Structural Studies of Secondary and Multi-Centre Bonding

in Compounds of the Non-Metals

By

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Copies of the available papers are included in Appendix **B**.

To My Parents

ABSTRACT

In this thesis the results of several crystal structure determinations are discussed in terms of their multi-centre inter- and intra-molecular bonding interactions. In Section 1 the structures reported form part of a systematic investigation into the importance of secondary bonding in determining the crystal packing and influencing primary geometry in compounds of the non-metals. In pursuance of this aim, the following crystal structures have been determined:-

(1) The diethyl tin dihalides, Et_2SnX_2 (X = Cl, Br, I).

(2) The solid solvate $SeOCl_2 \cdot$ Dioxane and the compound iodoxybenzene.

(3) The compounds iodobenzene diacetate and iodobenzene bis-(dichloroacetate).

(4) cis-3,5-Dibromo-4-oxo-2,2,6,6-tetramethylpiperidin-1-yloxy, a derived bis nitroxide and (Z, Z) 2,4-Dibromo-1,5-diphenylpenta-3-one.

(5) The novel pseudo polyhalide anion $[Me_2N(ICl)_2]^-$ as its tetramethylammonium salt.

Each of these structures is discussed in relation to similar examples. In some cases no secondary bonds were found, and possible reasons for this are given. In others, a three-centre overlap of a σ^* orbital with two lone pairs is proposed as a viable alternative to the principal linear arrangement X-A...Y of primary and secondary bonds found in most examples. A discussion of the significance of these structures in relation to current stereochemical and bonding models, including charge transfer descriptions of the interactions, and possible methods to quantify the strengths of these interactions are given in Chapter VI.

In Section 2 the topological descriptions of the structures of the boron hydrides and related compounds are discussed in terms of their multi-centre bonding interactions, and the classification of the geometries of the boron polyhedra as closo , nido , arachno and

hypho . The hypho class is by far the least well-known, and the crystal structures have been determined of three new examples isoelectronic with the hypothetical hypho $B_5H_{11}^{2-}$ ion, viz. $B_5H_9 \cdot L$ [L = $(Ph_2P)_2CH_2$, $(Ph_2PCH_2)_2$ and $(Me_2NCH_2)_2$]. The geometries of these compounds are significantly different, illustrating the diversity possible within such a related series. The structural relationships between these compounds are discussed in terms of the involvement of phosphorus 3d orbitals in the bonding of the phosphine adducts, and the contribution of vacant orbital valence structures to the structure of the tetramethylene diamine adduct.
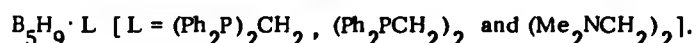
CONTENTS

LIST OF TABLES [†]

[†] In some cases an abbreviated title has been given to indicate the subject of the Table only.

Introduction

1. Secondary Bonding in Non-Metal Complexes

The initial definition of the term secondary bonding and a collation of the majority of the known structures in which this type of bonding interaction is prominent was published in a review which appeared in Advances in Inorganic Chemistry and Radiochemistry in 1972. Prior to this review, the chemical and structural significance of the weaker of these solid state interactions were not discussed in much detail and, in a vast number of cases, was completely omitted from discussion or else confined to a few values in tables of non-bonded contact distances. The exceptions to this were amongst the stronger (shorter) examples of this type of interaction, and these were included under the all-embracing title of charge transfer interactions or else were described as weak acid-base interactions. Several reviews have, in fact, included many of the compounds in the secondary bonding review under these latter descriptions. Whilst the charge transfer nomenclature is not incorrect, the secondary bonding interactions can be more specifically defined.

Thus, in the original thesis, the secondary bonding model considers that in non-metal complexes containing intra-molecular distances longer than normal bonds and/or inter-molecular distances that are shorter than van der Waals distances, these interactions can be considered as secondary bonds if certain criteria are satisfied. These criteria are:-

(a) the interacting neighbour(s) are not in the most favourable positions for non-directed forces, and/or

(b) the interacting neighbour(s) are in stereochemically significant positions.

These criteria are the same as those used for recognising bonding interactions compared to non-directional interactions of the van der Waals type. The stereochemically significant arrangement that was found to be important in virtually all of the known interactions was a linear system $Y-A...X$, where $Y-A$ is a normal bond and $A...X$ is a short inter-molecular (or intra-molecular) distance. Since then a series of compounds have been recognised (Chapter III) in which a significantly different stereochemical

arrangement occurs. It has also been observed (Chapter I) that inter-
actions are not always significantly shorter than the van der Waals
distance.

Having given the criteria whereby a secondary bond can be defined, it
is perhaps important at this stage to indicate briefly the theoretical bonding
description of these interactions. As can perhaps be seen from the nature
of the criteria, a simple electrostatic description can be relatively easily
dismissed. In fact the favoured view of these interactions is in terms of
three-centre four-electron (3c, 4e) molecular orbitals. In a system of
the type Y-A...X, the secondary bond A...X is formed by donation from a
lone pair on X into the σ^* orbital of the Y-A primary bond. Alternatively
(and equivalently) the interaction of the three σ-symmetry atomic orbitals
(on Y, A and X) gives a filled bonding molecular orbital concentrated
between A and Y, a filled non-bonding or weakly bonding orbital concentrated
between A and X, and an empty antibonding orbital. The overall scheme is
identical to the MO description of the hydrogen bond.

It is the intention in the first section of this thesis to describe the
results of recent crystallographic studies in several areas of non-metal
chemistry which have formed part of a systematic investigation of secondary
bonding. Several factors affecting the strength of these interactions have
been found. These and other conclusions about the role of secondary bonding
in non-metal compounds are discussed in the final chapter of the section.

2. The Hypho Boranes

Whilst the majority of the interactions described in Section 1 of the
thesis can be explained using 3c-4e molecular orbitals, the bonding in the
boron hydrides, their ions, the closely related carbaboranes and similar
compounds must be described using well-established 3c-2e molecular
orbitals (and, in a relatively few cases, higher n-centre m-electron M.O's)
since there are too few valence electrons available to provide a pair of
electrons between every pair of atoms close enough to be regarded as
covalently bonded (that is, by 2-centre-2-electron single bonds). These
3c-2e molecular orbitals result in a few basic structural features such as

hydrogen bridge bonding and three-centre open (and closed) triangular BBB face bonding being common to the majority of the structures. Lipscomb has described a topological model in which all the various theoretical valence structures based on these structural features are obtained from a set of rules. Alternatively (or equivalently) a good idea of the structure can be obtained from another set of simple rules due to Wade (and separately to Rudolph). These rules allow the structural class and hence the geometry, to be predicted from the number of skeletal electron pairs in the structure. These rules are described in detail in Chapter VII. The first three structural types resulting from these rules are closo, nido and arachno, representing closed polyhedra and closed polyhedra missing one and two vertices respectively. These descriptions cover the majority of the boron hydrides and related structures. However, an extension of Wade's rules allows a fourth class to be recognised which was given the name HYPHO from the Greek for net. HYPHO structures may be described as being based on closed polyhedra with three vertices missing. The application of these rules is seen from the description of the crystal structures of several hypho boranes in Chapter VII of this thesis.

SECTION 1

CHAPTER I

The crystal and molecular structures of the dialkyl tin dihalides; tetrahedral versus octahedral geometries

(I.1.) Introduction

There have been a wealth of physical measurements made on organotin compounds since tin is readily adaptable to many physical techniques and these compounds have immense commercial value.   The two common oxidation states of tin are $Sn(II)$ and $Sn(IV)$, and although the structures of their compounds might be expected to be based on a simple tetrahedral arrangement of ligands and lone pairs, extensive X-ray crystallographic investigations have established a marked tendency for the co-ordination number of the tin atom in these compounds to increase above four so that wide variety of structural types are known.   The description of some of the higher stereochemistries varied in the past depending on what significance was given to certain inter- and intra-molecular contact distances in the crystal which are less than the sum of the van der Waals radii for the atoms concerned and which appear to have significant effect on the primary geometry and also the packing in the crystal via dimers or polymeric lattice type arrangements. In the majority of cases these interactions can be included into the secondary bonding model.[1]

In this chapter, the crystal structures of diethyl tin dichloride, -dibromide and di-iodide and some preliminary results on dimethyl tin dibromide and dibutyl tin dichloride are reported, and the significance of the secondary bonds in distorting the molecular structures so that they are intermediate between tetrahedral and octahedral is discussed in relation to other known examples.   Some related organo $Sn(II)$ systems will be briefly covered.

(I.2.)   Structural Tin Chemistry

Several reviews of the crystal chemistry of tin up to <u>ca</u>. 1972 have been published.[2]   Probably the best method of classifying these structures is in terms   of the co-ordination number of the tin atom.   The inclusion and importance of secondary bonds in describing the overall stereochemistry can then be discussed. In particular, two research groups - those of Harrison and co-workers and Pelizzi and co-workers - have published the majority of the recent structures of organotin compounds, those of Harrison <u>et al</u>. normally being complexes of the organotin halides with Schiff's bases[3] whilst Pelizzi <u>et al</u>. have concentrated on a series of organotin complexes containing nitrate groups which have various stereochemistries depending on what other ligands are attached to tin.[4]

(I.2.1.)   Three co-ordinate tin

A single example of three co-ordinate tin will be discussed. This is the structure of the monomeric stannylene derivative $[(Me_3Si)C]_2SnCr(CO)_5$ which from an X-ray analysis contains the Group IV atom in an unusual three co-ordinate trigonal environment, the two carbon atoms, Sn and Cr being coplanar with a surprising low CSnC angle (98°).   There are no further intermolecular contacts less than 5 Å.[5]

(I.2.2.)   Four co-ordinate tin

In the crystal, tetra-aryl and tetra-alkyl tin compounds all contain tetrahedral molecules separated by van der Waals forces only.   A compilation of recent structural determinations of tetra-aryl tin compounds can be found in ref. 6 where it is noted that molecular symmetry S_4 is consistently observed despite considerable variation in the molecular packing due to the aryl substituents. This strongly suggests that in these crystals, which all have tetragonal symmetry, conformations with S_4 symmetry must be energetically favoured.[6]   A tetrahedral arrangement of bonds about tin is also

found in the majority of compounds with dialkyl- and trialkyl tin-groups bonded to transition metals (e.g. $Me_3SnMn(CO)_5$ and $Ph_3SnMn(CO)_5$[2c]) although there are some unusual distortions in these compounds. Notably, in the transition metal carbonyl derivatives, the $M-C\equiv O$ axes are found to deviate from linearity so as to bring the carbonyl groups towards the tin atom in an "umbrella effect".[2c]

(I.2.3.) Five co-ordinate tin

Perhaps the earliest example of five co-ordinate tin observed was the pyridine adduct of trimethyl tin chloride.[7] The normal geometry for this co-ordination number is trigonal bipyramidal and virtually all examples have this geometry albeit distorted to varying degrees. The bond lengths to the more electronegative axial ligands may be symmetrical or unsymmetrical but tend to be longer than those to the equatorial ligands. An arrangement of planar SnR_3 (R = alkyl or aryl) groups linked into polymeric chains via the axial ligands is quite common and can be found in trimethyl tin formate,[3c] methoxide[8], fluoroacetate and acetate[9] and glycinate[10] to give but a few examples. In these complexes it is quite common for the axial bonds to be unsymmetrical.

Five co-ordinate structures can also be obtained by intra-molecular interactions involving either unsymmetrically bidentate ligands or by the formation of long dative interactions involving chelate rings of various sizes. An example is C,N-{2[(dimethyl-amino)methyl]phenyl} diphenyl tin bromide in which penta co-ordination results from using a structured ligand. The dimethyl-amino group and bromine atoms are axial.[11] The structure of (1,3-diphenylpropane-1,3-dionato)triphenyl tin(IV) similarly achieves penta-co-ordination by intramolecular co-ordination.[12] In these two structures, the intramolecular co-ordinate bond is significantly shorter and the resulting geometry more regular than several other examples of systems containing a secondary bond to

complete the trigonal bipyramidal geometry , notably in 4-bromo
<u>cis</u> <u>cis</u> tetraphenylbutadienyldimethyltin(IV) bromide .[13] (see
section I.5). Similarly dimethyl tin chloride N N-dimethyldithio-
carbamate has been described as being distorted trigonal
bipyramidal due to an axial intra-molecular Sn...S contact of
2.79(1) Å from the bidentate dithiocarbamate. The electronegative
chlorine is also axial with an Cl-Sn...S angle of 154°.[14]

The second way Sn can obtain penta-co-ordination is seen in a
series of stannocanes where the fifth bond is intra-molecular
involving an oxygen or sulphur atom in the backbone of a fairly
large chelating ring. Examples of this type of co-ordination are
summarised in ref. 15.

Finally for Sn(II) compounds trigonal bipyramidal structures
appear to be extremely common although SnO is a rare example with
a square pyramidal structure.[16]

(I.2.4.) Six co-ordinate tin

This stereochemistry is based on an octahedron or distorted octahedron,
especially in complexes of the diorgano- and triorgano-tin halides with Lewis
bases. Again in these compounds the degree of distortion
of the octahedral arrangement can be related to the strength of the
inter- and intra-molecular secondary bonding amongst other factors.
In some cases there may be some ambiguity in the description of
the overall geometry which may be intermediate between tetrahedral
and octahedral. The dialkyl tin dihalides are a case in point.

(I.2.5.) Higher co-ordination numbers (> 6)

Examples of tin with co-ordination numbers of 7 or 8 are rare.
A summary of the known seven co-ordinate structures and a
description of their geometries can be found in ref. 17 where some
of the factors affecting this structural class are discussed. Whilst
three basic polyhedra possible for these seven co-ordinate
structures are the 1:3:3 capped octahedron (C_{3v}), the 1:4:2 mono-

capped trigonal prism (C_{2v}) and the 1:5:1 pentagonal bipyramid
(D_{5h}) ; with one exception all the known structures have the last
D_{5h} structure. The exception does not fit either the C_{3v} or the
C_{2v} descriptions.[17]

The known 8-co-ordinate structures are tin tetraacetate,[18]
tin tetranitrate and bis(phthalocynaninato)tin(IV).[19] The
geometries of these three structures are distorted dodecahedral,
dodecahedral and square antiprismatic respectively.

(I.2.6.)   Structural and related work on the Group IV organo-
metal halides and pseudohalides

Of the four diorganotin(IV) dihalides whose crystal structures
are known, Me_2SnF_2 has the Sn atoms octahedrally co-ordinated
by forming two _trans_-bonds to methyl groups and four equal Sn-F
bonds (2.14 Å), giving a regular two-dimensional layer lattice.[20]
In both Me_2SnCl_2 (ref. 21) and $(CH_2Cl)_2SnCl_2$ (ref. 22) the tin
atoms can be regarded as being four-co-ordinate, but it is also
possible to distinguish infinite chains in the crystal held together
by weak inter-molecular interactions.   The tin atoms are strongly
distorted from the expected tetrahedrally co-ordinated arrangement
by further secondary bonds to chlorine atoms of other molecules.
In the crystal structure of Ph_2SnCl_2 the original authors described
the structure in terms of isolated molecules without any inter-
molecular tin-chlorine bridging.[23]   This has been criticised by
Bokii et al.[22] who point out that the Sn-Cl bond lengths are different,
and that the chlorine atoms involved in the longer of the Sn-Cl bonds are
also involved in short inter-molecular interactions of 3.77 - 3.78 Å
with the tin atoms of neighbouring molecules.   These interactions
produce linear groups of four molecules, the two terminal tin atoms
remaining four-co-ordinate while the central tin atoms can be viewed
as six-co-ordinate.

As well as the diorganotin(IV) dihalides, the crystal structures
are known of several nominally four-co-ordinate dialkyltin(IV)
compounds containing pseudohalides[24] and many trialkyl- and triaryl-

tin(IV) halides and pseudohalides.[25]   Three review articles have
discussed the inter-molecular bonding in the organometallic pseudo-
halides of several heavy atoms including tin in terms of donor-
acceptor bonding.   Most of these compounds are also associated in
the crystal and the secondary bonds to the O, S and N ligands appear
to be much stronger than those to chlorine.   It also appears that
some compounds which are not associated by secondary bonding at
room temperature may be associated at lower temperatures.   This
is seen in triphenyltin(IV) chloride whose room-temperature crystal
structure shows discrete molecules with the valence angles about the
tin being very close to normal tetrahedral values.[27]   The authors
suggested that the significant difference in the ^{35}Cl n.q.r. spectra at
303 and 77 K (ref. 28) was due to the appearance of a polymeric
structure with trigonal bipyramidal tin and a weak secondary bond
Sn...Cl (as has been suggested[29] for Me_3SnCl) at the lower temperature.
However, a recent series of Mössbauer measurements over a range of
temperatures has failed to discover any gross structural changes in
Ph_3SnCl, whilst the association in Me_2SnCl_2 becomes stronger at
lower temperatures.[30]

In comparison, structural studies of the other Group IV di- and tri-
organometal halides are sparse, although it appears that associated
structures are likely to be found.   In the case of lead, only diphenyl-
lead dichloride has been investigated crystallographically[†] by means of
2D projections.   Significantly the structure has been found to consist
of infinite planar Cl_2PbCl_2 chains with equivalent Pb-Cl bonds (2.80 Å)
mutually perpendicular.   The phenyl rings are normal to the chain
axis with the Pb-C bonds (2.12 Å) nearly perpendicular to the plane
of the chain.[31]   The polymeric nature of the other tri-phenyl and
trimethyl lead halides and the dimethyl and diphenyl lead dihalides

† Presumably because of the rapid photodecomposition shown by
   organo lead halides (ref. 32).

in the solid state has also been inferred from evidence including their low solubilities in non-polar solvents, high melting points and most significantly the lowering of the infra-red metal-halogen stretching vibrations in the solid state compared with the corresponding values in solution (when soluble). Furthermore, it appears from these measure-ments that the molecular association in the organo lead compounds is greater than in the corresponding tin compounds.[33]

The majority of the organo germanium halides are liquids at room temperature. Gas phase electron diffraction studies on Me_2GeF_2, $MeGeF_3$, Me_2GeBr_2 and $MeGeBr_3$ have recently been published[34] but little crystallo-graphic work has been performed with the exception of a few complexes of $GeCl_2$[35] and several organogermyl complexes including the germanium analogues of the stannocanes mentioned above.[15] A structure associated via Ge-F-Ge bridged interactions in the solid state has been deduced from i.r. and other measurements for bis(trifluoromethyl)germanium difluoride.[36]

Crystallographic studies of organo silicon compounds are, however, more numerous, and have been the subject of several reviews. Of recent structures published, triphenyl silicon thiocyanate consists of isolated molecules, whilst bis(triphenyl silicon)carbo di-imide consists of a linear Si-N=C=N-Si chain along a three-fold axis.[37]

(I.3.) Experimental Results

(I.3.1.) General

Crystal samples R_2SnX_2 (R = Me, X = Br and I; R = Et, X = Cl, Br and I; and R = Bu, X = Cl) were kindly provided by Dr. D.A. Armitage. The crystal quality varied from sample to sample but was, however, somewhat poor even after recrystallisations from dry isopentane. The compounds were also sensitive to air-moisture hydrolysis and so handling and mounting of each compound was performed in a modified nitrogen 'dry box' fitted with a microscope and heating wire, using Lindemann capillary tubes which had been baked in vacuo for several hours. Even then, several crystals had to be mounted before one of sufficient quality for use on the diffractometer was found. Density measurements were not made because of the moisture sensitivity of the crystals and their solubility in most organic solvents, although calculated values, D_c, are in reasonable agreement with the values

TABLE I.1

Unit cell data for the dialkyl tin dihalides R_2SnX_2 ($R = Me$, $X = Br$ and I; $R = Et$, $X = Cl$, Br and I; and $R = Bu$, $X = Cl$)

Compound	System	Space group	a(Å)	b(Å)	c(Å)	β(°)	μ(Å³)	Z	D_c g/cm³	μ(Mo-Kα) cm⁻¹
Me₂SnBr₂	Monoclinic	C2/e (?)	12.437(2)	9.212(1)	24.791(4)	91.95(1)	2838.5(9)	16	2.89	154.07
Me₂SnI₂	Monoclinic	—	14.433(6)	10.279(4)	22.351(9)	94.03(3)	3307.8(23)	16	3.23	105.40
Et₂SnCl₂	Monoclinic	P2₁/c	9.677(3)	9.835(3)	9.243(3)	102.73(2)	858.1(4)	4	1.92	35.35
Et₂SnBr₂	Orthorhombic	C222₁	9.786(2)	10.006(3)	9.494(2)	–	929.7(4)	4	2.40	117.70
Et₂SnI₂	Orthorhombic	Pbcn	13.469(4)	5.385(2)	13.733(4)	–	996.0(6)	4	2.87	87.61
Bu₂SnCl₂	Monoclinic	P2₁ (?)	14.059(4)	9.407(2)	19.407(3)	96.79(2)	2548.8(10)	8	1.58	23.79

quoted for Me_2SnCl_2 and Ph_2SnCl_2. The unit cell constants, their standard deviations and space group data (where known) for the compounds are listed in Table I.1. Unit cell constants were obtained from least-squares refinement of the diffracting positions of up to 15 reflections on a Syntex $P2_1$ diffractometer by use of

$Mo-K_\alpha$ radiation ($\lambda = 0.71069$ Å). No further work was performed on the crystal of Me_2SnI_2 used, and although data sets have been collected for both Me_2SnBr_2 and Bu_2SnCl_2 they have been of very poor quality and need recollection.

(I.3.2.) Data collections

(I.3.2(i) Et_2SnCl_2,   compound (1)

Data were collected using a needle shaped crystal of dimensions 0.052 x 0.052 x 0.48 mm bounded by the faces (00 ± 1), (0 ± 10), (± 100).   Systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$, indicate space group $P2_1/c$.   Reflections were measured using a $\theta - 2\theta$ scan and scan range $(K_{\alpha1} -0.95)$ to $(K_{\alpha2} +0.95)$ to a maximum 2θ of 50°. A variable scan-rate of 1.3^o/min to 29.5^o/min depending on the intensity of a preliminary 2 s count was used.   Background counts were recorded at each end of the scan.   The intensities of three standard reflections were monitored every 80 reflections.   These showed a steady loss of intensity and the collected data were rescaled according to the equation $F = Fo(1 + 0.00065t)(1 + 0.00254 \sin \theta/\lambda.t)$. The maximum rescale factor was 1.1458.   1709 data were collected, of which 811 were considered observed ($I/\sigma(I) \geq 3.0$).

(I.3.2(ii) Et_2SnBr_2 , compound (2)

Data were collected using a crystal of dimensions 0.211 x 0.260 x 0.343 mm bound by the faces (± 110), (-1 ± 10), (00 ± 1). Systematic absences hkl , $h + k \neq 2n$, and $00l$, $l \neq 2n$ indicate space group $C222_1$, with the Sn on special positions, symmetry 2. Reflections were measured using a $\theta - 2\theta$ scan over a range $(K_{\alpha1} -0.9)$ to $(K_{\alpha2} +0.9)$ and variable scan rate of 1.5^o min^{-1} to 29.3^o min^{-1}

to a maximum 2θ of 55°. The intensities of four standard reflections were recorded after every 50 reflections and again showed a steady loss in intensity. The collected data were rescaled according to the equation

$$F = F_{o}(1 + 0.0004024t)\ (1 + 0.0012724\ \sin\ \theta/\lambda.t)$$

(Maximum rescale factor was 1.0524). 1263 data were measured including systematic absences due to the centering condition of which 289 were considered observed ($I/\sigma(I) \geq 3.0$).

(I.3.2(iii)) $\underline{Et_{2}SnI_{2}}$, compound (3)

Data were collected using a needle shaped crystal needle axis $\underline{a}$, (dimensions unknown). Systematic absences $\underline{0kl}$, $k \neq 2n$; $\underline{h0l}$, $l \neq 2n$; $\underline{hk0}$, $\underline{h} + \underline{k} \neq 2n$; indicates space group $\underline{Pbcn}$ with the Sn on special positions, symmetry 2. Reflections were measured using a $\theta - 2\theta$ scan over a range ($K_{\alpha_{1}} - 0.9$) to ($K_{\alpha_{2}} + 0.9$) and variable scan rate of 3° min^{-1} to 29.3^{o} min^{-1} to a maximum 2θ of 52°. The intensities of three standard reflections were recorded after every 60 reflections and showed a steady drop in intensity. The collected data were rescaled in two sections according to the equations

$$F = F_{o}(1 + 0.007655t)(1 - 0.004628\ \sin\ \theta/\lambda.t)\ \text{for}\ t \leq 15.18$$

$$F = F_{o}(1 + 0.002832t)(1 - 0.0009608\ \sin\ \theta/\lambda.t)\ \text{for}\ t > 15.18$$

The maximum rescale factor was 1.0682. 1187 data were measured, of which 342 were considered observed ($I/\sigma(I) > 3.0$).

(I.3.2(iv)) $\underline{Me_{2}SnBr_{2}}$ and $\underline{Bu_{2}SnCl_{2}}$

Crystals of $Me_{2}SnBr_{2}$ are colourless needles. Several attempts were made to collect a complete 3-dimensional set of data for $Me_{2}SnBr_{2}$ using several different crystals. However, crystal decomposition and crystal movement at each attempt drastically limited the amount and quality of the data collected, and prevented the solution of the structure.

Crystals of dibutyl tin dichloride were thin colourless plates with poorly-defined edges. One reasonable-looking flake was mounted in a Lindemann capillary and used for data collection.

Crystal data:

Monoclinic, $\underline{a}$ = 14.059(4), $\underline{b}$ = 9.407(2), $\underline{c}$ = 19.407(3) Å, β = 96.79(2) Å^3. D_c = 1.58 g/cm^3 for Z = 8. Mo-K$_\alpha$ radiation, λ = 0.71069 Å, μ(Mo-K$_\alpha$) = 23.79 cm^{-1}.

Unit cell dimensions and standard deviations were obtained by least squares fit to 15 strong reflections collected after the data collection had finished. Data were collected using θ - 2θ scans over a scan range (K$_{\alpha 1}$ - 1.1°) to (K$_{\alpha 2}$ + 1.1) using scan speeds from 2.0 to 29.3 $^\circ$/min. Several shells of data were collected. Some of these were later recollected due to crystal movement and the crystal was frequently recentred. Including duplicated data and standards 6305 reflections were eventually collected which, when reduced, gave only 660 observed reflections (I/σ(I) $\geq$ 2.58) due to the marked pseudo-absences in the data. The three standards collected every 100 reflections showed a gradual loss of intensity which was corrected for by rescaling the data in several sections, using several linear equations $F = F_o(1 + at)$.

(I.3.3.) Structure Solution

(I.3.3.1.) The diethyltin dihalides, compounds (1-3)

For compounds (1) and (2) Lorentz, polarisation and absorption corrections were applied, the last with the program ABSCOR. For (3), Lorentz and polarisation corrections were made, but crystal

decomposition prevented any measurement of the crystal for absorption correction. In all three cases, structure solution was attempted successfully using 3-dimensional Patterson maps to locate the heavy atoms and Fourier maps to locate the other non-hydrogen atoms. Block diagonal least squares refinement using anisotropic temperature factors for all atoms with correction for the effects of anomalous dispersion produced final R factors of 0.047(1), 0.058(2) and 0.049(3). The weights used were based on counting statistics.

Final co-ordinates and temperature factors are listed in Table I.2, significant bond lengths and angles in Table I.3. Structure factors for the three compounds are listed in Appendix

(I.3.3.2.) Dibutyl tin dichloride

The data contains several well marked pseudo-absences so that the choice of space group at this initial stage is somewhat arbitrary. The Patterson map reflects the pseudo I-centring of the heavy tin and chlorine atoms in the unit cell. Consistent with the observed pseudo-absences $\underline{hkl}$, $\underline{k} \neq 2n$, $\underline{hkl}$ $\underline{l} \neq 2n$ [and hence $\underline{hkl}$, $\underline{k} + \underline{l} \neq 2n$, $\underline{h} + \underline{k}/2 + \underline{l}/2 \neq 2n$] there are peaks at $(0,0,0)$; $(0, \frac{1}{2}, 0)$; $(0, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$ of approximately equal weight. Hence a feasible set of tin positions which would fit this map are given by

$$(0, 0, 0) \qquad\qquad (\frac{1}{2}, \frac{1}{4}, \frac{1}{4})$$
$$(0, \frac{1}{2}, 0) \quad\text{and}\quad (\frac{1}{2}, \frac{3}{4}, \frac{1}{4})$$
$$(0, 0, \frac{1}{2}) \qquad\qquad (\frac{1}{2}, \frac{1}{4}, \frac{3}{4})$$
$$(0, \frac{1}{2}, \frac{1}{2}) \qquad\qquad (\frac{1}{2}, \frac{3}{4}, \frac{3}{4})$$

There are at present 8 monoclinic space groups available and with suitable origin shifts the above combination of Sn positions can be fitted to all of these space groups. In some, this would involve placing some or all of the Sn atoms on special positions. It is very unlikely that the molecules would have $\overline{1}$ symmetry which rules out some possibilities. This still leaves several

possibilities, all of which need to be tested. Several alternatives have been tried with similar progress in each space group: that is, the Sn and Cl atoms can be located and in refinement show large correlation effects. The R factor for Sn and Cl atoms is $\approx$ R = 12% at which point the C atoms in the n-butyl groups can be observed in the difference Fourier with a strong suggestion that one chain is disordered at the α-position. However, due to the poor quality of the data and the problems of refining the C atoms in a acentric space group with a dominant centric distribution of heavy atoms , no reasonable bond distances and angles have yet been obtained. Even on reducing the data into the pseudo (primitive) cell (following a similar procedure to that in ref. 38, where disorder is blamed for the poor refinement in the true cell) no improvement was attained.

(I.4.)   Discussion of the Diethyl Tin Dihalides

(I.4.1.)   General

In the crystal structures of all three diethyl tin dihalides, Et_2SnX_2 (X = Cl, Br and I), the individual molecules interact to form chains. Probably as a result, there are significant angular distortions from tetrahedral values in the individual molecules. The values of the angles C-Sn-C and X-Sn-X are respectively 134.0(6) and 96.0(1) for (1), 135.9(10) and 98.5(1) for (2) and 130.2(11) and 104.0(2)$^\circ$ for (3).

Although there are few other Sn-C(Et) bond distances available for comparison, there should be little difference between Sn-C(Me) and Sn-C(Et). The Sn-C(Et) bond in dichloro(ethyl)hydroxotin [39] is 2.20(3) Å and a large number of Sn-C(Me) distances in the solid state for a variety of distorted geometries at tin give Sn-C from 2.07 to 2.22 Å. [40] The Sn-C distance in $SnMe_4$ has been determined most recently by gas-phase electron diffraction as 2.144(3) Å. [41] The present values are quite close to those quoted, but they do seem to show a slight systematic increase from (1) to (3). For Sn-Cl

TABLE I.2†

Atomic co-ordinate (x 10^4) and anisotropic temperature factors(x10)† for the diethyl tin dihalides with standard deviations in parentheses. †exp$[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$

(1) Et₂SnCl₂

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Sn	2788(1)	2312(1)	7006(1)	37.8(4)	43.8(5)	48.2(5)	-0.4(5)	8.3(3)	-0.9(5)
Cl(1)	2774(5)	705(4)	5071(4)	75.9(25)	47.0(20)	50.1(18)	-7.8(15)	10.4(17)	-1.5(17)
Cl(2)	2738(4)	672(4)	8898(4)	72.4(24)	48.7(19)	56.4(18)	7.4(15)	20.5(17)	1.0(17)
C(1)	751(14)	3238(15)	6542(16)	13(7)	74(9)	92(9)	1(7)	-2(6)	11(6)
C(2)	-413(20)	2217(25)	6152(34)	30(10)	135(15)	275(26)	-53(17)	0(13)	-9(11)
C(3)	4912(16)	3100(15)	7494(16)	40(7)	67(9)	74(8)	-1(6)	10(6)	-13(6)
C(4)	6028(16)	2021(18)	7800(20)	18(7)	90(11)	143(12)	8(9)	11(8)	10(8)

(2) Et₂SnBr₂

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Sn	431(3)	0(0)	5000(0)	58.4(14)	63.2(14)	52.3(13)	-4.1(65)	0(0)	0(0)
Br	2100(3)	48(21)	3002(3)	68.4(18)	117.0(28)	57.6(17)	1.6(73)	11.3(13)	-19.0(62)
C(1)	-420(26)	1956(25)	4745(31)	51(11)	65(12)	13(19)	-10(11)	-7(12)	-11(13)
C(2)	393(28)	300(31)	5366(61)	56(13)	70(15)	108(49)	-27(20)	-45(23)	10(15)

(3) Et₂SnI₂

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
I	1245(1)	965(5)	1531(1)	56.6(10)	64.0(13)	55.5(9)	-6.5(14)	16.2(8)	2.0(18)
Sn	0(0)	4080(6)	2500(0)	43.6(11)	40.2(15)	37.9(10)	0(0)	-4.8(10)	0(0)
C(1)	904(19)	5829(54)	3644(15)	83(15)	20(12)	50(11)	1(17)	-30(11)	7(17)
C(2)	1501(21)	3739(77)	4220(17)	89(17)	118(27)	58(12)	-28(22)	-40(12)	18(27)

TABLE I.3

Bond distances (Å) and bond angles (°) with standard deviations in parentheses.

(a) Distances

Compound	Ref.	Sn-X	Sn-C	C-C	Sn...X	Δ [a]	Sn...X [b]	X...X
Me$_2$SnCl$_2$	21	2.40(4)	2.21(8)		3.54(5)	1.14		
(CH$_2$Cl)$_2$SnCl$_2$	22	2.37(2)	2.18(7)		3.71(3.21)[c]	1.34(0.84)	3.85	
Et$_2$SnCl$_2$	d	2.385(3)	2.132(13)	1.452(25)	3.483(4)	1.08		3.544(6)
		2.384(4)	2.167(15)	1.471(22)	3.440(4)			
Et$_2$SnBr$_2$	d	2.505(4)	2.162(26)	1.456(46)	3.777(4)	1.27	3.95	3.795(4)
Et$_2$SnI$_2$	d	2.719(4)	2.178(27)	1.573(49)	4.284(5)	1.565	4.08	5.383
Ph$_2$SnCl$_2$ (1)	23	2.353(2)	2.119(5)		3.78		3.85	
		2.336(2)	2.105(5)					
(2)		2.357(2)	2.118(5)		3.77			
		2.336(2)	2.112(6)					

a Δ = (Sn...X) minus (Sn-X)

b van der Waals distance from A. Bondi, J. Phys. Chem., 1964, 68, 441

c Value in parentheses is Sn...Cl intramolecular distance(s)

d This work

Table I.3 continued

(b) Angles

Compound	X-Sn-X	C-Sn-C	C-Sn-X	Sn-C-C	X...Sn-X	Sn...X-Sn
Me$_2$SnCl$_2$	93.0(20)	123.5(45)	109.0(45)			
(CH$_2$Cl)$_2$SnCl$_2$	97.0(20)	135.0(60)	105.0(20)			
Et$_2$SnCl$_2$	96.0(1)	134.0(6)	106.3(4)	112.1(12)	173.0(1)	104.0(1)
			105.4(4)	113.6(10)	172.0(1)	102.8(1)
Et$_2$SnBr$_2$	98.5(1)	135.9(10)	97.5(9)	114.0(20)	179.5(5)	98.2(1)
Et$_2$SnI$_2$	104.0(2)	130.2(11)	105.6(8)	110.0(21)	158.0(1)	98.0(1)
Ph$_2$SnCl$_2$ (1)	101.7(1)	123.9(2)	106.0(2)	108.8(2)		
			106.5(2)	107.8(2)		
Ph$_2$SnCl$_2$ (2)	97.8(1)	127.0(2)	110.1(2)	105.0(2)		
			107.1(2)	105.9(2)		

a Δ = (Sn...X) minus (Sn-X)

b van der Waals distance from A. Bondi, J. Phys. Chem., 1964, 68, 441.

c Value in parenthesis is Sn...Cl intramolecular distance.

d This work
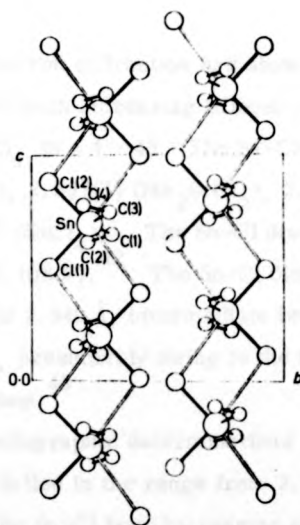
FIGURE 1 Et₂SnCl₂ projected down *a*; primary bonds are shown closed; secondary bonds open
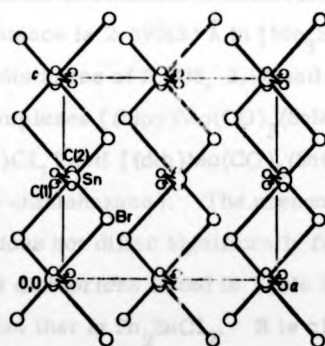
FIGURE 2 Et₂SnBr₂ projected down *b*
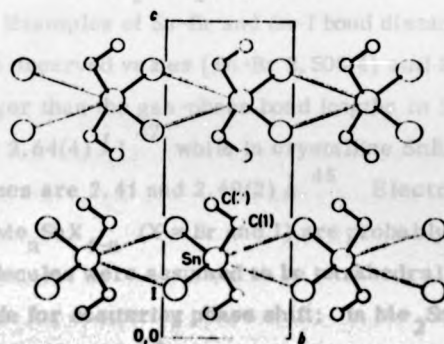
FIGURE 3 Et₂SnI₂ projected down *a*

Figs 1·1-3

bonds, electron diffraction has shown a regular contraction in the bond length with increasing halogen substitution in the series $Me_{4-n}SnCl_n$ (n = 1 - 4). The Sn-Cl distances are 2.351(7) (Me_3SnCl), 2.327(3) (Me_2SnCl_2), 2.304(3) ($MeSnCl_3$), and 2.281(4) Å ($SnCl_4$). The Sn-Cl distances are essentially constant (2.104 - 2.108 Å).[42] The Sn-Cl distance in (chloromethyl)trichloro-stannane is 2.340 Å, intermediate between those for Me_2SnCl and Me_2SnCl_2, presumably owing to the inductive effect of the chloro-methyl group.[43]

Crystallographic determinations of the Sn-Cl bond length have generally fallen in the range from 2.318 to 2.584 Å,[44] with the length of the Sn-Cl bond increasing as the co-ordination of the tin changes from tetrahedral to octahedral. The longest recorded Sn-Cl distance is 2.693(3) Å in $[Me_3SnCl_2]^-$,[45] although bridging Sn...Cl distances of 2.805, 2.96 and 2.78 Å occur in transition-metal complexes $[(bipy)Mo(CO)_3(SnMeCl_2)Cl]$, $[(dth)-W(CO)_3-(SnMeCl_2)Cl_7]$ and $[(dth)Mo(CO)_3(SnCl_3)Cl]$[46] (bipy = $\alpha\alpha'$-bipyridyl, dth = 2,5-dithiahexane). The present mean Sn-Cl bond length 2.384 Å does not differ significantly from those for the other two dialkyltin dichlorides listed in Table 3 although it is ca. 0.04 Å longer than that in Ph_2SnCl_2. It is clearly considerably longer than that in Me_2SnCl_2 in the gas phase.[42]

Examples of Sn-Br and Sn-I bond distances are less numerous. The observed values [Sn-Br 2.505(4) and Sn-I 2.719(4) Å] are again longer than the gas-phase bond lengths in $SnBr_4$ and SnI_4 [2.44(2) and 2.64(4) Å][47] while in crystalline $SnBr_4$ and SnI_4 the respective values are 2.41 and 2.69(2) Å.[48] Electron-diffraction measurements on Me_nSnX_{4-n} (X = Br and I) are probably not very accurate as the molecules were assumed to be tetrahedral and no allowance was made for scattering phase shift; in Me_2SnX_2, Sn-Br was 2.45(2) and Sn-I 2.69(3) Å, and for this series a contraction was reported

with increasing halogen substitution,[49] although the values quoted above for SnX_4 seem not to bear this out.

Considering solid state values, the observed Sn-Br value is in good agreement with that [2.504(5) Å] in (4-bromo-1,2,3,4-tetraphenyl-*cis*, *cis*-1,3-butadienyl)dimethyltin bromide which is also distorted from tetrahedral geometry by secondary bond interactions.[13] In the two isomers of bis-[1,2-bis(ethoxycarbonyl)-ethyl]tin dibromide, Sn-Br distances of 2.516(6), 2.588(6) and 2.504(5) Å were found in distorted octahedral structures.[50] However, in the crystal structure of C,N{2[(dimethylamino)methyl]-phenyl} diphenyl tin bromide, intra-molecular co-ordination from the dimethylamino group of the built-in ligand results in a penta-co-ordinate tin atom and a significantly longer axial Sn-Br bond of 2.630(2) Å [N-Sn-Br = 171.0(1)°].[11] The only other examples of solid state Sn-Br distances are for organotin-transition metal compounds, where more complex bonding and packing effects occur, *e.g.* [$(Br_3Sn)Fe(CO)_2(\pi-C_5H_5)$] mean 2.501(2), [$(Br_2Sn)\{Mn(CO)_5\}_2$] 2.548(2), and [$(BrSn)\{Co(CO)_4\}_3$] 2.520(5) Å.[51] The mean value for [$(Br_3Sn)Mo(\pi-C_5H_5)Br$] is 2.506(8) Å, but this compound also possesses a long bridging Sn-Br distance of 3.411 Å (*cf.* ref. 24) which results in trigonal bipyramidal geometry at the tin atom.[51d]

The observed Sn-I for (3) also agrees with that of 2.729(3) Å in 1,4-bis(iododiphenylstanna)butane which contains a tetrahedral tin atom.[52]

(I.4.2.) <u>Inter-molecular interactions</u>

The strength of the inter-molecular interactions can be deduced from the length of the secondary bonds and the angles around tin (especially C-Sn-C). In Et_2SnCl_2 and Et_2SnBr_2 the lengths of the secondary bonds (see Table 3) are 0.39 and 0.17 Å less than the sum of their appropriate van der Waals radii. The weakest interaction occurs in Et_2SnI_2, where the Sn...I secondary bond distance [4.284(5) Å] is greater than the sum of the tin and iodine

van der Waals radii. However, it can be argued that the interaction is still present since the value of the C-Sn-C angle [$130.2(11)^o$] is much larger than the tetrahedral value. Taking into account only the difference between the secondary bond distance and the sum of the van der Waals radii, it would appear that the strength of the secondary bonding is in the order $Cl > Br > I$. However, if the apparent difference in the C-Sn-C angle is genuine, then the order may be $Cl \approx Br > I$. It has also been suggested, from n.q.r. measurements, that bromine bridging is stronger than chlorine bridging.[53] Zahrobsky,[54] by use of a simple stereochemical model which optimises the van der Waals forces between the bonded and neighbouring atoms (regarded as spheres), has predicted inter-molecular distances of 3.81 and 4.11 Å for Me_2SnBr_2 and Me_2SnI_2. The distances quoted are reasonable although the steric requirements of the larger ethyl group might affect these results. However, this model calculates the C-Sn-C angles as being only 125 and 124° respectively.

The mode of bridging in the Et_2SnCl_2 and Et_2SnBr_2 chains is also different from that in Et_2SnI_2 where both bridging secondary bonds Sn...I involve the halogen atoms on the same neighbouring molecule (Fig. 3). In Et_2SnCl_2 and Et_2SnBr_2 the distorted octa-hedral arrangement around each tin is completed by two secondary bonds involving the halogen atoms of two neighbouring molecules (Figs. 1 and 2). Both $(CH_2Cl)_2SnCl_2$ and Ph_2SnCl_2 associate in the same chelating manner as does Et_2SnI_2; Me_2SnCl_2, however, has the second bridging type of association. It is not readily apparent which type of bridging arrangement a system containing secondary bonds will adopt, but the chelating bridges seems to be favoured with the longer weaker bonds. Brown and Shannon[55] have attempted to classify the bridging environments in certain inorganic structures using the bond valences of the bridging atoms, and this method may be applicable to secondary bonded systems.

The lengths of the Sn...Cl secondary bonds (Table 3) can be compared to that [3.486(7) Å] for quinolinium trichlorodimethyl-stannage(IV) where this bond links two $Me_2SnCl_3^-$ ions into dimeric units.[56] The cation here is very important since in [Me_2Sn(ter-pyridyl)]$^+$[Me_2SnCl_3]$^-$ the anion shows no Sn...Cl contacts < 3.7 Å;[57] nor does the ion [Me_3SnCl_2]$^-$ in [$Mo_3(\eta^5$-$C_5H_5)S_4$]$^+$[Me_3SnCl_2]$^-$, although it does contain a very long Sn-Cl distance (2.696 Å).[45]

The Sn...Br secondary bond in Et_2SnBr_2 has the same length [3.774(5) Å] as the intra-molecular interaction of bromine with tin in (4-bromo-1,2,3,4-tetraphenyl-cis, cis-1,3-butadienyl)dimethyltin bromide (resulting in an axially substituted trigonal bipyramid with equatorial organic groups).[13] In that compound also, the C(buta-dienyl)-Sn-C(Me) angle has opened to 129.0° and C(Me)-Sn-Me to 112.7°. A series of analogous 4-chloro - and 4-bromo-compounds has been investigated in which Sn-Ph replaces Sn-Br. In these compounds, the interaction is drastically weakened so that the Sn...Cl (4.28) and Sn...Br distances (4.35 Å) are both greater than the sum of the two corresponding van der Waals radii. The difference in the two Sn...Br distances is 0.57 Å. Similarly the C(butadienyl)-Sn-C(Me) angles are reduced to 116.5 (4-chloro) and 117.1° (4-bromo).[58] Furthermore, in the crystal structures of triphenyltin 2-methylthiophenolate and -2,6-dibromo-4-fluoro-thiophenolate, the Sn-S-C angles involving the thiophenolate rings are the same [98.6(8) and 101(2)° respectively] indicating that no intra-molecular co-ordinative interactions are occurring. The resulting intra-molecular Sn...Br distances of 4.26 and 4.29 Å again show that a Sn...Br van der Waals contact distance of 4.1 (after Bondi) is essentially correct.[59]

(I.4.3.) Factors affecting inter-molecular interactions

A CNDO calculation of the valence electron distribution in a series of Sn^{IV} compounds has shown that for isolated halogeno-(dimethyl)stannanes the 5s and 5p orbital occupancies are strongly

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(I.4.3.)   Factors affecting inter-molecular interactions

A CNDO calculation of the valence electron distribution in a series of Sn^{IV} compounds has shown that for isolated halogeno-(dimethyl)stannanes the 5s and 5p orbital occupancies are strongly

dependent on the electronegativity of the halogen.[60] Although the methyl groups donate electrons to the tin, they are unable to replace all the electron density removed by the halogen atoms, leaving a slightly electron-deficient tin atom which can then form secondary bonds. The decreasing electronegativity of the halogens and decreasing overlap with the more diffuse orbitals on bromine and iodine would then qualitatively explain the observed strengths of the secondary interactions. There is also a clear connection between secondary bond strength and the nature of the organic group.

In Me_2SnCl_2, Et_2SnCl_2 and Et_2SnBr_2 the secondary bonding is considerably stronger than in Ph_2SnCl_2. The effect of replacing methyl by ethyl in R_2SnCl_2 is to strengthen the inter-molecular bonding by shortening the secondary bond from 3.54(5) to 3.461(4) (mean) $\mathring{A}$ with the corresponding C-Sn-C angle opening out from 123(4) to 134.0(6)$^{\circ}$. These angles are still considerably less than in the more associated dimethyltin pseudo-halide compounds $Me_2Sn(CN)_2$ [148.7(3.5)$^{\circ}$] and $Me_2Sn(NCS)_2$ [145.9(1.4)$^{\circ}$]. The phenyl group produces a significant weakening of the secondary interaction as can be seen from Table 3 and from the dimethyl-(tetraphenylbutadienyl)tin compounds already mentioned. This is presumably due to the ability of the phenyl group to involve available orbitals on the tin atom in inductive and mesomeric interactions so that they cannot overlap effectively with further orbitals. Similarly the chloro-methyl group, with a reasonably strong inductive effect, also weakens the secondary bonding. However, the C-Sn-C angle of 135(6)$^{\circ}$ in $(CH_2Cl)_2SnCl_2$ compared with 123.9(2) and 127.0(2)$^{\circ}$ in the two crystallographically independent Ph_2SnCl_2 molecules suggests a stronger interaction in the former. If the viewpoint of Bokii et al.[22] is accepted, the difference of 4° between the C-Sn-C angles in the two Ph_2SnCl_2 molecules is directly attributable to secondary bonding effects.

(I.4.4.) Hybridisation models and other physical measurements

The C-Sn-C angle is important when describing any tin hybridisation model and in interpreting other physical measurements made on tin.   Sham and Bancroft[40] using a simple theoretical model, have correlated the Sn^{119} Mössbauer quadrupole splittings with the C-Sn-C angle in a number of distorted Me_2Sn^{IV} compounds. They find that Me_2SnCl_2 and $Me_2Sn(NO_3)_2$ lie in intermediate positions between the two predicted curves for Me_2SnL_2 and Me_2SnL_4.   Recent Mössbauer results have also shown that the amount of tin 5s character in the bonds from tin to (transition) metals and organic groups in the series of compounds $X_nR_{3-n}SnM$ [$X = Cl$, Br or C_6F_5; $R = Me$ or Ph; $M = Mn(CO)_5$ or $Fe(CO)_2$- (π -C_5H_5)] decreases in the order: Sn -$Fe(CO)_2(\pi$ -$C_5H_5) > Sn$ -$Mn(CO)_5$ $> Sn$ -$Me > Sn$ -$Ph > Sn$ -$C_6H_5 > Sn$ -$Cl \approx Sn$ -Br.   By use of this series they have rationalised the known distortions from tetrahedral geometry in several tin compounds.[61]

The values of the coupling constants J ^{119}Sn -CH_3 also indicate that the s character in the Sn-Me bonds decreases substantially as the C-Sn-C angle decreases.[62]   There should be a corresponding increase in the Sn-C distance, which is not always readily seen owing to the difficulty of determining this distance accurately.   The idea of a linear relationship between the J ^{119}Sn -Me values and the percentage s character in the Sn-C bonds was advanced by Holmes and Kaesz[63] but has been criticised by McFarlane.[64]   Van den Berghe and van der Kelen[65] have since suggested that the coupling constants are proportional to the percentage s character of sp^n hybrid orbitals only, since any d orbital involvement in bonding would increase orbital overlap and hence bond strength, whilst not increasing the amount of s character of the hybrid orbital.

In trans -octahedral complexes, the bonding may, therefore, be described in terms of sp_z hybridisation of the tin with p_x and p_y orbitals used in the equatorial bonds.[66]   The resulting equatorial bonds should then be longer than those observed for tetrahedral

compounds as is generally found (cf. Ph_2SnCl_2 and Et_2SnCl_2).
In the present compounds (1) - (3), which are clearly intermediate
between tetrahedral and trans -octahedral, the tin hybridisation
must be intermediate between sp^3 and sp and involvement of the
3d orbitals is possible. The Mössbauer parameters and other
physical measurements have been made on the present compounds
as well as on a series of related mixed-halogen species.[67]

(I.5.)   References

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CHAPTER II

The Crystal and Molecular Structures of the Solid Solvate Seleninyl
Dichloride. Dioxane and of Iodoxybenzene; Distorted Octahedral
Arrangements of Primary and Secondary Bonds

II.1.   Introduction

In the previous chapter, the central tin atoms of the diethyl tin dihalides
were regarded as distorting under the influence of secondary bonds from
neighbouring molecules so that the resultant geometries are intermediate
between tetrahedral and octahedral.   In this chapter it is intended to
discuss further octahedral and distorted octahedral arrangements of
primary and secondary bonds, and perhaps show considerable variance in
the role of any lone pairs in affecting the secondary bonds and hence the
resultant structures.   In particular two systems will be used to illustrate
these points.   The first involves the several known solid solvates of
seleninyl dichloride and in particular the crystal structure of the 1:1 solvate
with dioxane.   The second will involve a discussion of the crystal
structure of iodoxybenzene in relation to these solvates and other compounds,
all of which have considerably more distorted arrangements of primary and
secondary bonds.

V.2. The Solid Solvates of Seleninyl Dichloride[†]

The non-aqueous solvent seleninyl dichloride has for some time been
known to form solid solvates with a variety of metal halides and organic
acids and bases.[1]   Wise[2] performed much of the original work back in 1923,
but he found that, apart from the problems of excluding all traces of
moisture, the resulting solvates often form   gelatinous melts from which
it is very difficult to isolate pure (crystalline) materials. Single crystals
suitable for X-ray work have been isolated for a few of the solvates by
conventional or zone-melting techniques, and the results of these studies
have been reviewed by Hermodsson[3] and Cordes[4]. The interest in the
structural properties of these solvates concerns the multi-functional role

[†] Also known as selenium oxychloride or dichloro selenium(IV) oxide.

of the selininyl dichloride molecules and the importance in identifying specific solute-solvent interactions. In $SnCl_4 \cdot SeOCl_2$ [5] and $SbCl_5 \cdot SeOCl_2$ [6] the solvent acts as a Lewis base using a lone pair of electrons on oxygen in the co-ordination bond, whilst in the adduct $SeOCl_2 \cdot 2C_5H_5N$,[7] the seleninyl dichloride behaves as a Lewis acid, expanding its valence shell to give a distorted square pyramidal structure with _trans_ chlorine and nitrogen atoms. Finally, in the complex $(CH_3)_4N^+Cl^- \cdot 5SeOCl_2$ there is a centrosymmetric cluster $(2Cl \cdot 10SeOCl_2)^{2-}$ in which the seleninyl dichloride solvates chloride ions via a variety of weak inter-molecular contacts.[8] In fact, in all of the solvates of seleninyl dichloride studied so far, the selenium atoms have been found to form Se...O and Se...Cl contacts which may be described as secondary bonds. Inclusion of these contacts results in the geometry about the selenium atoms being based on an octahedral arrangement of three primary and three secondary bonds, although in some cases the third secondary bond opposite the Se-O bond may be significantly longer than the other two secondary bonds. The geometry in those cases has been described in terms of a square pyramid with the lone pair assumed to point in the direction of the third longer contact, although the octahedral description of the primary and secondary bonds is more complete. Furthermore there are other examples where a secondary bond has been replaced by two longer contacts, and it may be inferred from these results that the steric role of the lone pair of electrons on $SeOCl_2$ varies in importance. In those cases where an octahedron can be observed, the angles X-Se...Y (X, Y = O or Cl) have been found to lie in the range 142 - 173[o], and there appears to be no clear way of deciding which atoms, chlorine or oxygen, are going to form the secondary bonds.[9] The present structure of $SeOCl_2 \cdot$ dioxane is, however, the first in which $SeOCl_2$ is involved in three secondary bonds to oxygen with the $SeOCl_2$ being classed as amphoteric. The octahedral environment of selenium in this compound will be compared to several analagous systems of 3 primary and 3 (or 4) secondary bonds in Section (II.5.).

II.3. Iodoxybenzene

The preparation of many organotervalent iodine compounds proceeds via iodosobenzene, which is most conveniently prepared by reacting iodo-benzene dichloride with aqueous sodium hydroxide.[10] During one such preparation, using an excess of water, several thin crystalline plates were noticed amongst the yellow powdery product. In the belief that these were crystalline iodosobenzene which would be expected from previous studies of organotervalent iodine compounds to have extensive inter-molecular interactions or secondary bonds (Chapter III), a low temperature data set was collected. The structure solution, however, showed the compound to be another possible product, namely iodoxy-benzene. Nonetheless, the structure of this compound again contains several important intermolecular interactions which are described as being part of a more strongly distorted octahedral arrangement of primary and secondary bonds due to the more prominent importance of the iodine lone pair. Again, analagous systems will be quoted, and the inter-relation between these two diverse systems will be qualitatively discussed.

II.4. Experimental

II.4.1. Preparations and Data Collections

(II.4.1.(i)) SeOCl$_2$·Dioxane

Dropwise addition of a carbon tetrachloride (dried over CaCl$_2$) solution of seleninyl dichloride (BDH Chemicals Ltd.) to a carbon tetra-chloride solution of dioxane (dried over sodium) gave immediate precipitation of clear, colourless needle-shaped crystals of the 1:1 solvate. These crystals are extremely moisture sensitive and needed to be mounted in Lindemann capillaries baked for several hours in vacuo to minimize crystal decomposition.

Crystal data: C$_4$H$_8$Cl$_2$SeO$_3$, orthorhombic, $\underline{a}$ = 8.884(2), $\underline{b}$ = 12.066(3), $\underline{c}$ = 8.410(3) Å, $\underline{U}$ = 901.5(5) Å^3, D$_c$ = 1.870 g/cm^3 for Z = 4. Mo K$_\alpha$ radiation, λ = 0.71069 Å, μ(Mo-K$_\alpha$) = 50.10 cm^{-1}, F(000) = 496.0 . Systematic absences O$\underline{kl}$, $\underline{k} + \underline{l} \neq 2n$ and $\underline{hOl}$, $\underline{h} \neq 2n$ indicate space groups Pnam (No. 62 non-standard) or Pna2$_1$ (No. 33).

Unit cell dimensions and data were collected using the diffracto-
meter, and a crystal of size 0.194 x 0.104 x 0.093 mm. Reflections
were measured using θ-2θ scans to a maximum 2θ of 55°. A
variable scan rate of 3.0°/min to 29.3°/min depending on the
intensity of a preliminary 2 sec count was used. Background counts
were recorded at each end of the scan, each for one quarter of the
scan time. The intensities of four standard reflections were recorded
every 55 reflections. These showed gradual crystal decomposition
complicated by slight movements of the crystal in the capillary. The
effects of the crystal movement were reduced by recentering at
frequent intervals and increasing the scan range of $(K_{\alpha_1} - 1.0^{\circ})$ to
$(K_{\alpha_2} + 1.0^{\circ})$ to $(K_{\alpha_1} - 2.0^{\circ})$ to $(K_{\alpha_2} + 2.0^{\circ})$ after 480 reflections had
been collected. A correction for crystal decomposition was obtained
by scaling the collected data in small sections, using several linear
equations of the form $F = F_o(1 + at)$ where $\underline{a}$ = a linear scaling
coefficient and t = time.

1190 unique reflections were collected of which 640 were considered
observed, $(I/\sigma(I) \geqslant 3.0)$, and used in refinement.[†] Lorentz, polarisation
and absorption corrections were applied, the last with the program
ABSCOR.

(II. 4. 1. (ii)) Iodoxybenzene

As mentioned above, during the standard preparation of iodosobenzene
by the hydrolysis of iodobenzene dichloride,[10] an excess of water was used
and the product was left overnight to react. Amongst the expected iodoso-
benzene product, a fine yellow powder normally, was a small amount of
thin, clear, approximately hexagonal crystalline platelets. Several of these
crystals were separated and extinguished sharply under polarised light.
Many were too thin, however, to scatter X-rays well. A much thicker,
roughly hexagonal crystal of size ca. 0.19 x 0.16 mm and thickness 0.021
mm was eventually found and used for the data collection. As a precaution

[†] Two reflections (01-1) and (200) were later removed because of large
extinction effects.

against the known tendency of organoiodine compounds to undergo rapid photo-decomposition in X-rays (see Chapter III) it was decided to cool the crystal down to -100° C using the Syntex LT-1 attachment to the diffractometer.

Crystal data:

$C_6H_5IO_2$, M.W. = 236.0, monoclinic, $\underline{a}$ = 12.9041(23), $\underline{b}$ = 6.4023(14), $\underline{c}$ = 4.0115(7) Å, β = 99.018(14)°, $\underline{U}$ = 327.32(11) Å³, at -100° C D_c = 2.394 g/cm³ for Z = 2. Mo K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 48.66 cm⁻¹, F(000) = 220.0. Systematic absence O$\underline{k}$O, $\underline{k}$ ≠ 2n indicates space group P2$_1$ (No. 4).

Unit cell dimensions and data were collected using the diffractometer. Reflections were measured using θ-2θ scans to 2θ of 60° in three shells, using a scan range (K$_{\alpha_1}$ - 0.75) to (K$_{\alpha_2}$ + 0.75) and scan speed 0.7 - 29.3 °/min. Other conditions were the same as in (II.4.1.(i)). Four standards collected every 60 reflections showed only statistical fluctuations throughout the data collection. 1080 reflections were eventually processed (thus excluding several blocks of data recollected using a better orientation matrix and a block of reflections with low values due to problems with the generator (also recollected)). Of these, 801 were observed (I/σ(I) ⩾ 3.0); averaging symmetry equivalent reflections reduced this further to a final set of 775 data.

II.4.2.   Structure Solution and Refinement

(II.4.2.(ii)) SeOCl$_2$·Dioxane

Initially the centric space group Pnam was assumed but was rejected at an early stage. The co-ordinates of the selenium atom were located in a Patterson map and Fourier maps revealed the remaining light atoms. Hydrogen atoms in the dioxane molecule were placed in calculated positions (C-H = 0.95 Å) with temperature factors of 0.06 In the final cycles of least squares refinement, anisotropic temperature factors were used for all non-hydrogen atoms with the hydrogen atom parameters fixed. The weights used were given by ω = X·Y where, if sin θ < 0.35, X = sinθ/0.35 otherwise X = 1 and if F$_{obs}$ > 27.0 then Y = 27.0/F$_{obs}$ otherwise Y = 1. This scheme gave unit weights to most

reflections, but downweights those reflections with large F_{obs} and/or low sin theta.

The refinement, including corrections for anomalous dispersion, converged to a final R of 0.052 and weighted R of 0.064; in the final cycle no parameter shift was greater than 12% of its standard deviation. The final difference Fourier was featureless except for residual peaks near the selenium. There was virtually no difference in refinement with the two alternative 'hands' of the molecule, with negligible differences in bond distances and bond angles.

(II. 4. 2. (ii)) Iodoxybenzene

The co-ordinates of the iodine atom were readily located from the Harker plane $U\frac{1}{2}V$ in the Patterson. In space group $P2_1$, with a single heavy atom, the y co-ordinate can be arbitrarily fixed (y = 0) to define the position of the molecule with respect to the polar 2_1 axis. As a consequence the phases based on this iodine have the centrosymmetric values 0 and 180°, and the resulting Fourier contained a mirror plane at $y = \frac{1}{2}$ relating different images of the true molecule. The immediate observation from the original Fourier was that the compound was not iodosobenzene as expected, but iodoxybenzene, another likely reaction product. However, the normal process in locating all the atoms in the correct mirror image of the molecule is to break the pseudosymmetry in the map by including a second heavy atom in the calculation. In the present case, there were some difficulties encountered before the present atomic arrangement was obtained, because the positions of the carbons in the phenyl ring did not help discriminate between the alternative oxygen positions, all of which gave similar R-factors when refined. However, of the alternatives, two sets of oxygen positions resulted in a bad O...O contact of ~ 1.75 Å and a third resulted in a close C...O contact, leaving the present arrangement as the most chemically reasonable.

Hydrogen atoms for the phenyl ring were included in calculated positions with fixed temperature factors. In the final cycles of least squares refinement, anisotropic temperature factors were used for the iodine and
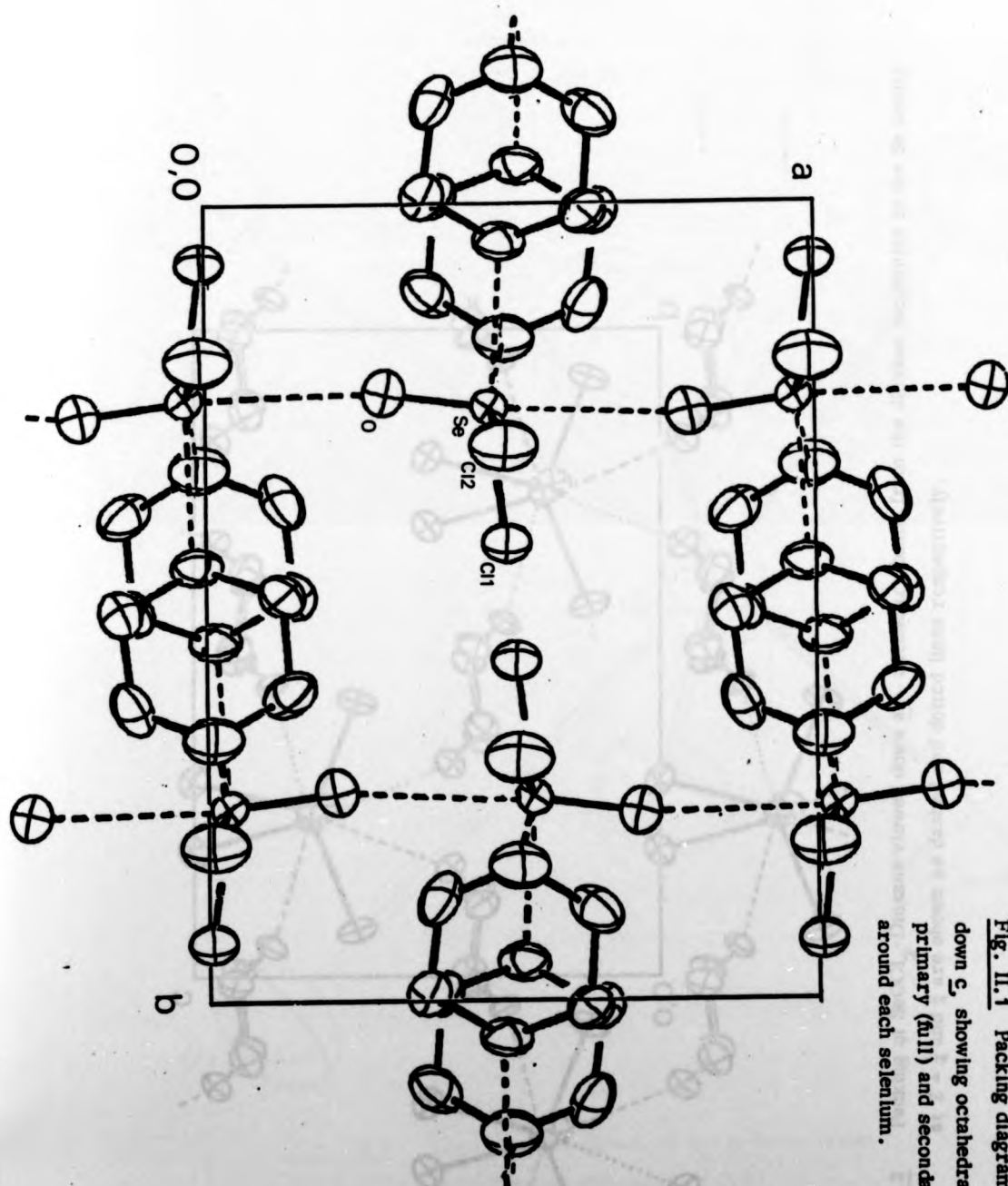
Fig. II.1 Packing diagram for SeOCl$_2$·Dioxane down c, showing octahedral arrangement of primary (full) and secondary (broken) bonds around each selenium.
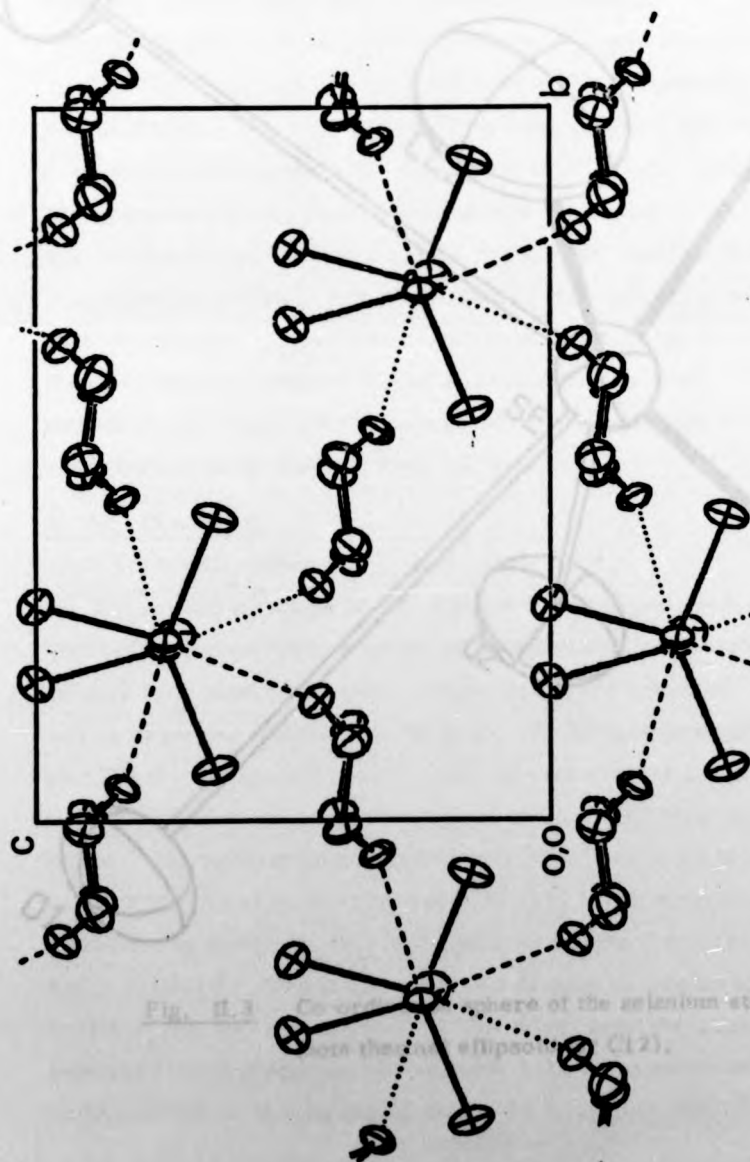
Fig. II.2 Packing of $SeOCl_2 \cdot Dioxane$ viewed down $\underline{a}$. Secondary bonds from the dioxane molecules to the Se atoms at $Z = \frac{1}{4}$ and $\frac{3}{4}$ are shown as dashed and dotted lines respectively.

target atoms and the reflections were given weights given by
$w= [\sigma^2 + (0.02 F)^2]^{...}$ where (i) X = F/10.0 if F<10.0, otherwise X = 0
and (ii) Y = sin $\theta/2.0$, ... if sin $\theta < 0.25$, ... The refinement, including
correction for anomalous dispersion and extinction, converged to 1.0 ...
R and 0.04 and weighted R of 0.040. In the final cycle no parameter
shift was greater than 0.25% of its standard deviation.

... Final positional parameters for the complex, both structures are listed
in Table II, ... along with listings of the equivalent temperature factors
for these atoms. ... Tables of the final structure factors for each
compound are in Appendix ... . Selected bond lengths, contact distances
and related angles for both compounds are tabulated in Tables II. 2 and
information on the dihedral angles, the distance between the ... molecules
and molecular planes to hydroxybenzene are recorded in Tables II.3 and
II. 4 respectively. Two views of the molecular packing in the anhous and
the co-ordination sphere of the Se atom are given in Figs. II. 1-3; the
molecular packing of hydroxybenzene and the ... of the iodine
atom are similarly shown in Figs. II. 4 ... II ...

II. 5.   Discussion

(II. 5. 1.) SeOCl$_2$·dioxane

The crystal structure of the anhydrous ... dioxane with selenium
dichloride contains infinite sheets of ... dichloride molecules
bridged by dioxane molecules. ... These sheets are linked into a periodic
lattice by further interactions via Se-Cl ... Se bridges forming chains
parallel to c ... (Figs. II. 1 and 2). The co-ordination about each selenium
atom is a distorted octahedron of three primary and three secondary ...
bonds. ... The primary co-ordination consists of two Se-Cl bonds of 2.225(1)
... , 2.202(1) Å and an Se-O bond of 1.974(1) Å with the octahedron
completed by three cis Se...O contacts of lengths 2.618(12), 2.726(15)
and 2.902(11) Å. ... Two slightly different dioxane molecules with Cl-Se...O
angles of ... they occupy ... shield ... from the oxygen atom of an
adjacent selenonyl ... molecule ... take the layers together with the
O-Se...O and Se...O...Se angles being 166.5(13)° and 105.5(14)°. (Fig. II. 3).

**Fig. II. 3   Co-ordination sphere of the selenium atom
(note thermal ellipsoid for Cl 2).**

oxygen atoms and the reflections were given weights given by
$\omega = X*Y*(1/\sigma(F))^2$ where (1) X = F/10.0 if F < 10.0, otherwise X = 1
and (2) Y = sin θ/0.30 if sin θ < 0.30 . The refinement, including
corrections for anomalous dispersion and extinction, converged to a final
R of 0.048 and weighted R of 0.046. In the final cycle no parameter
shift was greater than 0.25% of its standard deviation.

Final positional parameters for all atoms in both structures are listed
in Table II.1 along with listings of the anisotropic temperature factors
for these atoms. Tables of the final structure factors for each
compound are in Appendix B. Significant bond lengths, contact distances
and related angles for both compounds are included in Table II.2 and
information on the dihedral angles in the dioxane molecule of the solvate
and molecular planes in iodoxybenzene are included in Tables II.3 and
II.4 respectively. Two views of the molecular packing in the solvate and
the co-ordination sphere of the Se atom are given in Figs. II. 1-3; the
molecular packing of iodoxybenzene and the co-ordination of the iodine
atom are similarly shown in Figs. II. 4 and 5.

II. 5.   Discussion

(II.5.1.) SeOCl$_2$·dioxane

The crystal structure of the solid solvate of dioxane with seleninyl
dichloride contains infinite layers of seleninyl dichloride molecules
bridged by dioxane molecules. These layers are linked into a polymeric
lattice by further interactions via Se-O...Se bridges forming chains
parallel to c . (Figs.II.1 and 2). The co-ordination about each selenium
atom is a distorted octahedron of three primary and three secondary
bonds. The primary co-ordination consists of two Se-Cl bonds of 2.235(5)
and 2.202(7) Å and an Se-O bond of 1.571(11) Å with the octahedron
completed by three cis Se...O contacts of lengths 2.614(13), 2.724(15)
and 2.902(11) Å. Two involve different dioxane molecules with Cl-Se...O
angles of 168.1(4) and 167.5(4)$^\circ$. The third, from the oxygen atom of an
adjacent selenenyl oxychloride molecule links the layers together with the
O-Se...O and Se-O...Se angles being 168.6(12)$^\circ$ and 166.2(14)$^\circ$. (Fig. II.3).

The Se...O contact distances should be compared with the sums of the covalent and van der Waals radii for oxygen and selenium (1.80 and 3.42 Å respectively).

In the seleninyl dichloride moiety, the two Se-Cl bonds appear to be significantly different but this is almost certainly due to anisotropy of the thermal motion of Cl(2). No corrections for this effect has been made. The average Se-Cl bond length of 2.22 Å should be compared to a value of 2.204(5) Å determined in a gas-phase electron-diffraction study of seleninyl dichloride. In the same study, the Se-O bond length was determined as 1.612(5) Å and the angles Cl-Se-Cl and Cl-Se-O were found to be 96.8(7)° and 105.8(7) respectively.[11] The present study has found a Se-O bond length of 1.571(11) Å, Cl-Se-Cl angle of 95.6(3)° and Cl-Se-O angles of 101.6(7)° and 103.6(12)°. Clearly, the differences between the seleninyl dichloride in the solvate with the parameters observed for the molecule in the gas phase are slight.

In other solvates the Se-Cl bond length has an average value of 2.123 Å (based on 6 measurements ranging from 2.09(1) - 2.141(9) Å) when $SeOCl_2$ acts as a base and 2.235 Å (based on 16 measurements ranging from 2.17(1) -2.251(6) Å) when $SeOCl_2$ acts as an acid.[4] In the present case, the $SeOCl_2$ is somewhat amphoteric in using the lone pair on oxygen in one Se...O secondary bond (that is, acting as a Lewis base) whilst at the same time accepting electron density from the bridging dioxane molecules (Lewis acid behaviour). The Se-Cl distance would, however, indicate that the Lewis acid behaviour is more significant.

In other solvate structures the Se-O bond lengths in the $SeOCl_2$ moiety depend on its function. Thus, in those solvates where it acts as a Lewis base forming a co-ordinate bond via the oxygen atom, the Se-O bonds are lengthened (1.67(1) Å in $SnCl_4 \cdot 2SeOCl_2$[5] and 1.685(24) Å in $SbCl_5 \cdot SeOCl_2$[6]) compared with other solvates where lengths of 1.57 - 1.62 Å* have been observed. It is difficult to see further correlations between the individual values and the strength of the other inter-molecular contacts, partly

---

* The anomalous Se-O value of 1.82 found in $[SeOCl_2 \cdot (C_6H_5)_3PO]_2$ is due to rotational disorder.[3]

Fig. II.4   Two views of isolated molecule of iodoxybenzene.
(a) down b , (b) viewed down the I-C bond.
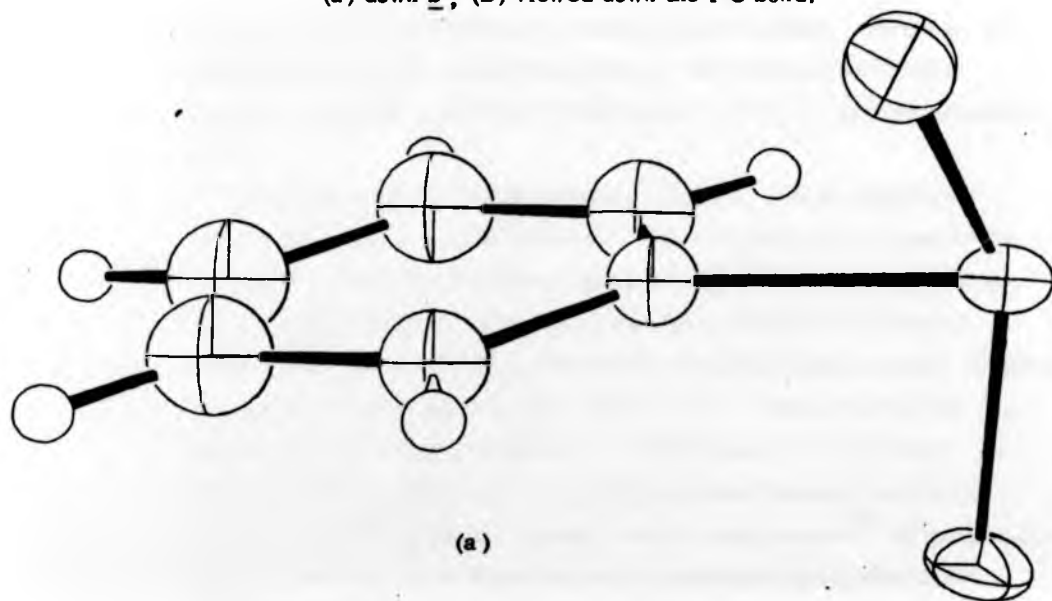
(a)
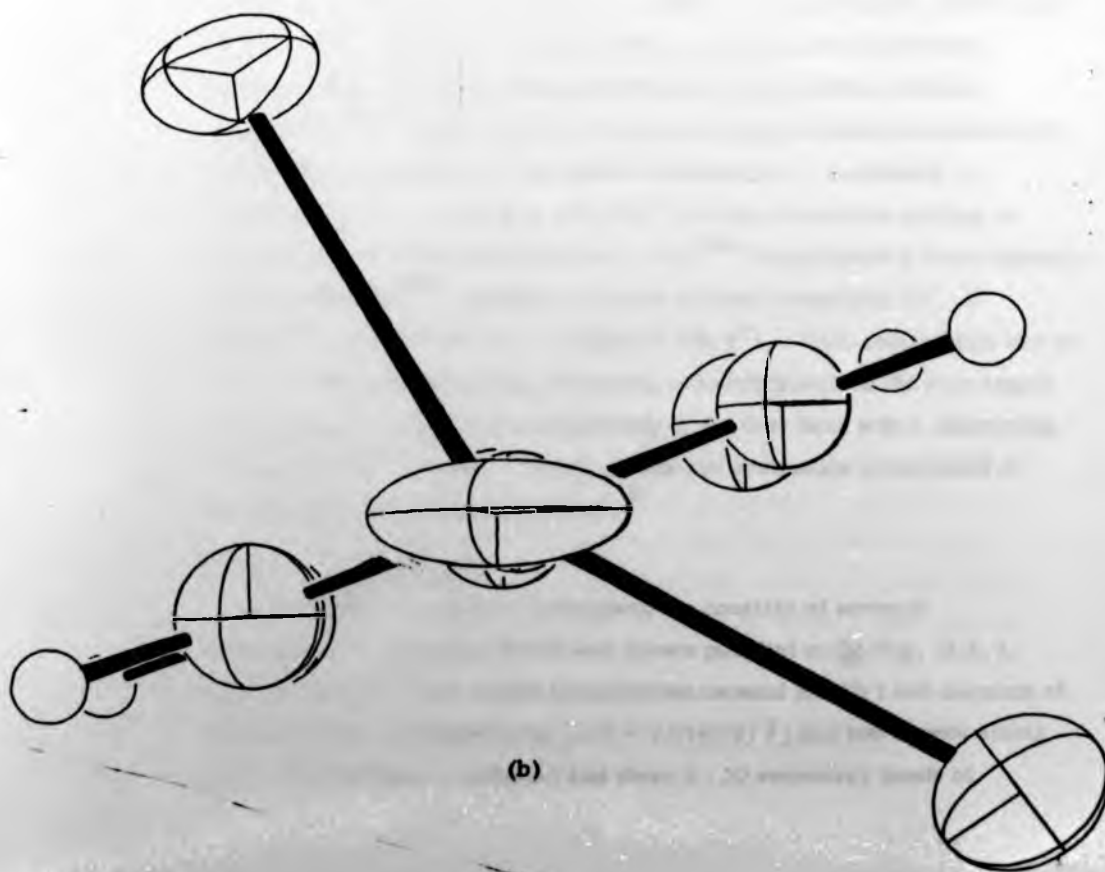
(b)

because of the limited accuracy of some of these values. However, in the present structure, considering that the Se-O bond is involved in bridging interactions, the Se-O bond length (1.57(1) Å) appears somewhat short.

The dihedral angles for the dioxane molecule, which exists in the chair conformation, are in Table II.3. The distances and angles in the molecules are similar to those of dioxane itself.[12] The bridging role of the dioxane giving polymeric layers here has similarly been noted in several other structures of dioxane with molecules such as iodine, bromine and oxalyl chloride where infinite chains occur. Similar behaviour also occurs with the related molecules 1,4-dithiane and 1,4-diselenane, and the short contacts involving the oxygen, sulphur or selenium atoms have generally been described as charge transfer interactions.[13] In the present example, the Se...O contacts involve the equatorial lone pairs of the oxygen atoms.

The Se...O distances in $SeOCl_2 \cdot$ dioxane fall in the middle of the range (2.47 - 3.14 Å) observed in other $SeOCl_2$ solvates, and in the intra-molecular Se...O contact distances found in several other selenium compounds.[14,15] Examples of the latter are bis(o-nitrobenzeneselenenyl) sulfide, in which there are two intra-molecular Se...O contacts of 2.574(8) Å (S-Se...O angle is 171.9(2)°) and the molecular packing is further dictated by Se-S contacts of 3.48 Å;[14a] structure of o-formylphenyl-selenenyl bromide[14b] similarly contains an intra-molecular Se...O contact of 2.31(2) Å (Br-Se...O angle is 176.8°). This contact also has an effect on the o-formyl group, producing a downfield shift of the nmr signal of the aldehyde proton and a lengthening of the C=O bond with a shortening of the adjacent C-C bond. These effects are even more pronounced in the analagous tellurenyl compounds.[16]

(II.5.2.) Iodoxybenzene

The crystal structure of iodoxybenzene consists of strongly distorted ClO_5 octahedra linked into layers parallel to bc (Fig. II.5.). The arrangement about iodine is somewhat unusual for I(V) and consists of primary bonds to a phenyl ring [I-C = 2.014(12) Å] and two oxygen atoms [I-O = 2.021(9) and 1.924(9)Å] and three I...O secondary bonds of

lengths 2.578(8), 2.660(10) and 2.733(9) Å. (Fig. II.5.). The
distortion produced by these secondary bonds is shown in the angles
between the primary bonds. Instead of a tetrahedral AX_3E arrangement
typical of I(V) structures (as found in iodates[17]) the O-I-O angle has
opened to 147.8(4)^O with the C-I-O closing to 91.1(4) and 76.3(4)^O so
that the geometry is intermediate between AX_3E and a typical AX_3E_2
trigonal bipyramidal arrangement normally associated with I(III).[†]

In chemical terms the present geometry should perhaps be regarded
as polymeric. Then the I-O bond lengths, which are long compared with
other IO_3^- structures based on an octahedron of 3 primary and 3 secondary
bonds, would be similar in length to bridging I-O distances in other
polymeric ions such as HI_3O_8.[18]

The deviation of the present geometry from an ideal T-shaped
arrangement can be seen from the difference between the angle O-I-O
[147.8^O] and the sum of the two C-I-O angles [167.4^O] and the displacement
[1.83 Å] of C(1) from the OIO plane. The considerable distortion in
the primary geometry also forces a close intra-molecular I...C(2)
repulsive contact. Other evidence of this repulsive contact can be seen
from the I-C-C angles which are significantly different [116(1) cf.
122(1)^O]

As a result of the pseudosymmetry present in the refinement, the
other distances and angles in the phenyl ring are less accurate and no
conclusions can be drawn although the effect of the iodine atom would be
expected to slightly alter some of the ring angles. (See discussion of
dppm and dppe ligands in Chapter VII).

If the present geometry is regarded as distorted trigonal bipyramidal,
the phenyl ring being less electronegative than oxygen would be expected
to be equatorial. The observed I-C distance is very close to normal
I-C distances observed in other complexes (see Chapter III), and the sum
of the covalent radii [2.10 Å]. The I-C distance in the closely related

[†] The normal geometry of an AX_3E_2 arrangement is T-shaped with the lone
pairs and the least electronegative ligand · in the equatorial plane, since
this minimises lone pair-bonding pair repulsions (cf. Chapter III).
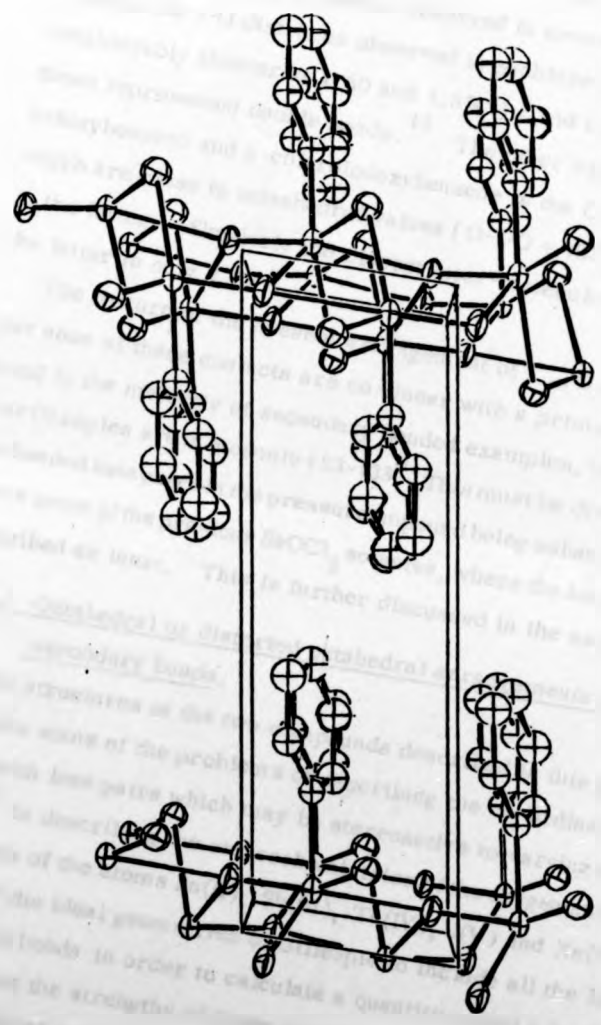
Fig. II.5   Packing diagram for Iodoxybenzene viewed down b.

p-chloroiodoxybenzene [19] is 1.93(5) Å.   However, this determination
is probably of limited accuracy.   The I-O distances are also
close to <u>single</u> bond distances observed in several other complexes
although the I-O distances observed in p-chloroiodoxybenzene are
considerably shorter at 1.60 and 1.65(5) Å and it was suggested that
these represented double bonds. [19]   The other significant difference between
iodoxybenzene and p-chloroiodoxybenzene is the O-I-O and C-I-O angles
which are close to tetrahedral values [O-I-O = 103°; C-I-O = 94 and 95°]
in the latter.   Similarly the closest inter-molecular I...O contact in
the latter is only 2.72 Å .

The feature of the present arrangement of I...O secondary bonds is
that none of these contacts are co-linear with a primary bond as has been
found in the majority of secondary bonded examples. The largest A-I...O (A =
C or O) angles are in fact only 125-133°. This must be directly attributable to the
non-bonded lone pairs in the present compound being substantially more important
than in some of the previous $SeOCl_2$ solvates, where the lone pairs should be
described as inert.   This is further discussed in the next section.

(II.6.)   Octahedral or distorted octahedral arrangements of primary and secondary bonds.

The structures of the two compounds described in this chapter
illustrate some of the problems of describing the co-ordination around
atoms with lone pairs which may be stereoactive to varying degrees.
Brown [17] in describing the stereochemistries of the oxygen and fluorine
complexes of the atoms Sn(II), Sb(III), Te(IV), I(V) and Xe(VI)
redefined the ideal geometries of Gillespie to include all the longer
(secondary) bonds in order to calculate a quantity called a bond valence
to represent the strengths of these additional interactions.   All five of
these redefined geometries are shown in Figure II.6 and can be
described as follows:-

$\mathcal{A}$ ≡ AX_2Y_2E + two secondary bonds of ≈ equal strength (bonds X5 and X6) ≡ $AX_2Y_2s_2E$ overall.

$\mathcal{C}$ ≡ AX_3E + three secondary bonds of ≈ equal strength ≡ AX_3s_3E overall.

$\mathcal{E}$ ≡ AXY_4E + one secondary bond if E stereoinactive ≡ AXY_4CE overall, otherwise AXY_4E.
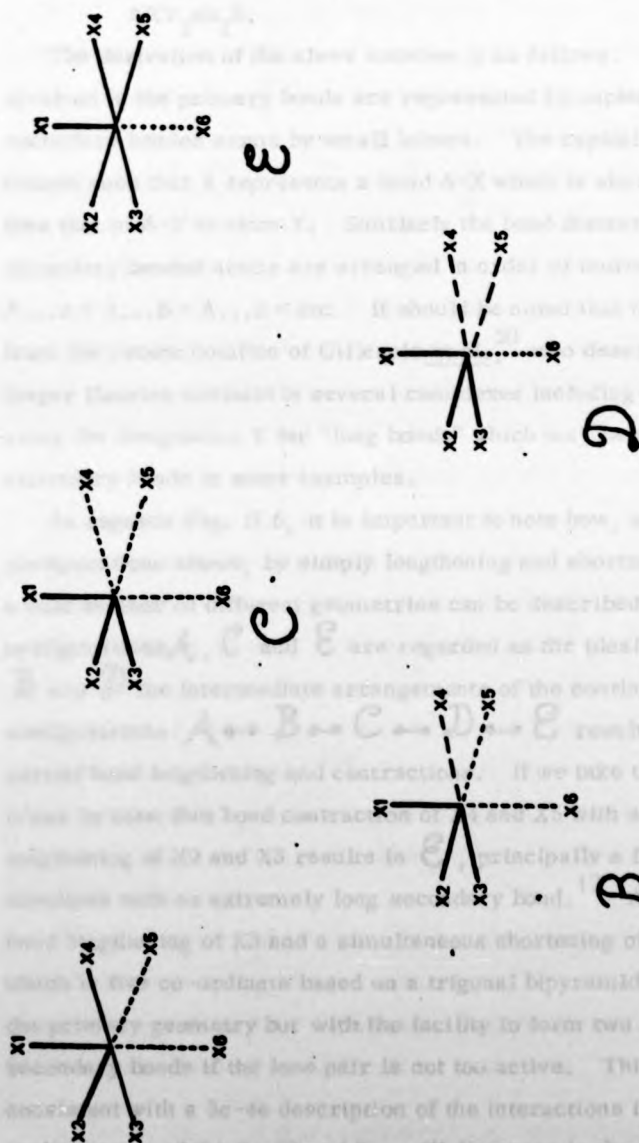
Fig. II.6 Characteristic arrangements of bonds around Sn(II), Sb(III), Te(IV), I(V) and Xe(VI) according to Brown.[17]

$\mathcal{B}$ $\equiv AX_2YE$ + three secondary bonds of different strengths $\equiv$ AX_2Ya_2bE.

$\mathcal{D}$ $\equiv AXY_2E$ + three secondary bonds of different strengths $\equiv$ AXY_2ab_2E.
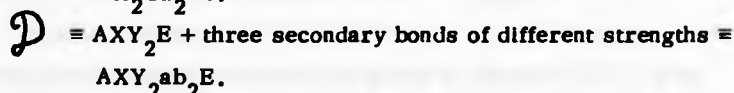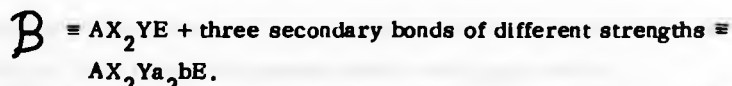
The derivation of the above notation is as follows. The atoms involved in the primary bonds are represented by capital and the secondary bonded atoms by small letters. The capital letters are chosen such that X represents a bond A-X which is shorter (stronger) than that of A-Y to atom Y. Similarly the bond distances to the secondary bonded atoms are arranged in order of increasing length:- A...a < A...b < A...c < etc. It should be noted that the above differs from the recent notation of Gillespie et al.,[20] who described the longer fluorine contacts in several complexes including the ion $[Sb_2F_4]^{2+}$ using the designation Y for "long bonds" which may be equivalent to secondary bonds in some examples.

As regards Fig. II.6, it is important to note how, using the configurations shown, by simply lengthening and shortening trans bonds a vast number of different geometries can be described. The three configurations $\mathcal{A}$, $\mathcal{C}$ and $\mathcal{E}$ are regarded as the ideal geometries with $\mathcal{B}$ and $\mathcal{D}$ the intermediate arrangements of the continuous set of configurations $\mathcal{A} \leftrightarrow \mathcal{B} \leftrightarrow \mathcal{C} \leftrightarrow \mathcal{D} \leftrightarrow \mathcal{E}$ resulting from partial bond lengthening and contractions. If we take the arrangement $\mathcal{C}$ it can be seen that bond contraction of X4 and X5 with simultaneous lengthening of X2 and X3 results in $\mathcal{E}$, principally a five co-ordinate structure with an extremely long secondary bond.[17] Alternatively, a bond lengthening of X3 and a simultaneous shortening of X4 results in $\mathcal{A}$ which is five co-ordinate based on a trigonal bipyramid as regards the primary geometry but with the facility to form two additional secondary bonds if the lone pair is not too active. This idea is consistent with a 3c-4e description of the interactions involved. Cordes[4] in discussion of the Se-Cl and Se...Cl distances in the $SeOCl_2$ solvates has already commented that there are three types of Se-Cl bonds "short",

"long" and "intermediate" - arranged short-long, intermediate-inter-
mediate, etc. to give a constant sum to the trans-bonds.

Further discussion of the bond valence calculations associated with
these co-ordination polyhedra are given in Chapter VI.3. It is
sufficient to say that there are many examples available in the literature
of other complexes of the non-metals bonded to ligands other than O and F
whose co-ordination polyhedra can reasonably be assigned one of the
descriptions A, B, C, D and E from a simple qualtitative analysis
of individual bond distances and angles.[22] Those complexes in which more
than six primary and secondary bonds are involved have higher co-ordination
polyhedra which may be seen to be related to the octahedral arrangements
by simple deformation mechanisms in which one or more of the secondary
bonds in the octahedral arrangement are replaced by several weaker
interactions. The normal cause of this change octahedral → higher
co-ordination is an increased stereoactivity of a lone pair of electrons
which are defined as non-bonding rather than inert[21] (see Chapter VI.).
This appears to be the case with iodoxybenzene. The arrangement about
the iodine in this compound is not very easily defined using any of these
octahedral arrangements, and is probably defined as $AX_3a_3E_2$.

The other complex described in this chapter has a regular[†] octahedral
arrangement of three primary and secondary bonds which has been found in a
number of other examples.[22a] The primary geometry in each case is based
on a tetrahedral AX_3E arrangement of ligands X and lone pair E, although
the overall geometry about the selenium could be described either as
AX_3Y_3E or AX_3a_3E.

A feature of the present octahedral arrangement is that the angles
Y-Se-Y between the cis oxygen contacts are less than 90°. This is
somewhat surprising as the lone pair, if stereochemically active, would
point in a direction bisecting the three Y contacts, and as a consequence

[†] Regular in the sense that secondary bonds are virtually co-linear with
the primary.

the cis angles Y-Se-Y would be expected to be greater than 90° because of repulsive interactions. Furthermore, as the Cl-Se-Cl and Cl-Se-O angles are also intermediate between tetrahedral angles of 109.5^O and angles of 90° based on an octahedron, the stereochemical role of the lone pair may be reduced in the present example and should be defined as inert.[21]

From a qualitative analysis it can readily be seen that the solid solvates of seleninyl dichloride contain selenium co-ordination polyhedra which range from A to E . The present geometry of the dioxane solvate is probably best described as C . Interestingly, the crystal structure of trifluoromethyl selenium trichloride[23] contains a D type configuration about each selenium, the structure contrary to its original description can be regarded as $(CF_3)SeCl_2^+$ ions interacting via extensive Se...Cl interactions. The arrangement in $SeOCl_3^-$ "dimers" of $C_5H_7N_2SeOCl_3$ is very similar $(B)^4$; an E configuration can be found in $SeOCl_2 \cdot 2py.$[7]

Although the $SeOCl_2$ moiety has been extensively investigated in the other known solvates, no low temperature crystal structure of $SeOCl_2$ itself has yet been determined, although Hermoddson attempted a determination without success.[3] However, the analagous seleninyl difluoride structure was recently determined at -35° C. As expected, the $SeOF_2$ is pyramidal [Se-O = 1.62 Å mean, Se-F = 1.70 Å] but forms a layer arrangement through secondary bonds to two oxygens (mean Se...O 2.76 Å) and a fluorine (Se...F 3.03 Å) so that the overall arrangement about the selenium is a distorted octahedron which is very similar to the SeF_3^+ complexes $[SeF_3][Nb_2F_{11}]$, $[SeF_3][NbF_6]$ and the $SeOF_2$ solvate with $NbF_5.$[24] Again these appear to have C configurations.

(II.6.) References

1. I. Lindquist, 'Inorganic Adduct Molecules of Oxo-Compounds', Springer-Verlag, 1963; J. Jackson and G.B.L. Smith, J. Am. Chem. Soc., 1940, 62, 544; M.J. Frazer, J. Chem. Soc., 1961, 3165; J.C. Sheldon and S.Y. Tyree, J. Am. Chem. Soc., 1959, 81, 2290; B. Edgington and J.B. Firth, J. Chem. Ind., 1936, 192.

TABLE II.1

Atomic co-ordinates (x 10^4) with standard deviations in
parentheses.

(a) $SeOCl_2 \cdot Dioxane$

Atom	$\underline{X}$	$\underline{Y}$	$\underline{Z}$
Se	5350(1)	2554(1)	7500(0)
Cl(1)	5070(7)	4263(4)	6522(9)
Cl(2)	5111(10)	3039(5)	10011(8)
O	7090(12)	2370(11)	7300(40)
O(1)	5152(18)	474(10)	8342(18)
O(2)	4905(22)	-1692(12)	9519(18)
C(1)	6426(22)	-95(17)	9102(29)
C(2)	6236(22)	-1283(18)	8881(31)
C(3)	3653(25)	-1126(17)	8833(32)
C(4)	3773(21)	104(16)	9019(28)
H(11)	6347	10	10364
H(12)	7324	174	8854
H(21)	6225	-1384	7754
H(22)	7075	-1681	9309
H(31)	2762	-1408	9322
H(32)	2653	-1260	7749
H(41)	2913	458	8668
H(42)	3748	246	10259

(b) Iodoxybenzene

ATOM	X	Y	Z
I	572.3(5)	0.0	3182.2(14)
O(1)	1097(7)	2586(15)	5807(21)
O(2)	468(7)	-1561(17)	-955(18)
C(1)	2053(9)	-968(21)	3098(28)
C(2)	2268(11)	-2952(26)	4128(35)
C(3)	3263(12)	-3761(32)	4200(38)
C(4)	4023(13)	-2502(28)	3065(41)
C(5)	3804(11)	-506(25)	1995(34)
C(6)	2800(8)	331(29)	1973(24)
H(2)	1728	-3810	4791
H(3)	3440	-5157	5000
H(4)	4716	-3036	3080
H(5)	4334	320	1225
H(6)	2640	1750	1277

TABLE II.1 (cont.) Anisotropic temperature factors † (× 10³) with standard deviations in parentheses

(a) SeOCl₂.Dioxane

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se	29.0(5)	27.7(5)	45.1(6)	-1.5(7)	-0.3(15)	1.2(11)
Cl(1)	52(3)	36(2)	86(4)	-1(2)	1(3)	19(2)
Cl(2)	103(6)	59(3)	50(3)	-1(3)	4(3)	-11(2)
O	38(5)	51(7)	72(14)	3(5)	-3(9)	3(10)
O(1)	61(9)	33(5)	50(8)	-2(5)	8(8)	13(6)
O(2)	80(13)	50(7)	50(8)	-2(7)	5(9)	13(6)
C(1)	42(10)	51(10)	67(15)	5(9)	-1(11)	5(10)
C(2)	43(10)	67(12)	59(12)	20(9)	-3(10)	15(11)
C(3)	60(12)	51(10)	64(13)	-16(10)	-21(10)	10(10)
C(4)	45(10)	43(9)	63(14)	6(8)	-16(10)	15(9)

(b) Iodoxybenzene

Atoms H(11)-H(42) all have U = 0.07

ATOM	U11	U22	U33	U12	U13	U23
I	26.3(3)	91.6(7)	14.9(3)	-1.6(10)	2.9(2)	0.5(16)
O(1)	31(4)	35(6)	32(4)	1(4)	5(3)	-5(4)
O(2)	39(5)	48(7)	16(3)	-9(5)	8(3)	-8(4)

ATOM	U	ATOM	U	ATOM	U	ATOM	U
C(2)	26(2)	C(1)	42(3)	C(3)	48(3)	C(4)	51(4)
C(6)	46(4)	C(5)	32(3)	H(2)	52	H(3)	57
H(5)	61	H(4)	56	H(6)	42		

† In the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$

TABLE II.2

Significant bond lengths (Å), contact distances and related

bond angles (°) with standard deviations in parentheses

(a)   SeOCl$_2$·Dioxane

Bond lengths [†]

Se-Cl(1)	2.235(5)	O(1)-C(1)	1.47(3)
Se-Cl(2)	2.202(7)	O(1)-C(4)	1.42(3)
Se-O	1.571(11)	O(2)-C(2)	1.39(3)
Se...O	2.902(11)	O(2)-C(3)	1.43(3)
Se...O(1)	2.614(13)	C(1)-C(2)	1.46(3)
Se...O(2)	2.724(15)	C(3)-C(4)	1.50(3)

Bond angles (°) [†]

Cl(1)-Se-Cl(2)	95.6(3)	Se-O...Se	166.2(14)
Cl(1)-Se-O	101.6(7)	Se...O(1)-C(1)	121.0(11)
Cl(2)-Se-O	103.6(12)	Se...O(1)-C(4)	117.9(11)
		Se...O(2)-C(4)	124.2(14)
Cl(1)-Se...O(1)	168.1(4)	Se...O(2)-C(3)	119.3(14)
Cl(2)-Se...O(2)	167.5(4)	C(1)-O(1)-C(4)	110.0(15)
O-Se...O	168.6(12)	C(2)-O(2)-C(3)	109.7(16)
O-Se...O(1)	87.7(7)	O(1)-C(1)-C(2)	108.3(17)
O-Se...O(2)	85.9(12)	C(1)-C(2)-O(2)	113.5(18)
O(1)...Se...O(2)	82.9(4)	O(2)-C(3)-C(4)	112.2(18)
O...Se...O(1)	88.8(5)	C(3)-C(4)-O(1)	109.3(16)
O...Se...O(2)	82.9(7)		

[†] The C-H bond lengths range from 0.89 Å to 1.07 Å; C-C-H angles range from 103.6° to 115.8°, OCH angles from 107.5° to 116.0° and HCH angles from 103° to 111°.

(b)   Iodoxybenzene [‡]

Bond lengths (Å)

Around iodine

I - O(1)	2.021(9)	I...O(1')	2.733(9)
I - O(2)	1.924(8)	I...O(2")	2.578(8)
I - C(1)	2.014(12)	I...O(2''')	2.660(10)
I...C(2)	2.872(15)		

Phenyl ring

C(1)-C(2)	1.351(21)	C(2)-H(2)	0.96
C(2)-C(3)	1.380(22)	C(3)-H(3)	0.96
C(3)-C(4)	1.400(26)	C(4)-H(4)	0.96
C(4)-C(5)	1.364(24)	C(5)-H(5)	0.95
C(5)-C(6)	1.400(19)	C(6)-H(6)	0.96
C(6)-C(1)	1.401(19)		

Bond angles (°)

Around iodine

O(1)-I-C(1)	91.1(4)	C(1)-I-O(1')	126.9(4)
O(1)-I-O(2)	147.9(4)	C(1)-I-O(2")	94.7(4)
O(1)-I-O(1')	126.4(3)	C(1)-I-O(2''')	132.8(4)
O(1)-I-O(2")	84.5(3)	O(1')-I-O(2")	59.4(3)
O(1)-I-O(2''')	66.9(3)	O(1')-I-O(2''')	98.6(3)
O(2)-I-C(1)	76.4(4)	O(2")-I-O(2''')	122.1(3)
O(2)-I-O(1')	83.3(3)	I-O(1)-I^{IV}	109.5(3)
O(2)-I-O(2")	125.4(4)	I-O(2)-I^{V}	125.4(5)
O(2)-I-O(2''')	100.2(3)	I-O(2)-I^{VI}	133.1(4)
		I^{V}-O(2)-I^{VI}	96.3(2)

Phenyl ring

I-C(1)-C(2)	115.7(10)	C(2)-C(3)-C(4)	118.3(17)
I-C(1)-C(6)	121.7(10)	C(3)-C(4)-C(5)	121.3(16)
C(6)-C(1)-C(2)	122.6(13)	C(4)-C(5)-C(6)	120.5(15)
C(1)-C(2)-C(3)	120.3(15)	C(5)-C(6)-C(1)	116.9(15)

[‡] Symmetry transformations are:

(i)   -x, $-\frac{1}{2}+y$, -z   (iv) -x, $\frac{1}{2}+y$, 1-z

(ii) x, y, 1+z   (v)   x, y, -1+z

(iii) -x, $\frac{1}{2}+y$, -z   (vi) -x, $-\frac{1}{2}+y$, 2-z

TABLE II.3

Dihedral angles in dioxane molecule

C(1)-O(1)-C(4)-C(3)	+ 57.5
O(1)-C(4)-C(3)-O(2)	-56.4
C(4)-C(3)-O(2)-C(2)	+55.0
C(3)-O(2)-C(2)-C(1)	-57.5
O(2)-C(2)-C(1)-O(1)	+59.1
C(2)-C(1)-O(1)-C(4)	-58.5

TABLE II.4

Equations of the least squares mean planes $PI + QJ + RK = S$[†] in orthogonal angstrom space for iodoxybenzene.

Plane	Defining Atoms	P	Q	R	S
1	I, C(1-6)	0.1290	0.3342	0.9336	1.2487
2	I, O(1), O(2)	0.8111	-0.4698	0.3485	0.8761
3	C(1), I, O(1)	-0.1448	-0.4937	0.8575	1.0031
4	C(1), I, O(2)	0.2609	0.8330	-0.4879	-0.4746

Angles between planes

(1)-(2)	74.16		(2)-(3)	65.58
(1)-(3)	51.91		(2)-(4)	69.53
(1)-(4)	81.75		(3)-(4)	29.84

Atomic displacements from these planes:-[‡]

Plane 1. O(1) by 1.59 Å
     O(2) by -1.85 Å
     O(1') by -0.43 Å
     O(2") by 1.77 Å
     O(2''') by -0.24 Å

Plane 3. O(2) by -0.93 Å
     O(1') by 1.43 Å
     O(2") by 2.56 Å
     O(2''') by -1.67 Å

Plane 2. C(1) by 1.83 Å
     O(1') by 0.87 Å
     O(2") by -0.93 Å
     O(2''') by -2.32 Å

Plane 4. O(1) by 1.01 Å
     O(1') by -2.06 Å
     O(2") by -2.10 Å
     O(2''') by 1.95 Å

[†] The orthogonal unit vector I is parallel to **a**, K is perpendicular to **a** in the **ac** plane and J is perpendicular to the **ac** plane.

[‡] Symmetry transformations are:

(i) $-x, -\frac{1}{2}+y, -z$ (ii) $x, y, 1+z$ (iii) $-x, \frac{1}{2}+y, -z$

(iv) $-x, \frac{1}{2}+y, 1-z$ (v) $x, y, -1+z$ (vi) $-x, -\frac{1}{2}+y, 2-z$

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CHAPTER III

The Iodobenzene Acetates;   planar pentagonal systems with three
centre overlaps

(III. 1.)   Introduction

Before 1970, crystallographic studies of compounds containing organo-
tervalent iodine were restricted to iodobenzene dichloride $(PhICl_2)$[1] and
the diphenyl iodonium compounds.[2]   However, recently many more
structures containing this oxidation state of iodine have been published.[3-5]
In particular, complexes containing the benziodozoline heterocyclic ring
have been investigated by Gougoutas and others to understand the solid
state topotactic transformations displayed by these compounds.[6]   In
all of these compounds the trivalent iodine atoms form three covalent
bonds to other atoms in slightly distorted T-shaped geometries as
predicted for five electron pairs.[7]   As well as covalent bonds, virtually
all of the known structures also contain weak inter- and intra-molecular
co-ordination bonds of remarkably constant orientation around the iodine
atoms.   The lengths of these co-ordination interactions are all less than
the sum of the van der Waals radii for the atoms concerned, and again
may be described as secondary bonds.[8]

There is some importance in considering these interactions in some
detail as one suggested explanation of the extensive molecular
re-organisations necessary for the polymorphic phase transformations in
the benziodoxoline compounds involves intermolecular bond delocalisation
with the weakening of the covalent bonds and strengthening of the weak
inter-molecular bonds.[6]

In this chapter, the crystal structures of iodobenzene diacetate and
iodobenzene bis(dichloroacetate) determined at -60° C are reported, and
the secondary bonding in these compounds is described in terms of a
possible three centre overlap of a σ^* antibonding orbital.   After the
completion of these structural studies, the structure of iodobenzene
diacetate was reported independently although without any discussion of
the longer intramolecular I---O contacts.[9]

(III.2.) Experimental

As mentioned above with the compounds of Gougoutas, there are some experimental difficulties when working with these organo tervalent iodine systems in that solid state topotactic transformations between reactant and preferentially orientated single crystal product phases can occur. A knowledge of the geometrical comparisons between the reactant and product phases can then be of some importance. However, in other examples, changes on irradiation of the crystals at room temperature are normally facile and complex. In the present examples, the crystals rapidly decomposed in the X-ray beam at room temperature, but on cooling the crystals to -60° C using a Syntex LT-1 attachment to the diffractometer, the problem of crystal decomposition was effectively solved. Curiously, in ref. 9, no decomposition was reported.

Both iodobenzene diacetate and iodobenzene bis(dichloroacetate) were prepared by reacting iodosobenzene with the appropriate acid, the iodoso-benzene having been prepared by hydrolysis of iodobenzene dichloride with aqueous sodium hydroxide.[10] In a typical reaction, 2 g iodosobenzene (as a yellow powder) is added to 6 cc of glacial acetic acid and the iodo-benzene diacetate precipitated by the addition of ether. Both acetates occur as colourless needle shaped crystals. The diacetate can be recrystallised from benzene , the bis(dichloroacetate) from carbon tetrachloride or ethanol.

(III.3.) Data Collection and Structure Solution
(III.3.1.) Iodobenzene diacetate (Compound 1)

For the data collection, the crystal used was obtained by cleaving a long thick needle perpendicular to the needle axis. At room temperature, the crystals rapidly decompose in the X-ray beam. However, by cooling the crystal to -60° C using a Syntex LT-1 attachment to the diffractometer, the problem of crystal decomposition was solved.

Crystal data:

$C_{10}H_{11}IO_4$, orthorhombic, a = 15.693(3), b = 8.477(2), c = 8.762(2), U = 1165.5(5) $Å^3$, D_c = 1.835 g/cm^3 for Z = 4. MoK$_\alpha$ radiation, λ = 0.71069 Å, μ(Mo-K$_\alpha$) = 27.75 cm^{-1}, F(000) = 624.0, T = -60° C.

Systematic absences $0kl$, $k + l \neq 2n$ and $h0l$, $h + l \neq 2n$ indicate space groups Pnnm (No. 58) or Pnn2 (No. 34).

Unit cell dimensions and data were collected using a Syntex $P2_1$ diffractometer. Reflections were measured using $\theta - 2\theta$ scans over a scan range $(K_{\alpha_1} - 1.0^O)$ to $(K_{\alpha_2} + 1.0^O)$ to a maximum 2θ of 51°. A variable scan rate of 1^O/min to 29.3^O/min, depending on the intensity of a preliminary 2 sec count, was used. Background counts were recorded at each end of the scan, each for one quarter of the scan time. The intensities of three standard reflections were monitored every 55 reflections. These reflections showed no significant loss in intensity. 1306 data were collected, of which 1063 were considered observed $(I/\sigma(I) \geqslant 3.0)$ and used in refinement.[†]

Lorentz, polarisation and absorption corrections were applied, the last with the program ABSCOR. A Patterson synthesis revealed the position of a single iodine atom. In space group Pnnm this position would impose mirror symmetry on the molecule. However, in a subsequent Fourier phased by this heavy atom, possible light atom positions were too close to their mirror images. The space group symmetry was relaxed to Pnn2 whereupon all light atom positions were located and successfully refined. Hydrogen atoms in the methyl groups were located in a difference Fourier, whilst the ring hydrogen atoms were placed in calculated positions (C-H = 0.95 Å). In the final cycles of least squares refinement, anisotropic temperature factors were used for all non-hydrogen atoms with the hydrogen atom parameters fixed. The weighting scheme used was $w = [1 + \{(F-31)/19\}^2]^{-1}$. The refinement, including corrections for anomalous dispersion and extinction, converged to a final R of 0.021 and weighted R of 0.026; in the final cycle no parameter shift was greater than 20% of its standard deviation. The final difference Fourier was featureless except for residual peaks up to 0.7 e/Å^3 near the iodine. The alternative 'hand' of the molecule was

[†] Two reflections (002) and (020) were too intense to be measured.

rejected because R = 0.022 and wR = 0.026, and distances around the iodine which should be expected to be equivalent differed significantly, (e.g. I-O(1) and I-O(3) were 2.191(5) and 2.130(5) $\mathring{A}$ respectively). The independent determination of (1) gives very similar dimensions (at room temperature), but the co-ordinates have been reported with the opposite hand (1-x, 1-y, z) relative to those in Table 1.[9]

(III.3.2.)   Iodobenzene bis(dichloroacetate) (Compound 2)

A thin needle crystal was used for the data collection.   Again, by cooling the crystal to -60° C, the crystal decomposition was minimal.

Crystal data:

$C_{10}H_7Cl_{21}IO_4$, triclinic, $\underline{a}$ = 10.462(3), $\underline{b}$ = 4.870(2), $\underline{c}$ = 15.445(5) $\mathring{A}$, $\underline{\alpha}$ = 101.03(3)^o, $\underline{\beta}$ = 99.89(3)^o, $\underline{\gamma}$ = 94.40(3)^o, $\underline{U}$ = 756.0(5) $\mathring{A}^3$, D_c = 2.02 g/cm^3 for Z = 2, D_m = 1.96 g/cm^3 (flotation).   MoK$_\alpha$ radiation, λ = 0.71069 $\mathring{A}$; $\mu(MoK_\alpha)$ = 28.49 cm^{-1}. F(000) = 440; T = -60° C. Possible space groups $\underline{P\bar{1}}$ and $\underline{P1}$.

Unit cell dimensions and data were collected using a Syntex P2$_1$ diffractometer.   Reflections were measured using θ-2θ scans over a scan range $(K_{\alpha_1} - 1.2^o)$ to $(K_{\alpha_1} + 1.1^o)$ to a maximum 2θ of 50° in two shells.   The scan rate varied from 1.5 ^{o}/min to 29.3 ^{o}/min and three standards were monitored every 100 reflections.   The crystal was recentred after the first shell of data was completed.   Towards the end of the data collection, the crystal showed signs of decomposition and the data were rescaled in groups using the equations

$F = F_o$ for t ≤ 15.42 hrs   (1)

$F = F_o*(1 + 0.0044985*t)$ for 15.43 < t ≤ 30.59 hrs   (2)

and $F = F_o*(1 = 0.00053*t)(1 + 0.0180*t*sin \theta/\lambda)$ for 30.59
≤ t hrs   (3)

2685 data were collected, of which 1580 were considered observed $(I/\sigma(I) \geqslant 3.0)$ and used in refinement.

Lorentz and polarisation corrections were applied. The absorption correction for the block-shaped crystal used is small and, because of the effects of crystal decomposition, no absorption corrections was performed.   The centrosymmetric space group P$\bar{1}$ was initially assumed

and confirmed by a satisfactory refinement. From a Fourier phased by an iodine atom located in a Patterson map, all remaining heavy atoms were located. In the final cycles of least squares, anisotropic temperature factors were used for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions, but were not refined. The weights used were $(1/\sigma(F))^2$ for reflections within the ranges $10.0 \leq F \leq 21.5$ and $0.29 \leq \sin \theta \leq 0.65$. Reflections outside these ranges are given weights $w = X*Y*(\frac{1}{\sigma(F)})^2$ where (1) $X = (\sin \theta/0.29)$ if $\sin \theta < 0.29$ or $X = (0.65/\sin \theta)$ if $\sin \theta > 0.65$ and (2) $Y = (F/10.0)$ if $F < 10.0$ or $Y = (21.5/F)$ if $F > 21.5$. Four reflections with bad $w* (\Delta F)^2$ values after the application of this weighting scheme were rejected from subsequent refinement cycles. The refinement, including corrections for anomalous dispersion, converged to a final R of 0.058 and weighted R of 0.054.

Final positional parameters for all atoms in both (1) and (2) are listed in Table III.1, bond lengths and angles are in Table III.2, and information on molecular planes in Table III.3. Table III.1 also contains listings of the anisotropic temperature factors for the atoms in (1) and (2). Final structure factors for both compounds are included in Appendix 3A. Views of the isolated molecular units are shown in Figures III.1 and 2, whilst the different crystal packing is given in Figures III.3 and 4.

(III.4)   Discussion of Structures

(III.4.1.)   General

In both (1) and (2) the primary geometry of the trivalent iodine is the familiar T-shaped arrangement with covalent bonds to a phenyl ring and two oxygen atoms of the acetate groups. In (1) the I-O distances are the same (2.156 Å av.) whilst in (2) they differ significantly (2.136(6) and 2.163(7) Å). The I-C distances in (1) and (2), however, are the same (2.08-2.09 Å). These bond lengths should be compared with values of 1.99 Å (I-O) and 2.10 Å (I-C) from the sum of the covalent radii. The corresponding C-I-O angles are 81.4(2) and 82.6(2)$^{\circ}$ for (1); 86.0(3) and 82.5(3)$^{\circ}$ for (2) so that the O-I-O angles are 164.0(2)$^{\circ}$ (1) and 167.1(4) (2). This T-shaped arrangement of covalent bonds has been
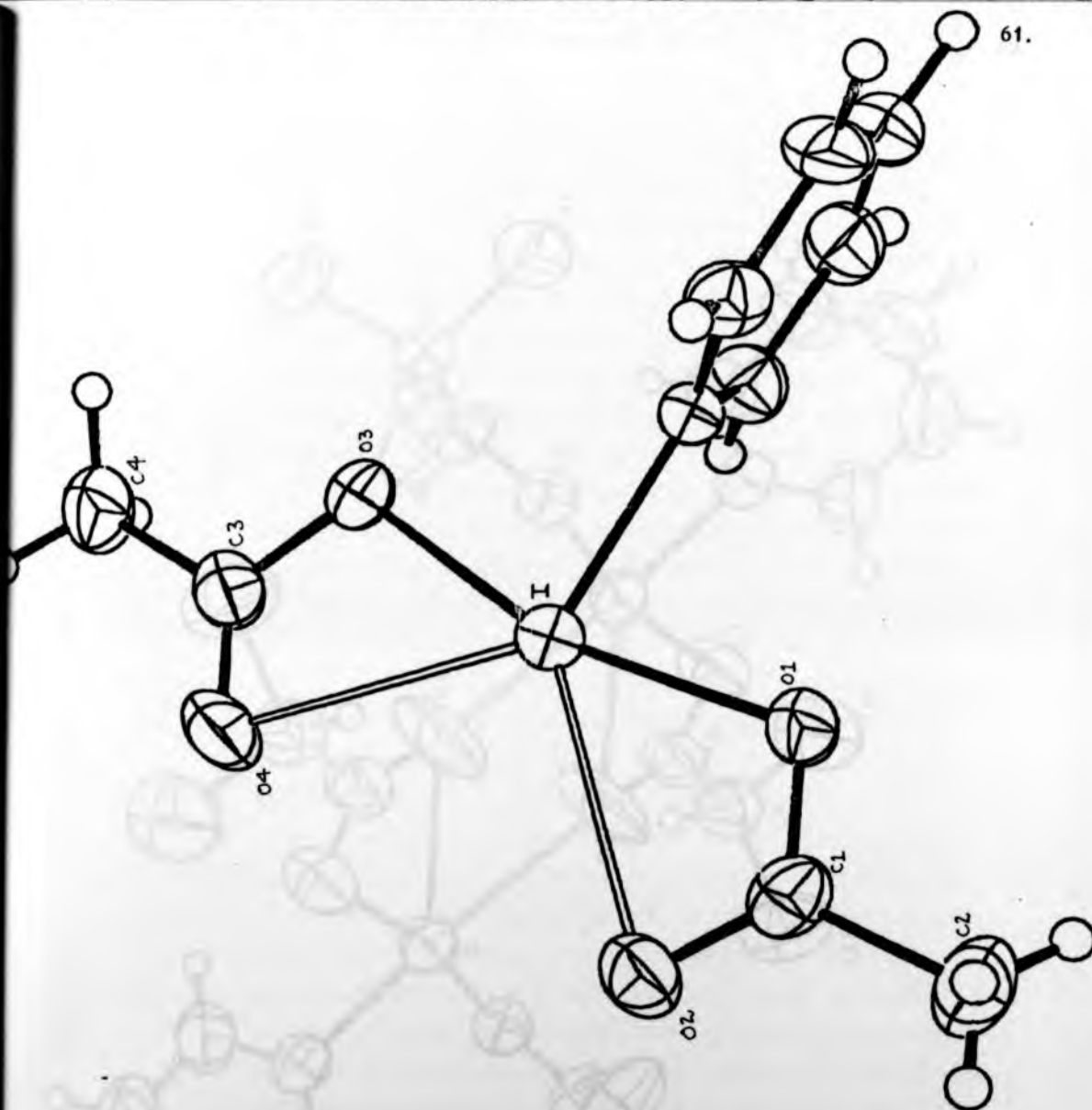
61.

Fig.III·1 ORTEP View of molecule 1 down b rotated 20° about c showing the pentagonal planar arrangement of primary(shaded) and secondary bonds.
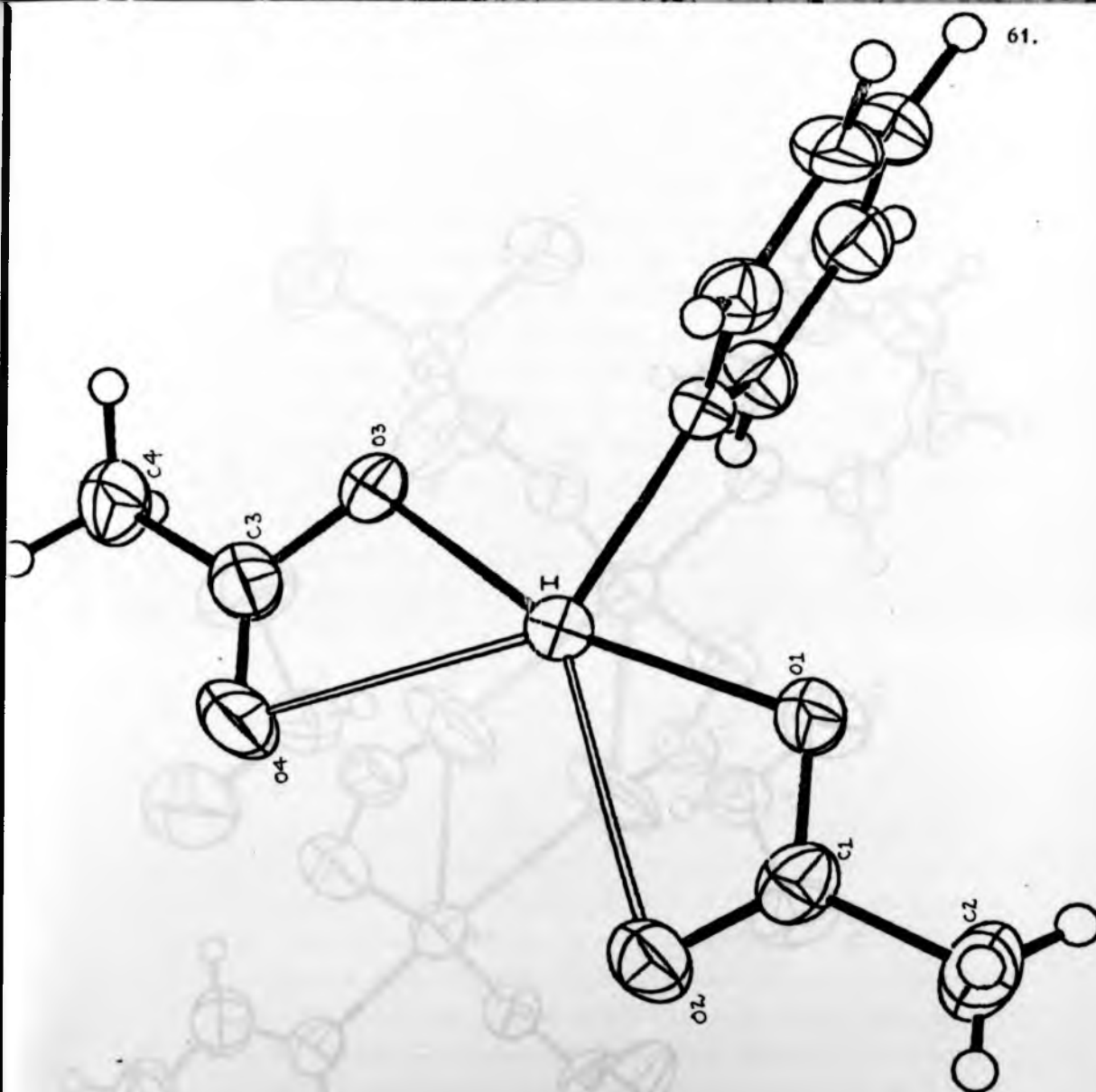
Fig.III·1 ORTEP View of molecule 1 down b rotated 20° about c showing the
pentagonal planar arrangement of primary (shaded) and secondary
bonds.
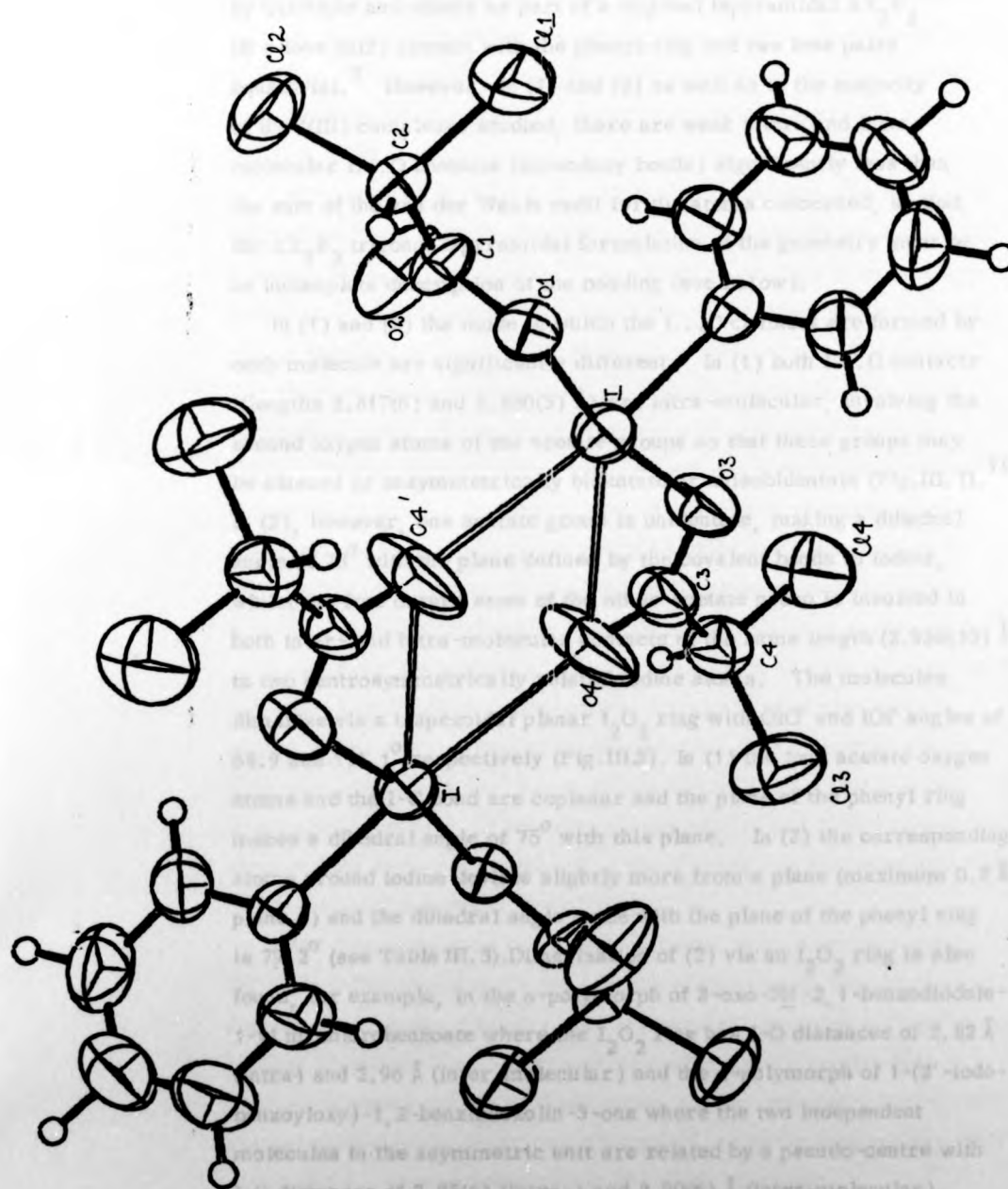
Fig III·2   ORTEP View of molecule 2 down b showing bimolecular units
linked by secondary bonds.

found in most compounds of I(III) investigated, and has been described by Gillespie and others as part of a trigonal bipyramidal AX_3E_2 (E = lone pair) system with the phenyl ring and two lone pairs equatorial.[7] However, in (1) and (2) as well as in the majority of the I(III) complexes studied, there are weak inter- and intra-molecular I...O contacts (secondary bonds) significantly less than the sum of the van der Waals radii for the atoms concerned, so that the AX_3E_2 trigonal bipyramidal formulation of the geometry must be an incomplete description of the bonding (see below).

In (1) and (2) the mode in which the I...O contacts are formed by each molecule are significantly different. In (1) both I...O contacts (lengths 2.817(6) and 2.850(5) Å) are intra-molecular, involving the second oxygen atoms of the acetate groups so that these groups may be classed as unsymmetrically bidentate or anisobidentate (Fig.III.1).[11] In (2), however, one acetate group is unidentate, making a dihedral angle of 78° with the plane defined by the covalent bonds to iodine, whilst the free oxygen atom of the other acetate group is involved in both inter- and intra-molecular contacts of the same length (2.936(10) Å) to two centrosymmetrically related iodine atoms. The molecules dimerise via a trapezoidal planar I_2O_2 ring with OIO' and IOI' angles of 68.9 and 111.1^o respectively (Fig.III.2). In (1) the four acetate oxygen atoms and the I-C bond are coplanar and the plane of the phenyl ring makes a dihedral angle of 75° with this plane. In (2) the corresponding atoms around iodine deviate slightly more from a plane (maximum 0.5 Å - plane 4) and the dihedral angle made with the plane of the phenyl ring is 79.2^o (see Table III.3).Dimerisation of (2) via an I_2O_2 ring is also found, for example, in the α-polymorph of 3-oxo-3H -2,1-benzodiodole-1-yl m chlorobenzoate where the I_2O_2 ring has I-O distances of 2.82 Å (intra-) and 2.96 Å (inter-molecular) and the α-polymorph of 1-(2'-iodo-benzoyloxy)-1,2-benzIodoxolin-3-one where the two independent molecules in the asymmetric unit are related by a pseudo-centre with I-O distances of 2.85(6) (intra-) and 2.90(6) Å (inter-molecular).

In the corresponding β-polymorph of the latter compound there is a conformational change in the molecule and the two weak co-ordination bonds to the trivalent iodine involve an oxygen atom intramolecularly and a further unique contact to the monovalent iodine atom in the iodo-benzoyloxy group of a centro-symmetrically related molecule I(III) - I(I) is 3.70 Å).[6]

The structures of (1) and (2) are furthermore very similar to the recently solved structure of 'iodobenzene dinitrate' which again contains a pentagonal planar geometry. The structure consists of two iodines linked by an oxygen bridge with all the oxygen atoms of the two nitrate groups involved in primary and secondary interactions to the iodines. The primary geometry of each iodine is again T-shaped, with bonds to the phenyl ring, the bridging oxygen and one oxygen of a nitrate group. The pentagonal planar arrangement about each iodine is then completed by two I...O contacts, one of which is intramolecular and the other involves an oxygen atom of the nitrate group attached to the other iodine which is not involved in any interactions with that iodine. Individual distances and angles involved are contained in Figure III.5.[12]

Apart from the pentagonal planar arrangement of three primary and two secondary bonds described above, trivalent iodine also forms a square planar arrangement of three covalent and one secondary bond. In iodobenzene dichloride[1] and N-chloro-3-aza-3H, 2, 1-benzodiodol-1-yl chloride[6] the I...Cl secondary bonds of 3.40 and 3.36 Å respectively complete the square arrangement of bonds giving dimeric units and chains of co-ordinated molecules respectively.

Etter has noted four basic packing modes in crystals containing trivalent iodine covering the two bonding arrangements described above.[6] Packing modes a and d are the square planar arrangement of three strong and one secondary bond whilst packing modes b and c involve the pentagonal planar system of three strong and two secondary bonds. Both (1) and (2) are of the latter type although (1) uniquely involves two intra-molecular I...O weak bonds and is in a class of its own.
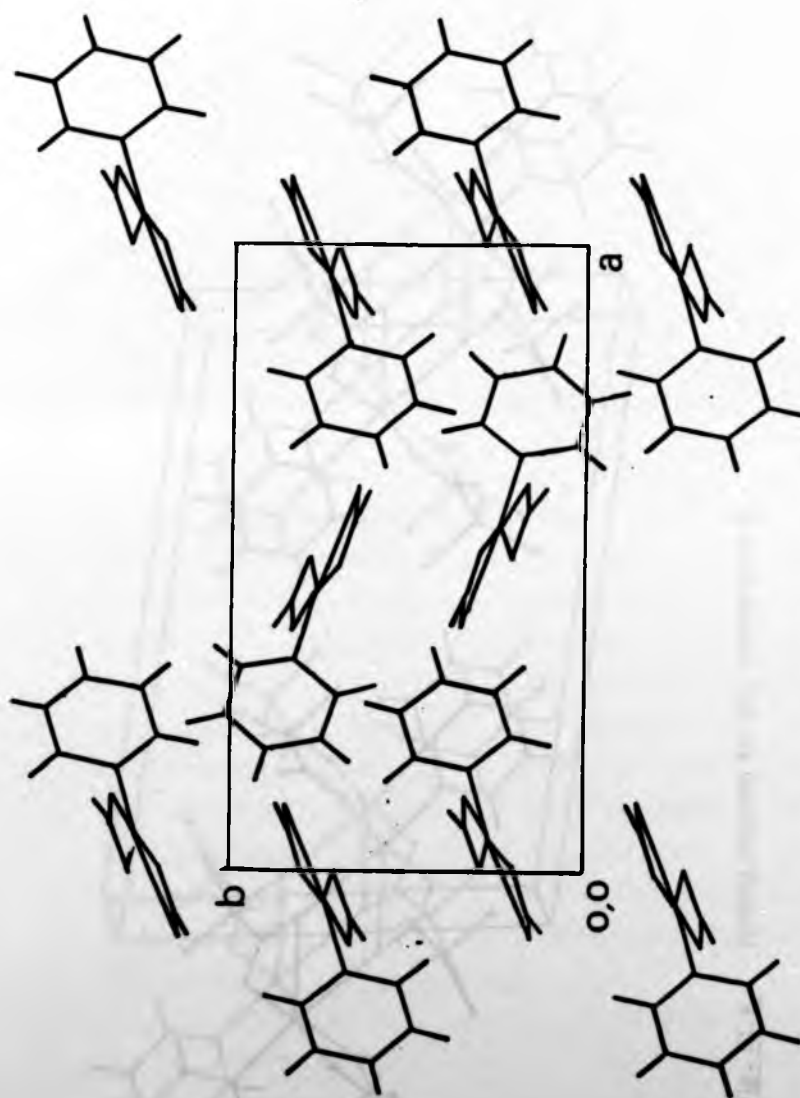
Fig. III.3. Packing diagram for (1), viewed down c.
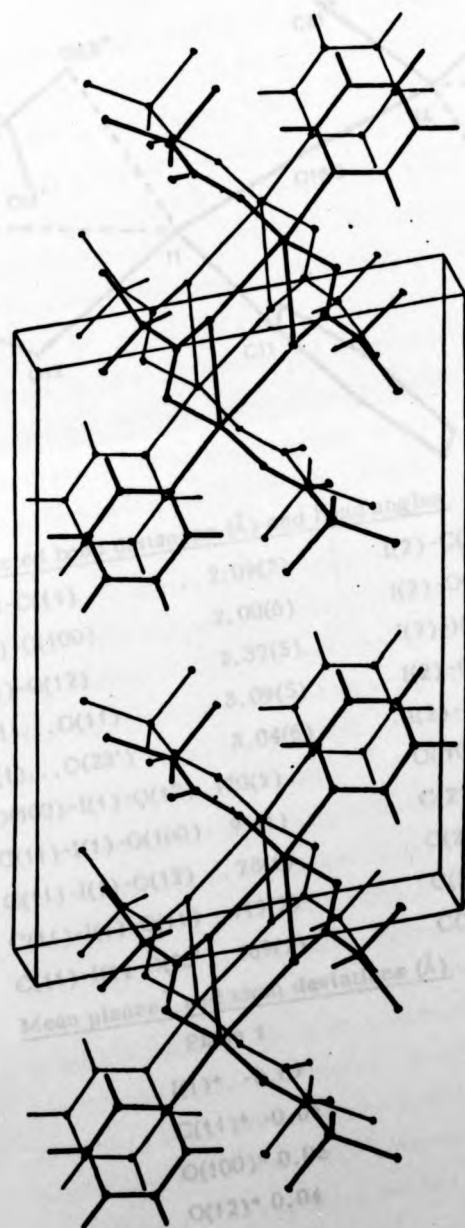
Fig. III. 4. Packing diagram for (2), viewed down b.

Fig. III.5 Structural parameters for "iodobenzene dinitrate".
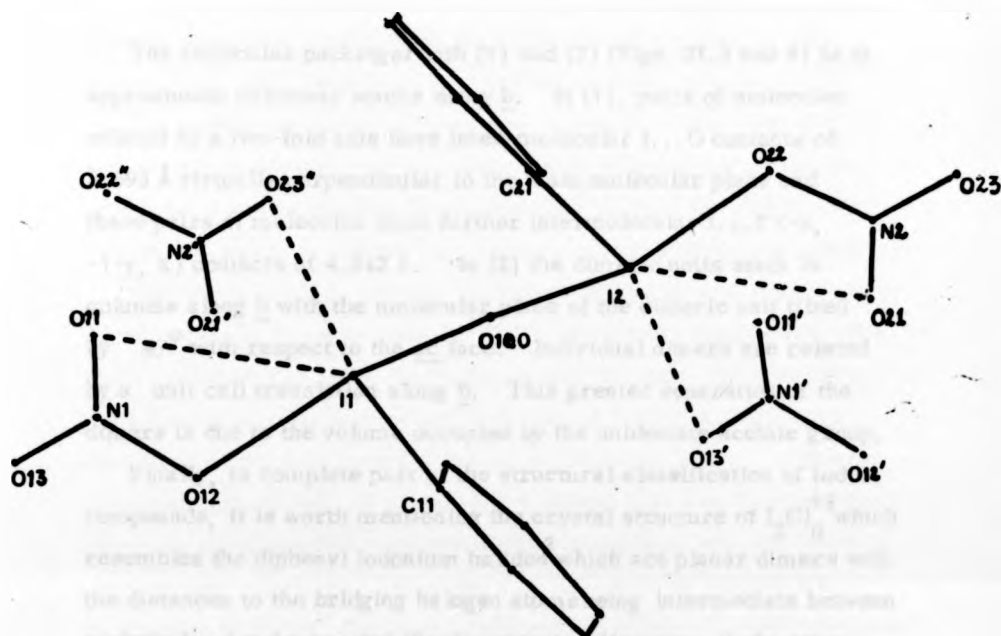
Selected bond distances (Å) and bond angles

I(1)-C(11)	2.09(2)	I(2)-C(21)	2.05(2)
I(1)-O(100)	2.00(6)	I(2)-O(100)	2.02(6)
I(1)-O(12)	2.37(5)	I(2)-)(22)	2.27(5)
I(1)...O(11)	3.09(5)	I(2)-O(21)	2.88(5)
I(1)...O(23')	3.04(6)	I(2)-O(13")	2.99(4)
O(100)-I(1)-O(12)	170(2)	O(100)-I(2)-O(22)	166(2)
C(11)-I(1)-O(100)	96(1)	C(21)-I(2)-O(100)	88(1)
C(11)-I(1)-O(12)	78(1)	C(21)-I(2)-O(22)	79(1)
C(11)-I(1)-O(11)	119(2)	C(21)-I(2)-O(21)	126(2)
C(11)-I(1)-O(23')	169(2)	C(21)-I(2)-O(13")	163(2)

Mean planes † and atom deviations (Å)

Plane 1		Plane 2	
I(1)*.	-0.09	I(2)*	0.08
C(11)*	-0.01	C(21)*	0.01
O(100)*	0.05	O(100)*	-0.05
O(12)*	0.04	O(22)*	-0.04
O(11)	-0.84	O(21)	0.52
O(23)	-0.58	O(13")	0.66

† Atoms defining plane marked with asterisks.

The molecular packing of both (1) and (2) (Figs. III.3 and 4) is in approximate columnar stacks along $\underline{b}$. In (1), pairs of molecules related by a two-fold axis have inter-molecular I...O contacts of 3.693 Å virtually perpendicular to the main molecular plane and these pairs of molecules form further intermolecular I...I' (-x, -1-y, z) contacts of 4.342 Å. In (2) the dimeric units stack in columns along $\underline{b}$ with the molecular plane of the dimeric unit tilted by 46° with respect to the $\underline{ac}$ face. Individual dimers are related by a unit cell translation along $\underline{b}$. This greater separation of the dimers is due to the volume occupied by the unidentate acetate group.

Finally, to complete part of the structural classification of iodine compounds, it is worth mentioning the crystal structure of I_2Cl_6[13] which resembles the diphenyl iodonium halides[2] which are planar dimers with the distances to the bridging halogen atoms being intermediate between a single bond and a van der Waals contact. However, in the other closely related diphenyl iodonium structures, diphenyl iodonium tetra-fluoroborate consists of separated diphenyliodonium and tetrafluoroborate ions whilst the structure of diphenyl iodonium nitrate[2b] consists of infinite zig-zag chains, -I-O-I'-O', with the square planar arrangement about the diphenyl iodonium group being completed by the I-O and I-O' contacts of 2.768(8) and 2.877(8) Å respectively; (C-I-O angles are 170.6 and 168.3° respectively).[14]

The bonding arrangements described above for iodine also occur with other non-metals as the central atom. The square planar arrangement is quite common, either with three primary and one secondary bond, or two primary and two secondary bonds.[8] The square planar arrangement of three primary and one secondary bond has been found, for example, in one crystalline form of bromo(ethylene thiourea) phenyl tellurium(II) and bromo(ethylene selenourea) phenyl tellurium(II) where the Te...Br secondary bonds are of lengths 3.821(1) and 3.849(2) Å (the C-Te...Br angles are 162.3° and 163.3° respectively).[15] The square planar arrangement of two primary and two secondary bonds is also found in

several examples, particularly the structures of the interhalogen cations ICl_2^+, BrF_2^+ and ClF_2^+ with the anions AsF_6^- and SbF_6^-.[8,16]

The pentagonal planar geometry is, however, much rarer for non-metal complexes. An equatorial plane of five bonds of varying strengths is known to occur in compounds with axial (or pseudo-axial) lone pairs, and also with the axial lone pair(s) replaced by a ligand(s).

With three primary and two secondary bonds, the pentagonal planar arrangement of bonds is found for Te(II) and Xe(IV) compounds. The XeF_3^+ cation in $XeF_3^+SbF_6^-$ is T-shaped with two axial Xe-F bonds of 1.91 Å and a shorter equatorial Xe-F bond of 1.84 Å and was again described as trigonal bipyramidal AX_3E_2 (E = lone pair).[17] However, there are further Xe...F contacts of 2.49 and 2.71 Å to fluorine atoms in two neighbouring SbF_6^- cations which are coplanar with the primary Xe-F bonds; the F-Xe...F angles are 153° and 143° respectively. In the case of Te(II), the anion $[Te(Etxan)_3]^-$ (Etxan = O-ethylxanthate) is pentagonal planar with three strong and two weaker bonds involving two unsymmetrically bidentate and one unidentate ligands.[18] Other Te(II) compounds are known with two strong covalent bonds and three weaker intra- and inter-molecular bonds coplanar with the covalent bonds. Thus in $Te[(S_2CNEt_2)_2]$ there is a planar TeS_4 group formed by the unsymmetrically bidentate ligands and the fifth Te...S contact of length 3.579(5) Å is made by a sulphur atom in a centrosymmetrically related molecule with this atom 0.5 Å out of the plane defined by the TeS_4 group.[19] The crystal structures of tellurium(II)(dimethylxanthate) and tellurium(II) di(ethylxanthate)[21] are similar: planar TeS_4 groups with unsymmetrical Te-S distances and a fifth inter-molecular contact (Te...S distances 3.51 and 3.61 Å respectively). The deviations of the S atoms forming these contacts from the planes defined by the TeS_4 groups are 1.10 and 0.65 Å respectively.

An equatorial arrangement of five pentagonal bonds of widely different strengths can also be found with axial substituents so that the geometry is derived from a pentagonal bipyramid. To give a few

examples, in bis(1-oxopyridine-2-thiolato)phenylbismuth there is an intermolecular Bi...O of 3.37 Å completing the equatorial pentagonal plane of bonds and results in dimeric units. The phenyl group and a lone pair are in axial positions.[21] In [Pb(O-ethylxanthate)$_3$]$^-$ an equatorial plane of two strong and three weak Pb-S distances occur with a further Pb-S bond and a lone pair presumed to be axial. A further even longer Pb-S inter-molecular contact close to the direction of the lone pair results in dimeric units again.[22] Even in dimethylthallium(I) dimethylxanthate three inter-molecular contacts appear to be in the same plane as the primary Te-S bonds with the methyl groups axial.[23]

(III.4.2.) Bonding Models [19]

Three possible bonding models can be considered for these planar pentagonal systems involving bonds of very different lengths. The simplest treats the primary covalent bonds as 2 centre-2 electron bonds and any additional interactions are considered to be electrostatic. This model, however, fails to explain why the primary and secondary bonds in these systems are, within reasonable limits, coplanar.

Secondly, it has been proposed for the anion [Te(Etxan)$_3$]$^-$ that it might represent an AX_5E_2 system on the Gillespie-Nyholm model.[18] With two lone pairs, the expectation of the geometry would presumably be the pentagonal planar arrangement. The two lone pairs would be in axial positions perpendicular to the plane, minimising lone pair bond pair interactions since the alternative of equatorial lone pairs would give (with all bonds equal) lone pair-bond pair angles of 72° in the plane. The drawback to this model is the difference in strength between the strong and weak bonds. One explanation for this, advanced to explain the asymmetric dithiolate ligands in [Te(Etxan)$_3$]$^-$ and related complexes, suggests that the repulsion between the bonding electrons of the short Te-S bond to the unidentate ligand and the axial lone pairs is stronger than other bond pair-lone pair interactions; this forces the lone pairs into an off-axial position away from the unidentate ligand.

The two Te-S bonds furthest from the unidentate ligand lengthen as a consequence of the increased repulsion from these off-axial lone pairs.[18] The asymmetry in the shorter Te-S bond lengths (one of 2.50 Å and two of 2.66 Å) seems, however, too modest to account for the substantial lengthening of the two other Te...S bonds.

Overcrowding might offer an alternative explanation for the difference in the bond lengths and a useful comparison is with uranyl complexes which often have pentagonal planar co-ordination around the axial UO_2^{2+} group. The geometrical constraints of these compounds are fairly well understood and it appears that non-bonded O...O contacts of 2.6 - 2.8 Å are the minimum to avoid distortions due to overcrowding which, if sufficiently strong, will cause the expulsion of a ligand.[24] In (1) the non-bonded O...O contacts in the AX_5 plane is 4.2 Å, whilst in (2) it is 3.32 Å. These will clearly not impose any steric constraints.

A third approach describes the longer I...O and Te...S interactions using the secondary bonding model. In its normal form (Introduction) it normally predicts a linear X-A...Y system. However, in the pentagonal planar examples, the long inter- and intra-molecular contacts are far from being colinear with a covalent bond; typically O-I...O, C-I...O or S-Te...S angles are in the range 140-150°.

It is, however, possible to modify the secondary bonding model to account for this geometry by considering the overlap of the I-C σ^* orbital not with one filled orbital (e.g. a p orbital on chlorine in $PhICl_2$) but with two. Thus, two "unco-ordinated" oxygen atoms of two acetate groups give two filled non-bonding or weakly bonding orbitals concentrated between the heavy atom and the oxygen atoms (Fig. III.6).The resulting molecular orbitals resemble the three centre bonding orbital description found in the triangular faces in boranes.[25] In the alternative case of the Te(II) compounds with two strong and three weak bonds, the secondary bonding description requires the formation of two separate three centre systems involving three lone pairs on sulphur atoms overlapping with the σ^* orbitals of the strong covalent Te-S bonds (Fig. III.6).
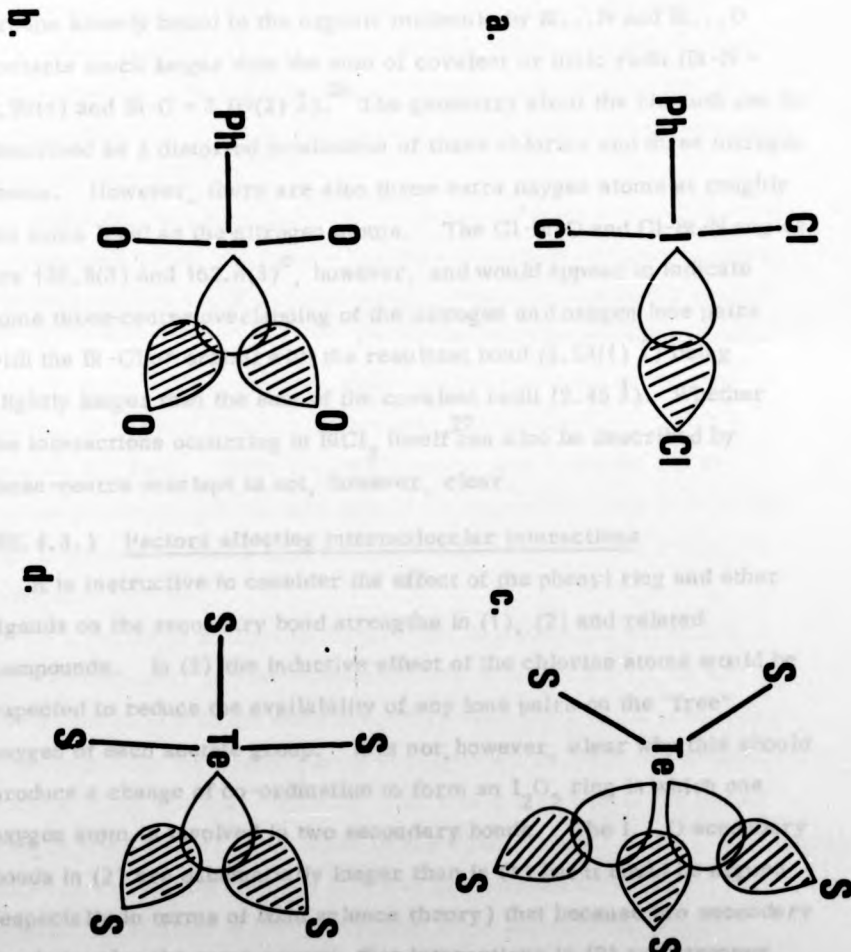
Fig. III.6. Two and three centre secondary bonding overlaps in (1), (2) (a. and b.) and related Te compounds (c. and d.). Shaded orbitals are filled.

This three-centre overlap model can be used to rationalise several other examples of anomalously long interactions. For example, the crystal structure of the pharmaceutically important molecule trichloro-tris)3-sulfanilamide-6-methoxy-pyridazine)bismuth(III) has three-fold symmetry, lying on the axis in space group $\underline{R}\,3$, and contains $BiCl_3$ groups loosely bound to the organic molecule by $Bi...N$ and $Bi...O$ contacts much longer than the sum of covalent or ionic radii ($Bi-N = 2.90(1)$ and $Bi-O = 3.09(2)$ Å).[26] The geometry about the bismuth can be described as a distorted octahedron of three chlorine and three nitrogen atoms. However, there are also three extra oxygen atoms at roughly the same level as the nitrogen atoms. The Cl-Bi-O and Cl-Bi-N angles are $139.8(3)$ and $162.6(3)^o$, however, and would appear to indicate some three-centre overlapping of the nitrogen and oxygen lone pairs with the Bi-Cl σ^* orbital with the resultant bond ($2.53(1)$ Å) being slightly longer than the sum of the covalent radii (2.45 Å). Whether the interactions occurring in $BiCl_3$ itself[27] can also be described by three-centre overlaps is not, however, clear.

(III.4.3.) Factors affecting intermolecular interactions

It is instructive to consider the effect of the phenyl ring and other ligands on the secondary bond strengths in (1), (2) and related compounds. In (2) the inductive effect of the chlorine atoms would be expected to reduce the availability of any lone pairs on the "free" oxygen of each acetate group. It is not, however, clear why this should produce a change of co-ordination to form an I_2O_2 ring in which one oxygen atom is involved in two secondary bonds. The I...O secondary bonds in (2) are substantially longer than in (1) but it could be argued (especially in terms of bond valence theory) that because two secondary bonds involve the same oxygen, that interactions in (2) are stronger overall. Why only the oxygen atom O3 is so co-ordinated is difficult to explain. Clearly there should be observable differences in the solid state i.r. between the vibrations of the two acetate groups in (2).

An alternative way of affecting the strength of the secondary bonds would be to reduce the availability of the I-C σ^* orbital with which the

lone pairs overlap. This will be affected by inductive and other
interactions with substituents on the phenyl ring. Interactions
involving the phenyl ring can also be observed cis as well as trans
to the I-C(Ph) bond. In phenylhydroxytosyloxyiodine, the phenyl
group occurs in the bar of the T so that there are no further atoms
trans to the equatorial I-O bond (cis to the phenyl) which would
complete a square planar arrangement (cf. $PhICl_2$). Furthermore,
there appears to be a lengthening of the equatorial bond so that the
I-O distance of 2.473 Å is significantly longer than in other compounds
(e.g. (1) and (2)).[5]

Although, in a brief report of the crystal structure of p-chloroiodo-
benzene dichloride, the system has been described as having a square
planar arrangement of 3 primary and 1 secondary bond very similar
to that of $PhICl_2$, the actual I...Cl distance and atomic co-ordinates
are not given.[1b] The inductive withdrawal of electrons by chlorine
through the phenyl ring would, however, be expected to produce a
weaker I-C bond. Hence the small energy gain when the I-C σ^*
orbital interacts with the lone pair of Cl intermolecularly will be less
and one could predict a longer I...Cl secondary bond in $ClPhICl_2$ as
compared to $PhICl_2$.

In a series of phenyltellurium(II) halide complexes PhTeLX (L =
ethylenethiourea, ethyleneselenourea and thiourea; X = Cl, Br and I),
the presence of a fourth weak secondary bond trans to the phenyl ring
and completing the square planar arrangement of bonds can be apparently
related to the dihedral angles made by either the plane of the phenyl
ring (a trans effect) or the plane of the ligand L (a cis effect), with the
plane containing the primary covalent bonds to the tellurium.[28] A
similar correlation of phenyl dihedral angle and secondary bond
formation is not so easy for I(III). In $PhICl_2$[1a] the phenyl ring is
perpendicular to the Cl-I-Cl line whilst in complexes containing the
benziodoxoline nucleus the phenyl ring is forced to be coplanar with
the bonds to iodine. In this latter case, there may be π-interactions

with any lone pair orbitals perpendicular to the plane of the molecule; with the phenyl ring perpendicular there may be repulsion between the ring π-orbitals and the I-Cl orbitals.

In comparing compounds (1) and (2) it is again clear that the secondary bonds are very sensitive to slight changes in ligands and the resulting conformational effects can be considerable. Similar conclusions have been reached on the basis of i.r. and Mössbauer evidence particularly for organotellurium compounds.[29]

(III. 4. 4.)   Conclusions

In selecting between the alternative explanations of the present geometries of (1) and (2) in terms of an AX_5E_2 system with axial lone pairs, or an AX_3E_2 system with two secondary bonds (forced into the same plane as the primary bonds by repulsion from the pseudo-axial lone pairs) the balance appears to lie towards the latter. In particular, it appears to offer a more satisfactory explanation for the essentially undisturbed T-shaped geometry of the primary bonds, and the large difference in bond length between the primary and secondary bonds. For the Te(II) compounds mentioned, a single bonding description cannot be used to cover both $[Te(Etxan)_3]_3$ and the two examples of tellurium(II) di(methylxanthate) and di(ethylxanthate). The former is again best described as AX_3E_2 plus secondary bonds, whilst the latter examples with two strong and three weak secondary bonds are probably classified as AX_2E_2 systems with the two lone pairs approximately tetrahedrally disposed with respect to the bonding pairs forcing the Te...S contacts into the same plane as the primary bonds. The alternative AX_3E_2 classification would have one of the weak secondary bonds in the same direction as one of the lone pairs. The XeF_3^+ examples are again best described as AX_3E_2 with two secondary bonds.

Table III·1 Atomic co-ordinates (x 10^4) with standard deviations in parentheses

(1) Iodobenzene diacetate

Atom	X	Y	Z
I	9508.5(2)	7393.9(3)	0(0)
O(1)	8791(3)	6610(5)	1960(5)
O(2)	10023(4)	7127(7)	3069(6)
O(3)	9911(3)	7959(5)	-2285(6)
O(4)	11106(3)	8549(5)	-1072(6)
C(1)	8875(5)	6155(9)	4626(7)
C(2)	9294(4)	6664(8)	3160(8)
C(3)	11069(5)	8786(9)	-3820(9)
C(4)	10705(4)	8424(6)	-2268(8)
C(5)	8381(4)	6768(7)	-1114(7)
C(6)	7846(4)	7971(7)	-1643(8)
C(7)	7111(4)	7513(8)	-2397(8)
C(8)	6933(4)	5955(10)	-2641(8)
C(9)	7466(5)	4811(8)	-2117(8)
C(10)	8205(4)	5210(7)	-1318(8)
H(11)	8243	6532	4569
H(12)	9188	6660	5452
H(13)	8908	4989	4672
H(31)	10981	9757	-3937
H(32)	10860	8291	-4524
H(33)	11524	8985	-3802
H(1)	7980	9043	-1546
H(2)	6733	8313	-2815
H(3)	6426	5665	-3219
H(4)	7335	3736	-2347
H(5)	8567	4434	-984

(2) Iodobenzene bis(dichloroacetate)

Atom	X	Y	Z
I	4256.8(8)	119.0(16)	1405.9(5)
Cl(1)	8639(3)	4349(9)	4122(2)
Cl(2)	6143(4)	5816(12)	4407(2)
Cl(3)	1289(4)	-5061(9)	-1741(2)
Cl(4)	1093(4)	-8047(8)	-325(2)
O(1)	5429(7)	3393(13)	2413(5)
O(2)	6831(10)	394(21)	2708(7)
O(3)	2825(8)	-3217(16)	585(5)
O(4)	3869(12)	-2677(31)	-495(6)
C(1)	7120(10)	5071(24)	3614(7)
C(2)	6441(12)	2669(25)	2880(7)
C(3)	2141(12)	-6380(27)	-832(8)
C(4)	3042(13)	-3886(30)	-212(8)
C(5)	3053(11)	-110(21)	2340(7)
C(6)	3413(13)	-1547(27)	3006(9)
C(7)	2662(19)	-1637(32)	3613(9)
C(8)	1578(19)	-495(38)	3547(10)
C(9)	1195(14)	932(36)	2888(12)
C(10)	1942(14)	1129(28)	2260(9)
H(11)	7248	6724	3350
H(31)	2710	-7749	-1049
H(1)	4211	-2396	3041
H(2)	2884	-2556	4107
H(3)	983	-541	4013
H(4)	335	1704	2823
H(5)	1694	2073	1752

TABLE III.1 (cont.)   78.

Anisotropic temperature factors Uij ($\times 10^3$) with standard deviations in parentheses.   *In the form $\exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$

(1) Iodobenzene diacetate

Atom	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
I	27.6(2)	36.1(2)	30.3(2)	-0.5(1)	-0.8(3)	-1.5(4)
O(1)	34(2)	53(2)	28(2)	-3(2)	6(2)	2(2)
O(2)	47(3)	108(4)	34(3)	-27(3)	-10(3)	1(3)
O(3)	37(2)	62(2)	26(2)	-12(2)	0(2)	1(2)
O(4)	43(2)	48(2)	38(2)	-10(2)	-6(2)	-1(2)
C(1)	58(4)	76(4)	31(4)	-11(4)	3(3)	1(3)
C(2)	44(4)	51(3)	34(4)	-5(3)	-3(3)	-3(3)
C(3)	61(5)	67(4)	36(4)	-19(4)	16(4)	-7(3)
C(4)	41(3)	33(3)	38(4)	-3(2)	8(3)	1(2)
C(5)	25(3)	42(3)	27(3)	-3(2)	0(2)	-5(2)
C(6)	35(3)	37(3)	40(3)	-1(2)	2(3)	5(3)
C(7)	29(3)	62(4)	44(4)	9(3)	-6(3)	8(3)
C(8)	32(3)	80(5)	38(4)	-11(3)	-3(3)	-11(3)
C(9)	46(3)	55(4)	46(4)	-14(3)	-0(3)	-15(3)
C(10)	43(3)	37(3)	42(4)	0(2)	-3(3)	-3(3)

Atoms H(11, 12, 13, 31, 32, 33) have U = 0.07
Atoms H(1, 2, 3, 4, 5) have U = 0.05

(2) Iodobenzene bis(dichloroacetate)

Atom	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
I	51.0(8)	51.3(6)	48.8(6)	0.0(3)	7.7(3)	5.1(3)
Cl(1)	64(2)	128(3)	83(2)	27(2)	-15(2)	11(2)
Cl(2)	91(3)	204(5)	58(2)	53(3)	18(2)	6(2)
Cl(3)	120(4)	115(3)	80(2)	-12(3)	-13(2)	21(2)
Cl(4)	118(3)	98(3)	93(3)	-42(2)	15(2)	14(2)
O(1)	55(5)	46(4)	48(4)	5(4)	9(4)	2(3)
O(2)	97(7)	57(6)	128(8)	12(5)	-29(6)	23(5)
O(3)	76(6)	69(5)	53(5)	23(4)	21(4)	-7(4)
O(4)	128(9)	212(13)	72(6)	-105(9)	54(6)	-23(7)
C(1)	46(7)	74(8)	48(6)	8(6)	1(6)	18(6)
C(2)	47(8)	45(7)	53(7)	4(6)	-8(6)	19(6)
C(3)	71(9)	86(9)	57(7)	-1(7)	13(7)	6(7)
C(4)	65(9)	97(10)	47(8)	-22(8)	12(7)	1(7)
C(5)	47(8)	42(6)	51(7)	0(6)	3(6)	5(5)
C(6)	84(10)	83(9)	68(8)	38(8)	24(8)	30(7)
C(7)	107(14)	97(11)	82(10)	28(10)	39(10)	40(9)
C(8)	85(12)	105(12)	75(10)	-12(10)	35(9)	5(9)
C(9)	56(10)	118(12)	106(12)	28(9)	17(9)	12(10)
C(10)	54(9)	84(9)	87(9)	11(8)	18(8)	33(7)

All hydrogen atoms have U = 0.08

Table III-2 Bond lengths (Å) and bond angles (°) with standard deviations in
parentheses*.

(1) Iodobenzene diacetate

(a) Bond lengths

(i) Around iodine

I-O(1)	2.159(5)
I-O(3)	2.153(5)
I-C(5)	2.090(6)
I...O(2)	2.817(6)
I...O(4)	2.850(5)

(ii) Acetate groups

C(1)-C(2)	1.506(10)	C(3)-C(4)	1.507(10)
C(2)-O(1)	1.316(8)	C(4)-O(3)	1.307(8)
C(2)-O(2)	1.211(9)	C(4)-O(4)	1.227(8)
C(1)-H(11)	1.04	C(3)-H(31)	0.84
C(1)-H(12)	0.97	C(3)-H(32)	0.82
C(1)-H(13)	0.99	C(3)-H(33)	0.73

(iii) Phenyl ring

C(5)-C(6)	1.400(8)	C(6)-H(1)	0.94
C(6)-C(7)	1.384(9)	C(7)-H(2)	0.97
C(7)-C(8)	1.368(11)	C(8)-H(3)	0.97
C(8)-C(9)	1.361(10)	C(9)-H(4)	0.96
C(9)-C(10)	1.396(10)	C(10)-H(5)	0.92
C(10)-C(5)	1.361(8)		

(b) Bond angles

(i) Around iodine

O(1)-I-O(3)	164.0(2)	C(5)-I-O(2)	131.9(2)
O(1)-I-C(5)	81.4(2)	C(5)-I-O(4)	132.7(2)
O(3)-I-C(5)	82.6(2)	O(1)-I-O(4)	145.8(2)
O(2)-I-O(4)	95.2(2)	O(3)-I-O(2)	145.2(2)

(ii) Acetate groups

I-O(1)-C(2)	108.1(4)	I-O(3)-C(4)	109.6(4)
O(1)-C(2)-O(2)	121.7(6)	O(3)-C(4)-O(4)	121.7(6)
O(1)-C(2)-C(1)	114.1(6)	O(3)-C(4)-C(3)	114.4(6)
O(2)-C(2)-C(1)	124.2(7)	O(4)-C(4)-C(3)	124.0(6)
I-O(2)-C(2)	79.6(4)	I-O(4)-C(4)	78.5(4)

(iii)   Phenyl ring

I-C(5)-C(6)	118.5(4)
I-C(5)-C(10)	118.7(4)
C(5)-C(6)-C(7)	116.9(6)
C(6)-C(7)-C(8)	121.1(6)
C(7)-C(8)-C(9)	120.6(6)
C(8)-C(9)-C(10)	120.5(6)
C(9)-C(10)-C(5)	118.0(6)

(2)   Iodobenzene bis(dichloroacetate)

(a)   Bond lengths

(i)   Around iodine

I-O(1)	2.136(6)
I-O(3)	2.163(7)
I...O(2)	3.049(10)
I...O(4)	2.936(10)
I-C(5)	2.083(12)

(ii)   Acetate groups

Cl(1)-C(1)	1.740(11)	Cl(3)-C(3)	1.784(13)
Cl(2)-C(1)	1.731(12)	Cl(4)-C(3)	1.696(14)
C(1)-C(2)	1.499(14)	C(3)-C(4)	1.533(16)
C(2)-O(1)	1.288(14)	C(4)-O(3)	1.275(16)
C(2)-O(2)	1.208(16)	C(4)-O(4)	1.199(20)
C(1)-H(11)	0.98	C(3)-H(31)	0.98

(iii)   Phenyl ring

C(5)-C(6)	1.369(18)	C(6)-H(1)	0.96
C(6)-C(7)	1.328(24)	C(7)-H(2)	0.96
C(7)-C(8)	1.298(28)	C(8)-H(3)	1.03
C(8)-C(9)	1.361(27)	C(9)-H(4)	1.00
C(9)-C(10)	1.358(25)	C(10)-H(5)	0.99
C(10)-C(5)	1.348(19)		

(b)   Bond angles

(i)   Around iodine

O(1)-I-O(3)	167.1(4)	O(1)-I-O(4)	143.3(3)
O(1)-I-C(5)	86.0(3)	O(3)-I-O(4')	116.8(3)
O(3)-I-C(5)	82.5(3)	I-O(4)-I'	111.1(4)
O(4)-I-O(4')	68.9(3)		
C(5)-I-O(4)	157.8(4)		
C(5)-I-O(4')	130.0(4)		

* O(4') is related to O(4) by 1-x, -y, -z.

(ii) **Acetate groups**

Cl(1)-C(1)-Cl(2)	110.0(6)	Cl(3)-C(3)-Cl(4)	111.4(7)
Cl(1)-C(1)-C(2)	112.1(9)	Cl(3)-C(3)-C(4)	106.7(10)
Cl(2)-C(1)-C(3)	109.2(8)	Cl(4)-C(3)-C(4)	114.7(9)
O(1)-C(2)-O(2)	123.8(9)	O(3)-C(4)-O(4)	124.5(11)
O(1)-C(2)-C(1)	111.4(10)	O(3)-C(4)-C(3)	115.8(12)
O(2)-C(2)-C(1)	124.7(11)	O(4)-C(4)-C(3)	119.7(12)
I-O(1)-C(2)	116.2(6)	I-O(3)-C(4)	111.5(8)
I-O(4)-C(4)	75.8(7)	I-O(2)-C(2)	73.3(7)

(iii) **Phenyl ring**

I-C(5)-C(6)	118.7(9)
I-C(5)-C(10)	119.0(9)
C(10)-C(5)-C(6)	122.3(13)
C(5)-C(6)-C(7)	118.7(14)
C(6)-C(7)-C(8)	120.3(16)
C(7)-C(8)-C(9)	122.1(18)
C(8)-C(9)-C(10)	119.8(16)
C(9)-C(10)-C(5)	116.7(14)

Table III·3   Equations of the least squares mean planes PI + QJ + RK = S[a]
in orthogonal angstrom space

(1)   Iodobenzene diacetate

Plane 1	P	Q	R	S	
	0.4926	0.0197	-0.8700	-0.4418	

Atom, dev.(Å)					
I*	0.018	C(7)*	-0.006	C(10)*	-0.021
C(5)*	-0.015	C(8)*	0.017	O(1)	-2.044
C(6)*	-0.005	C(9)*	0.010	O(3)	2.081

Plane 2	P	Q	R	S	
	-0.2989	0.9387	0.1717	-1.8387	

Atom, dev.(Å)					
O(1)*	0.003	C(2)*	-0.10	O(4)	0.005
O(2)*	0.004	I	-0.004	C(5)	-0.141
C(1)*	0.003	O(3)	-0.087		

Plane 3	P	Q	R	S	
	-0.3024	0.9493	0.0865	-1.7736	

Atom, dev.(Å)					
O(3)*	0.000	C(4)*	-0.001	O(2)	-0.316
O(4)*	0.000	I	-0.090	C(5)	-0.143
C(3)*	0.000	O(1)	-0.232		

Plane 4	P	Q	R	S	
	-0.3226	0.9350	0.1471	-1.8555	

Atom, dev.(Å)					
I*	0.039	C(1)	-0.027	C(6)	1.126
O(1)*	0.033	C(2)	-0.025	C(7)	1.038
O(2)*	-0.038	C(3)	-0.140	C(8)	-0.139
O(3)*	-0.012	C(4)	-0.043	C(9)	-1.248
O(4)*	0.008	C(5)*	-0.030	C(10)	-1.203

Angles between planes (°)

(1)-(2)	73.85	(1)-(3)	78.14	(1)-(4)	74.43
(2)-(3)	4.93	(2)-(4)	1.97	(3)-(4)	3.75

(III.5.) References

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  (b) For a classification of acetate co-ordination modes, see N.W. Alcock, V.M. Tracy and T.C. Waddington, J. Chem. Soc. Dalton, 1976, 2243.

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(2) Iodobenzene bis(dichloroacetate)

Plane 1	P	Q	R	S
	0.3372	0.8468	0.4114	2.2930

Atom, dev.(Å)

I*	0.004	C(7)*	0.015	C(10)*	-0.002
C(5)*	0.001	C(8)*	-0.005		
C(6)*	-0.015	C(9)*	0.002		

Plane 2	P	Q	R	S
	-0.6477	-0.3145	0.6940	-1.3723

Atom, dev.(Å)

O(1)*	-0.007	I	0.191
O(2)*	-0.009	C(5)	2.197
C(1)*	-0.006		
C(2)*	0.023		

Plane 3	P	Q	R	S
	0.6542	-0.6223	0.4298	3.3859

Atom, dev.(Å)

O(3)*	-0.002	I	0.160
O(4)*	-0.003	O(1)	0.256
C(3)*	-0.002	O(2)	2.447
C(4)*	0.007	C(5)	-0.132

Plane 4	P	Q	R	S
	0.5352	-0.6784	0.5033	3.2121

Atom, dev.(Å)

I*	0.002	C(8)	0.079	O(2)	2.147
O(1)*	-0.001	C(2)	1.142	O(4)	-0.302
O(3)*	-0.001	C(4)	-0.711	O(4)'	-0.523[b]
C(5)*	0.000				

Angles between planes (°)

(1)-(2)	78.51	(1)-(3)	82.55	(1)-(4)	79.22
(2)-(3)	85.97	(2)-(4)	77.53	(3)-(4)	8.64

(a) The orthogonal unit vector I is parallel to a, K is perpendicular to a in the ac plane and J is perpendicular to the ac plane.

(b) Related to O(4) by a centre of symmetry.

(III.5.)   References

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CHAPTER IV

The crystal and molecular structures of two new spin labels and of
α-α dibromobenzylidene acetone; pyramidal distortions of the
nitroxide group and the importance of Br...O secondary bonds in
the packing of organic molecules

(IV.1.) Introduction

Among the better known examples of relatively   stable free
radicals (i.e. $\tau_{\frac{1}{2}}$ > days) are a group of compounds known as nitroxides.[1]
These compounds are readily prepared by oxidation of the corresponding
secondary amine.   Nitroxides have secured an important place in
biochemistry as spin labels.[2]   The technique of spin labelling entails
covalent attachment of the nitroxide to a biologically active molecule
whereupon the resulting biological system can then be probed by electron
spin resonance spectroscopy.   In this way valuable information about
conformational change accompanying binding of a substrate to an
enzyme can be deduced.   Since e.s.r. spectroscopy is such a sensitive
technique (concentrations of paramagnetic species down to 10^{-14} M can
be detected) extremely small quantities of a nitroxide-labelled substrate
suffice for biochemical investigations.   As part of a research program
into adenosylcobalamin-dependent enzymatic reactions, several spin-
labelled probes for studying the biochemistry of β-lactam antibiotics were
prepared by other workers.   One objective was to prepare a stereo-
specific spin-labelled penicillin from 6-aminopenicillanic acid and an
achiral nitroxide such as 3-carboxy-2, 2, 5, 5-tetramethyl-3-pyrrolin-1-
yloxy.   Both 3, 5-dibromo-4-oxo-2, 2, 6, 6-tetramethyl-piperidin-1-
yloxy (compound 1) and its monobromo analogue were similarly
investigated as potential precursors of 3-(N-substituted)-aminocarbonyl-
2, 2, 5, 5-tetramethyl-3-pyrrolidin-1-yloxy radicals also of use in such
coupling reactions.

Whilst (1) was highly suitable for its intended purpose, the monobromo
analogue could not be readily prepared in pure form, and in any case was
found to be too unreactive for the direct acylation of primary and
secondary amines to give the 3-(N-substituted) radicals.

The 3,5-dibromo-4-oxo-2,2,6,6-tetramethyl-pyrrolin-1-yloxy
was prepared by oxidation of 3,5-dibromo-4-oxo-2,2,6,6-tetramethyl-
piperidine using m-chloroperbenzoic acid and details of this
preparation are given elsewhere.[3] The radical (1) is a highly reactive
acylating agent converting amines, amino-acid esters and amino-
alcohols to crystalline amides. It is, however, quite unreactive
towards hydroxyl groups and reaction with ethanolamine leads to
selective acylation of the amino function. During one reaction of (1)
with propan-2-ol in dichloromethane containing triethylamine, a
compound of molecular formula $C_{19}H_{26}Br_2N_2O_4$ (compound 2) was
obtained. This substance also arises from treatment of (1) with
triethylamine alone and is also a by-product from reactions between
(1) and amino compounds of relatively low basicity. The structure of
this compound was originally tentatively given as a dimer of the
putative intermediate (3) with the suggested structure (4). X-ray
analysis, however, has rigorously established this compound to be a
bis-nitroxide 4-[(2',2',5',5'-tetramethylpyrrolin-1'-yloxy)-3'-
carbonyloxy]-2,2,6,6-tetramethyl-3,5-dibromo-3,4-dehydropiperidin-
1-yloxy.[4]

In this chapter, the details of the X-ray analysis on compounds (1)
and (2) will be described. Apart from establishing the structure of
(2) as the bis-nitroxide, the analysis has given further valuable
information on the pyramidal distortions that occur at the nitrogen atom
of the nitroxide group. Furthermore, the packing in (2) is determined
by Br...O secondary bonds which was another important consideration
in attempting these structural analyses.

Also reported is the crystal structure of (Z,Z) 2,4-dibromo-1,5-
diphenyl-penta-1,4-dien-3-one which has similarly been determined to
gain information on Br...O secondary bonds, and secondly to establish
the molecular conformation. However, in both this compound and (1) above,
the molecular packing is that of a molecular crystal with no secondary
bonding involved. These three structures show a little of the difficulty
of establishing a priori whether secondary bonds will be found in a
particular structure.

(IV.2.) Data Collection and Structure Solution

(IV.2.1.)

3,5-Dibromo-4-oxo-2,2,6,6-tetramethylpiperidin-1-yloxy (Compound 1)

As crystals grown on crystals of (1) occurred only partially as elongated triangular prisms, the prism was crushed and used for data collection.

Crystal data: $C_9H_{14}Br_2O_2N$, orthorhombic, $a = 11.468(1)$, $b = 9.938(1)$, $c = 14.150(1)$, $V = 1613.3(4)$ Å^3, $D_c = 1.727$, $Z = 4$, MoK_α radiation, $\lambda = 0.71069$ Å, $\mu(MoK_\alpha) = 38.80$, $F(000) = 656$, systematic absences (h k l, h + k ≠ 2n, (h 0 l, l ≠ 2n indicate space groups Pnna or P2₁ a non-standard setting of Pna2₁ (No. 33)).

Unit cell dimensions and data were measured using θ – 2θ scans over a scan range (K_{α_1} – 0.65) to (K_{α_2} + 0.65) to a maximum 2θ of 55° in two shells. A variable scan rate of 1.0°/min to 29.2°/min depending on the intensity of a preliminary 2 sec count was used. Background measurements were recorded at each end of the scan, each for one quarter of the scan time. The total intensity of 3 standard reflections were monitored every 97 reflections. These reflections showed no significant loss in intensity. 1453 data were collected, of which 923 were considered observed and used in refinement (I/σI > 3σI).

Lorentz, polarisation and absorption corrections were applied. With four molecules in the unit cell, space group Pnna requires mirror symmetry in the molecule. A Patterson synthesis was successfully interpreted for the vectors generated by a single bromine atom in space group Pna2₁ and the subsequent satisfactory refinement confirms this choice. The remaining atoms were located in subsequent Fourier maps. Least squares refinement with anisotropic temperature factors for all non-hydrogen atoms produced a final R factor of 0.026 (weighted R of 0.025).

The weighting scheme used gives reflections within the ranges 15.0 < F < 45.0 and 0.35 < sin θ < 0.50 weights of $(1/\sigma(F))^2$. Other reflections are weighted by the equation $W = X*Y*(1/\sigma F^2)$, where $X =$

(IV.2.)   Data Collection and Structure Solution

(IV.2.1.)

3,5-dibromo-4-oxo-2,2,6,6-tetramethylpiperidin-1-yloxy.(Compound 1)

Air-stable orange-red crystals of (1) occur as chunky prisms or as elongated hexagonal plates.   One prism was mounted and used for data collection.

Crystal data: $C_9H_{14}Br_2O_2N$, orthorhombic, $\underline{a}$ = 11.665(2), $\underline{b}$ = 5.938(1), $\underline{c}$ = 16.067(3) Å, $\underline{U}$ = 1113.0(4) Å^3, D_c = 1.957, Z = 4.   Mo K$_\alpha$ - radiation, λ = 0.71069 Å; μ(Mo-K$_\alpha$) = 76.85, F(000) = 644.   Systematic absences $\underline{hk0}$, h $\neq$ 2n, $\underline{0kl}$, k + 1 $\neq$ 2n indicate space groups $\underline{Pnma}$ or $\underline{Pn2_1a}$ (non-standard setting of $\underline{Pna2_1}$ (No. 33)).

Unit cell dimensions and data were measured using θ - 2θ scans over a scan range (K$_{\alpha_1}$ - 0.65) to (K$_{\alpha_2}$ + 0.65) to a maximum 2θ of 55° in two shells.   A variable scan rate of 1.0^o/min to 29.5^o/min depending on the intensity of a preliminary 2 sec count was used. Background counts were recorded at each end of the scan, each for one quarter of the scan time.   The intensities of four standard reflections were monitored every 70 reflections. These reflections showed no significant loss in intensity.   1527 data were collected, of which 823 were considered observed and used in refinement (I/σI $\geq$ 3.0).

Lorentz, polarisation and absorption corrections were applied. With four molecules in the unit cell, space group $\underline{Pnma}$ requires mirror symmetry in the molecule. A Patterson synthesis was successfully interpreted for the vectors generated by a single bromine atom in space group $\underline{Pnma}$ and the subsequent satisfactory refinement confirms this choice.   The remaining atoms were located in subsequent Fourier maps.   Least squares refinement with anisotropic temperature factors for all non-hydrogen atoms produced a final R factor of 0.026 (weighted R of 0.025).

The weighting scheme used gives reflections within the ranges $15.0 \leq F \leq 45.0$ and $0.265 \leq \sin\theta \leq 0.50$ weights of $(1/\sigma(F))^2$.   Other reflections are weighted by the equation $W = X*Y*(1/\sigma(F))^2$ where X =

sin θ/0.265 if sin θ < 0.265 or X = 0.50/sin θ if sin θ > 0.50 and

Y = F/15.0 if F < 15.0 or Y = 45.0/F if F > 45.0 . Using this

weighting scheme, one reflection with a very bad ω*deltasq was

rejected from the refinement.

(IV.2.2.)

4-[(2',2',5',5'-tetramethylpyrrolin-1'-yloxy)-3'-carbonyloxy]-

2,2,6,6-tetramethyl-3,5-dibromo-3,4-dehydropiperidin-1-yloxy

(Compound 2)

Air-stable orange-red crystals of (2) slowly recrystallised from

boiling n-hexane as thin plates. One such plate was found to extinguish

under crossed polars along the diagonal of the plate.

Crystal data: $C_{18}H_{26}Br_2O_4N_2$, orthorhombic, $\underline{a}$ = 11.089(2), $\underline{b}$ = 30.477(6),

$\underline{c}$ = 12.970(2) Å, $\underline{U}$ = 4383.3(14) Å^3, D_c = 1.498, $\underline{Z}$ = 8, MoK_α -radiation,

λ = 0.71069 Å, μ(Mo-K_α) = 39.41 cm^{-1}, F(000) = 2000. Systematic

absences O$\underline{kl}$, $\underline{k}$ ≠ 2n; $\underline{h}$O$\underline{l}$, $\underline{l}$ ≠ 2n; $\underline{hk}$O, $\underline{h}$ ≠ 2n indicate space group

$\underline{Pbca}$ (No. 61).

Unit cell dimensions and data were measured using the diffractometer.

Reflections were measured using θ - 2θ scans over a scan range

(K_{α_1} - 0.7) to (K_{α_2} + 0.7) to a maximum 2θ of 50°. The intensities of

three standard reflections were monitored every 100 reflections. These

reflections showed no significant loss in intensity. Other conditions

were the same as in (IV.2.1.). 4399 data were collected, of which 1104

were considered observed and used in refinement (I/σ(I) ≥ 3.0).

Lorentz, polarisation and absorption corrections were applied.

The two bromine atoms were readily located on a Patterson synthesis

and the remaining light atoms found by Fourier methods. Least squares

refinement, using three blocks with anisotropic temperature factors for

all non-hydrogen atoms and including a correction for the effects of

anomalous dispersion, produced a final R factor of 0.048 (weighted R of

0.035). The weights used were based on counting statistics.

Final co-ordinates and temperature factors are in Table IV.1.

Significant bond lengths, bond angles and torsion angles are given in Table

II.2, and molecular planes in Table IV.3.Structure factors. are in

Appendix A

(IV.2.3.)

<u>(Z,Z) 2,4-Dibromo-1,5-diphenyl-penta-1,4-dien-3-one</u>. (Compound 3)

The sample of $(Z,Z)^{2,4}$Dibromo-1,5-diphenyl-penta-1,4-dien-3-one were prepared and supplied by Professor Shoppee.   The crystals (m.p. 97-98° C), recrystallised slowly from ethanol, form chunky needles (needle axis <u>c</u>).   One needle was mounted and used for all subsequent work.

<u>Crystal data</u>: $C_{17}H_{12}Br_2O$, monoclinic, <u>a</u> = 41.080(11), <u>b</u> = 6.527(2), <u>c</u> = 11.118(3) Å, β = 97.767(23)$^{\circ}$, <u>V</u> = 2953.7(16) Å^3 at 18° C, <u>Z</u> = 8, D_c = 1.71 g/cm^{-3}.   MoK$_{\alpha}$ - radiation, λ = 0.71069 Å; μ(MoK$_{\alpha}$) = cm^{-1}.   Systematic absences, <u>h0l</u>, <u>l</u> ≠ 2n, and 0<u>k</u>0, <u>k</u> ≠ 2n indicate space group <u>P2$_1$/c</u>.

Unit cell dimensions and data were measured on the diffractometer and the long <u>a</u> axis was confirmed by Weissenberg photographs.   There are two independent molecules in the asymmetric unit and also a marked pseudo-absence <u>hk</u>0, <u>h</u> ≠ 2n in the data.   However, there is no evidence from the Syntex autoindexing program or more particularly from the Weissenberg photographs of an orthorhombic system with a single molecule in the asymmetric unit.   Reflections were measured using θ - 2θ scans over a scan range $(K_{\alpha_1} - 0.9)$ to $(K_{\alpha_2} + 0.8)^{\circ}$ to a maximum 2θ of 50° in two shells.   In the first shell ($0 < 2\theta \leq 35^{\circ}$) all reflections were collected whilst in the second shell ($35 < 2\theta \leq 50^{\circ}$) a reflection was only collected if the intensity of a 8 sec preliminary count was greater than 40 counts per sec.   A variable scan rate of 1.0 - 29.3°/min depending on the intensity of the preliminary count was used.

The positions of the four Br atoms were located by applying the direct methods programs NORMAL and MULTAN (Germain and Woolfson, 1968) to the 274 reflections with E > 1.50 in the first shell of data.   Fourier and least squares refinement using the 1865 observed ($I/\sigma(I) \geq 3.0$) reflections in both shells located the remaining non-hydrogen atoms.   The final refinement was with Br, C and O with anisotropic temperature factors to an R factor of 0.081.   The

Fig. IV.1. General view of Compound (1). Primed and unprimed atoms are related by the mirror plane.

weighting scheme used was $1/\sigma^2(\omega) = 1/\sigma^2(\text{F}_0)(10^{-4} F^2 + 6)$. Hydrogen atoms were not included and no correction for absorption was applied.

(IV.2.) Discussion of Structures

(IV.2.1.) Compounds (1) and (2)

The crystals of (1) contain discrete molecules possessing mirror symmetry, the carbonyl and nitroxide bonds lying in the mirror plane. The conformation adopted by the piperidine ring is a slightly flattened chair with the bromine atoms equatorial (Figure IV. 1) The carbonyl group bisecting through the N–O bond makes an angle of 24, 2° with the C4N1C5 plane. The angular distortion at nitrogen towards the tetrahedral value is a result of fused rings containing the nitroxide bond and is discussed below (Section IV. 4.).

The bromine atoms of (1) prefer to be equatorial as a consequence of steric effects, which originates in the mutual repulsion of two bulky axial substituents. In the case with both bromine equatorial, the packaging in the ring, as seen in Figure IV. 2 increases the 1, 3-diaxial separations of the bulkier methyl groups and hence reduces non-bonding repulsions. Similar effects occur in 2-bromo- and 2, 6-dibromo-3, 3, 5, 5-tetramethylcyclohexanone which are both known from crystallographic results to contain equatorial bromine atoms. Other workers, using dipole moment measurements on the chemical shift of the bromomethine proton in brominated tetrahydropyran and cyclohexanone rings, have also shown that conformations with bromine equatorial may be favoured despite the intramolecular electrostatic repulsions between C–Br and C=O dipoles.

In the present structure the intramolecular Br...O (carbonyl) separation is 3.045 Å, less than the sum of the appropriate van der Waals radii. Comparatively short Br...O contacts of 2.97-2.99 were found in the two bromocyclohexanone structures noted above, and also in 2, 4-dibromo-1, 5-diphenyl pent-1, 4-dien-3-one (Compound 3) which has the ZZ configuration about the two double bonds, due again to the steric requirements of other bulkier groups, resulting in adjacent Br and O and Br...O of 2.93-2.95 Å. Other evidence of strain in the piperidine

weighting scheme used was $\sqrt{w} = 1.0/(186 - 335 \cdot \sin \theta)$. Hydrogen atoms were not included and no correction for absorption was performed.

(IV.3.) Discussion of Structures

(IV.3.1.) Compounds (1) and (2)

The crystals of (1) contain discrete molecules possessing mirror symmetry, the carbonyl and nitroxide bonds lying in the mirror plane. The conformation adopted by the piperidine ring is a slightly flattened chair with the bromine atoms equatorial (Figure IV.1).The carbonyl group is planar although the N-O bond makes an angle of 24.2^{o} with the CNC plane. This angular distortion at nitrogen towards tetrahedral is typical of six-membered rings containing the nitroxide bond and is discussed below (Section IV.4.).

Bromine atoms of (1) prefer to be equatorial as a consequence of the 'reflex effect'[5] which originates in the mutual repulsion of two bulky axial substituents. In this case, with bromine equatorial, the puckering in the ring, as seen in the torsion angles,Table IV.2,increases the 1,3-diaxial separations of the bulkier methyl groups and hence reduces non-bonding repulsions. Similar effects occur in 2-bromo- and 2,6-dibromo-3,3,5,5-tetramethylcyclohexanone which are both known from crystallographic results to contain equatorial bromine atoms.[6] Other workers, using dipole moment measurements or the chemical shifts of the bromo-methine proton in brominated tetrahydropyranone or cyclohexanone rings, have also shown that conformations with bromine equatorial may be favoured despite the intramolecular electrostatic repulsion between the C-Br and C=O dipoles.[7,8]

In the present structure the intramolecular Br...O (carbonyl) separation is 3.045 Å, less than the sum of the appropriate van der Waals radii. Comparatively short Br...O contacts of 2.97-2.99 were found in the two bromocyclohexanone structures noted above, and also in 2,4-dibromo-1,5-diphenyl penta-1,4-dien-3-one (Compound 3) which has the ZZ configuration about the two double bonds, due again to the steric requirements of other bulkier groups, resulting in adjacent Br and O and Br...O of 2.93-2.95 Å. Other evidence of strain in the piperidine

ring is the small C(2)-C(1)-C(2') angle (108.2(6)$^{\circ}$) which reduces
the repulsion between the C-Br and C=O dipoles.

The packing of the individual molecules of (1) is dictated by normal
van der Waals forces (Figure IV.3).There appears to be no close inter-
molecular interactions involving the nitroxide bond (in contrast to
9-aza-bicyclo[3,3,1]nonan-3-one-8-oxyl, for example , in which two
nitroxide bonds lie around a centre of symmetry forming a rectangle
with sides 1.289 and 2.278 Å).[9]

In (2) individual molecules contain nitroxide bonds in two different
ring environments (Figure IV.2).In contrast to (1) the crystal packing
(Figure IV.4)does seem to involve Br...O secondary bonds of 3.086(8) Å
between Br(1) and the oxygen of the pyrrolin-yloxy ring, resulting in
dimeric units about inversion centres.   This secondary
bond is 0.28 Å less than the sum of the van der Waals radii[†]: the
C-Br...O angle is 178.4(4)$^{\circ}$ and the N-O...Br angle is 114.2(6)$^{\circ}$.
The importance of these Br...O secondary bonds is discussed in
Section IV.5.

The C-Br distance in (1) is 1.941(3) Å whilst in ring 1 of (2) there
are two different C-Br distances of 1.988(12) (C(sp^3)-Br) and 1.916(11) Å
(C(sp^2)-Br as expected, since the hybridisation of the carbon atom
changes.   Accepted values for C(sp^2)-Br and C(sp^3)-Br are 1.89(1) Å
and 1.937(3) Å respectively,[10] but the value of 1.988 Å for C(3)-Br(2)
is significantly longer.   (The C-Br distance in (1) is typical of
C(sp^3)-Br however).   The lengthening of the C(3)-Br(2) bond is
probably a consequence of repulsive non-bonded contacts, although
several authors have commented that Sutton's values[10] for these bond
lengths may be under-estimated in the light of recent results.   The
conformation that ring 1 adopts also forces close intramolecular
contacts of 3.361(8) (Br(2)...O(2)) and 3.008(8) Å (Br(1)...O(2))
involving the bromine atoms.   The remaining distances and angles in
(1) and (2) are within normal ranges.

[†] After H. Bondi, J. Phys. Chem., 68, 441, (1964).

Fig. IV.3. Packing diagram for (1), viewed down c.
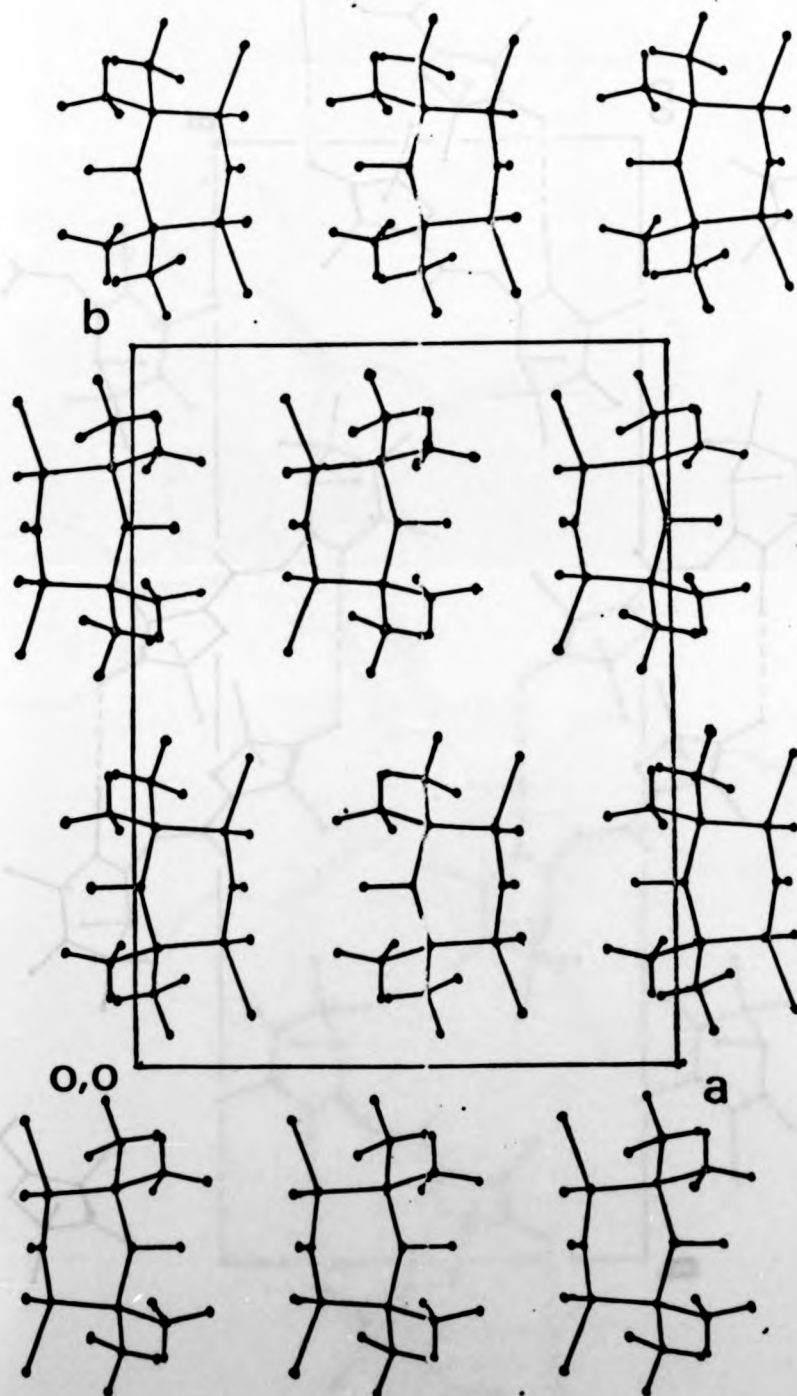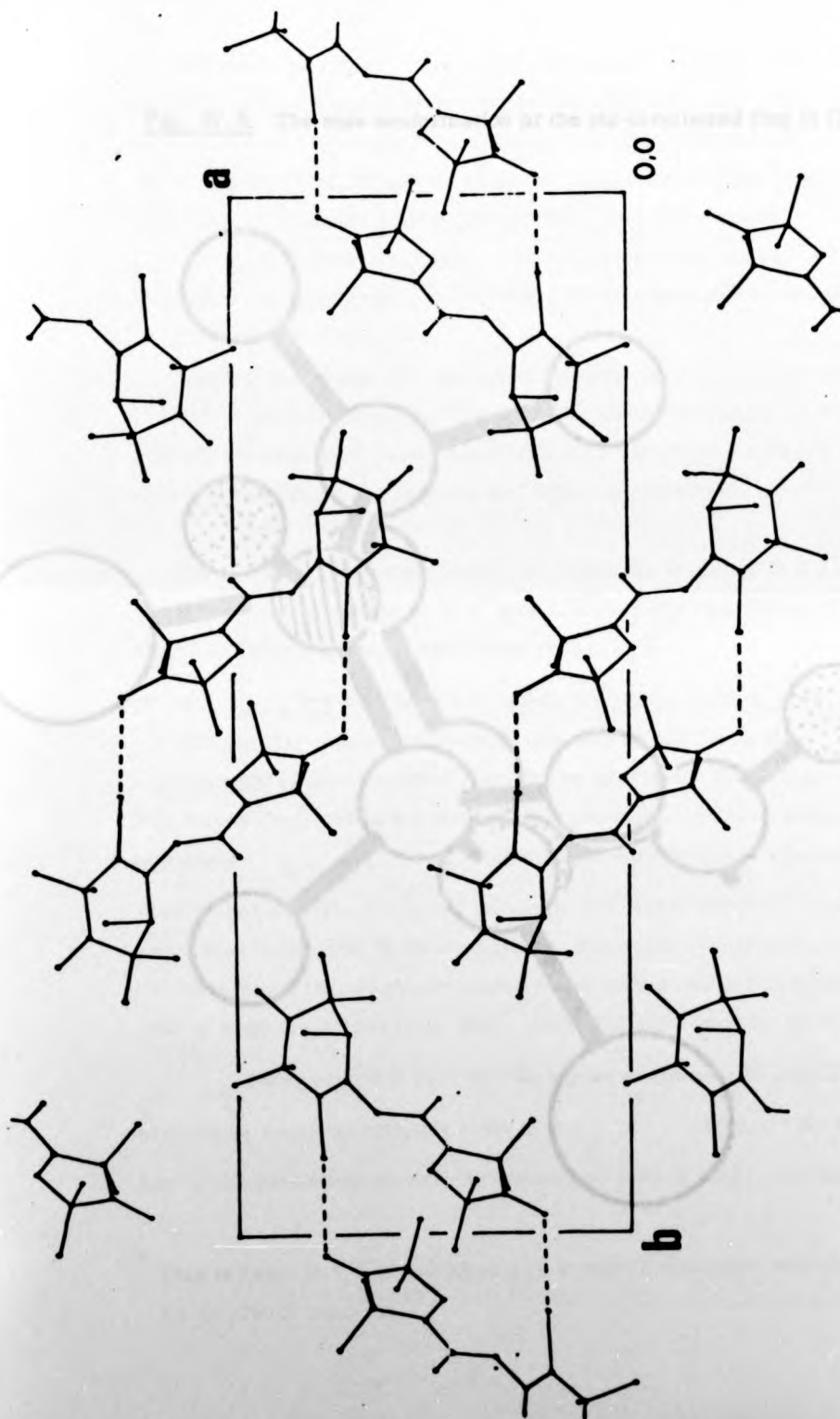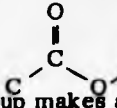
Fig. IV.4. Packing diagram for (2), viewed down c, showing dimeric units associated by Br...O secondary bonds (dashed).

Fig. IV.5. The sofa conformation of the six-membered ring in (2).
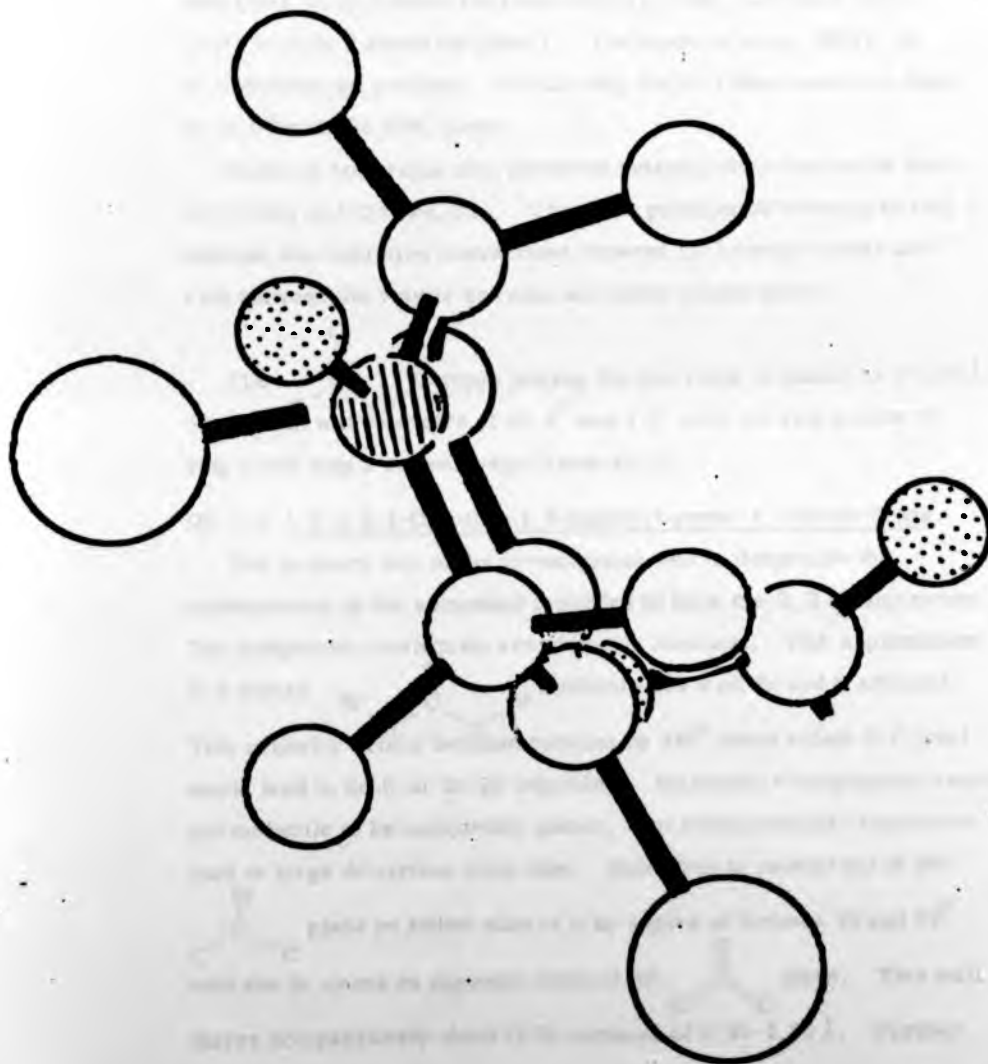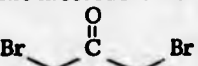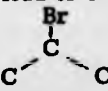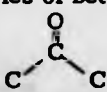
The pyrrolin-yloxy ring is virtually planar with atom C(13) deviating from the plane of the ring by only 0.025 Å. The nitroxide bond makes an angle of 0.5° with the CNC plane. The second six-membered ring, however, adopts a 'sofa' conformation (Figure IV.5) with C(4), 0.60 Å above the plane of N(1), C(2), C(3) and C(5). [C(1) is 0.08 Å above the plane]. The bromine atom, Br(2), is in a pseudoaxial position. In this ring the N-O bond makes an angle of 16.04°with the CNC plane.

Strain in both rings also produces twisting about the double bonds C(1)=C(2) and C(11)=C(12). The more pronounced twisting in ring 1 reduces the repulsive interactions between its bromine atoms and also between the vinylic bromine and ester oxygen atoms.

The ⟨C–O–C with =O⟩ group linking the two rings is planar to ± 0.02 Å. This group makes angles of 87.3° and 1.9° with the ring planes of ring 1 and ring 2 respectively (Table IV.3).

(IV.3.2.) Z-Z 2,4-Dibromo-1,5-diphenyl-penta-1,4-diene-3-one.

The primary aim of the investigation was to determine the conformation of the compound regarded to have the Z, Z configuration.[11] The independent molecules are virtually identical. Both approximate to a planar ⟨Br–C(=O)–Br⟩ conformation with Br and O adjacent. This probably arises because rotation by 180° about either C-C bond would lead to Br-H or Br-Br repulsion. Maximum π-conjugation requires the molecule to be completely planar, but intramolecular repulsions lead to large deviations from this. Each C=O is twisted out of the ⟨Br–C–C–C⟩ plane on either side of it by angles of between 22 and 32°, with the Br atoms on opposite sides of the ⟨C–C(=O)–C⟩ plane. This still leaves comparatively short O-Br contacts of 2.93-2.95 Å. Further,

* This is found in 1,5-diphenylpenta-1,4-dien-3-one itself, (investigated as its uranyl complex.[12])

Fig. IV. 6.

Views of the two molecules showing the deviations from
planarity.

Fig. IV. 7.
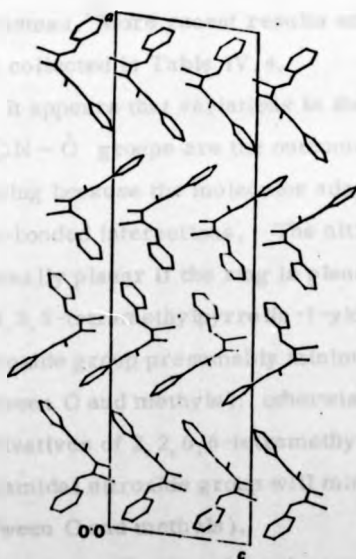
Packing diagram, viewed down b. The rows contain
respectively (from the bottom) molecules 1,2,1,2, those in
each row being related by the glide plane.

Figs. for Z-Z 2,4-Dibromo-1,5-diphenyl-penta-1,4-diene-3-one

the phenyl rings are twisted out of plane by between 24 and 32°
to increase the Br-H (ortho) contact distances resulting in
values between 2.61 and 2.78 Å (H in calculated positions)(Figure IV.6).
The (Ph)C-C$\overset{C}{\diagup}$ angles are also substantially larger than
expected, presumably for the same reason.   Other bond lengths
and angles have normal values (Figure IV.8).

The molecular packing (Figure IV.7)proved not to be controlled
by Br...O secondary bonds.   Instead, the phenyl rings take up
the typical herring-bone arrangement.

(IV.4)   The Nitroxide Group; distortions due to non-bonded
interactions
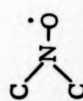
A tabulation of relevant distances and angles in molecules
containing the nitroxide group has been given by Lajzerowicz-
Bonneteau.[13] More recent results and data for acyclic nitroxides
are collected in Table IV.4.

It appears that variations in the dimensions and angles of the
$\overset{C}{\underset{C}{\diagup}}N-\overset{.}{O}$ groups are the outcome of geometrical constraints
arising because the molecules adopt conformations which minimise
non-bonded interactions.   The nitroxide group in ring systems is
normally planar if the ring is planar (e.g. in derivatives of
2, 2, 5, 5-tetramethylpyrrolin-1-yloxy where planarity of the
nitroxide group presumably minimises repulsive interactions
between O and methyls); otherwise it may be pyramidal (e.g. in
derivatives of 2, 2, 6, 6-tetramethylpiperidin-1-yloxy where a
pyramidal nitroxide group will minimise repulsive interactions
between O and methyls).

With acyclic nitroxides the non-bonded contact distances
involving the oxygen atom may force the nitroxide group to be
planar.   For example, in $Bu_2^t NO$ the O...C distance is already
short and any deviation at N would decrease this distance even
further.   Packing arrangements, especially when hydrogen bonds
are formed, can also alter the shapes of nitroxide groups.

TABLE IV.4

Structural Data on Nitroxides from Refs.(26-37)[a]

Nitroxide	N-O(Å)	CNC(°)	Δt	Conformation of 5-membered ring	Ref.
2,2,5,5-Tetramethyl-3-hydroxypyrrolidin-1-yloxy	1.265(5)	115.3	—	Twist	26
2,2,5,5-Tetramethylpyrrolidin-3-on-1-yloxy oxime[b]	1.272(5)	117.1(4)	—	Slightly distorted envelope	27
3-Aminocarbonyl-2,2,5,5-tetramethylpyrrolidin-1-yloxy	1.268(3)	115.0(2)	—	Virtually planar Twist	28
2,2,6,6-Tetramethyl-4-(hydroxyimino)piperidine-1-oxyl	1.27	125	25.8	Non-planar	29
exo-6-tetramethyl-3-azabicyclo[3,3,1]nonan-7-on-3-oxyl	1.28(1)	123.2(4)	17°	Non-planar	30
bis(2,2,6,6-tetramethylpiperidin-1-oxyl)carbonate	1.287	d	19.4°	Non-planar	31
2,2,6,6-tetramethyl-piperidine-1-iminoxyl-4-(N,2-hydroxy-1-naphthaldehydimine	1.28	d	22°	d	32
2,2,6,6-tetramethyl-1-piperidine-1-oxyl	1.283(9)	123.6(3)	e	Non-planar	33
bis(p-Anisyl)nitroxide	1.23(5)	124(5)	—	Planar	34
bis(t-Butyl)nitroxide	1.28(2)	124(5)	—	Probably planar	35
bis(Trifluoromethyl)nitroxide	1.26(3)	121(2)	—	Non-planar	35
Fremy's salt (K nitrosodisulphonate, triclinic form)	1.28(4)	c	—	Small deviation from planarity	36
t-Butylferrocenyl nitroxide	1.20		—	not given	37

a Other data on nitroxides in ref. 13.

b Data for optically active form. This molecule also crystallises as a racemate with two independent molecules in the asymmetric unit. The N-O bond lengths are 1.261(5) and 1.276(5) Å and the corresponding CNC are 115.3(4)° and 116.5(3)°.

c Corresponding angle SNS is 118(2)°.

d Δ is the angle the N-O bond makes with the CNC plane.

e Abstract only available; information not included in abstract.

f Molecule is disordered.

The theoretical geometry of the nitroxide group has been investigated by a CNDO calculation on bis (trifluoromethyl) nitroxide which found that r(N-O) = 1.26(1) Å, and a minimum energy for the molecule occurs with an angle of 10° between the N-O bond and the CNC plane. However, very little energy is required to change this angle in the range 0° to 30°.[14] An ab initio calculation on H_2NO reached similar conclusions: the out-of-plane angle is 26°, HNH is 116° and the N-O bond length is 1.34 Å.[15]

The observed N-O bond lengths are 1.285(9) Å for (1), 1.286(15) Å (ring 1) and 1.252(13) Å (ring 2) for (2). The corresponding CNC angles are $125.1(3)^O$ for (1), $121.7(10)^O$ (ring 1) and $113.1(10)^O$ (ring 2) for (2). The N-O distances are within the ranges quoted in ref. 13 and Table IV.4. The angles between the N-O bonds and the CNC planes in the six-membered rings are also within the observed range $(15.8 - 30.5^O)$.[‡ 13]

The two N-O distances in the six-membered rings are very similar, but the shorter N-O distance in the five-membered ring 2 of (2) is not significantly different. The deviation from planarity of a nitroxide group would be expected to decrease π-overlap between the N and O and hence slightly lengthen the N-O bond. Similarly the CNC would be expected to decrease and the C-N distance to increase. The evidence here and in other nitroxide structures, however, is not sufficiently accurate to prove these points conclusively.

(IV.5.) Halogen - Oxygen Secondary Bonding

In the last few years the successful introduction of direct methods programs such as MULTAN, LSAM, SINGEN and PHASE and others has meant that, for organic molecules especially, it is no longer a necessity to have a heavy atom in the structure for its solution by

‡ The value of 30.5^O is for 9-azabicyclo[3,3,1]nonan-3-one-9-oxyl,[9] where there is a repulsive interaction between the nitroxide and carbonyl bonds and a more reasonable range is perhaps 15.8 to 24.9^O.

Patterson methods. However, there have been and there still are a
large number of organic and inorganic molecules being published
in which the structures have been phased by the use of a heavy
halogen atom in the structure. Principally this is due to the
relative ease of producing relatively strong carbon-halogen bonds
or by crystallising an organic molecule as a halide. Whilst the
use of the halogen derivatives does ensure a relatively easy structure
solution, the introduced halogen atoms can drastically affect the
molecular packing arrangements in the crystal, and it is the
intention of this section to summarise some of the specific inter-
actions that are likely to involve the halogen atom, emphasising
some secondary bonded examples.

All three of the compounds in this chapter were investigated in
the hope that they might contain Br...O secondary bonds. Only
compound (2) has been found to contain this type of interaction,
although in both the other compounds the repulsive intra-molecular
Br...O contacts do have significant effects on the molecular
conformation. Apart from their involvement in secondary bonding
interactions it is also well documented that halogen substituents on
organic bases (in particular purine and pyrimidine bases) can
considerably affect the solid state base-stacking patterns and it has
been suggested that specific stacking interactions involving these
halogen substituents are contributing to the unusual physical and
biological properties of nucleic acids which contain halogenated
pyrimidines.[16] These latter interactions are however different
from linear secondary bonded systems since they normally involve
the molecules stacking in layers with partial base overlap so that
the halogen atom normally rests over the centre of a nucleotide
ring, and hence is involved in several close contacts to carbon and
nitrogen atoms (see also Section VI.3.2). In some cases crystal
structures may be found with both columnar stacking of approximately
planar molecules with short halogen contacts and also with the
halogen involved in lateral secondary bonds providing some cohesion
between the molecular stacks.[17]

As regards the secondary bonds in (2) they result in dimeric units about centres of symmetry which are tilted with respect to the ab face and are related by unit cell translations. Similar Br...O secondary bonds to those in (2) have been found to be important in determining the packing of several brominated steroids,[18] certain acid-base structures involving Watson-Crick pairs of molecules[19] and several other organic and inorganic structures.[20] A typical range of distances for the Br...O contact in these structures are from 2.91 to 3.35 Å (compared to the sum of van der Waals radii of 3.37 Å) and all involve nearly linear C-Br...O groups. They thus represent the simplest examples of secondary bonds and can be directly compared to hydrogen bonding in determining the crystal packing. In fact, both hydrogen and secondary bonds may occur together. Not only are the C-Br...O angles $\approx 180^\circ$ but the angles Br-O...X also suggest that the lone pair on oxygen involved in the interaction occurs in an sp^2 or sp^3 hybrid orbital.

Whilst C-Br...O interactions have been principally mentioned, these linear interactions are also found for the other halogen atoms (Cl and I) with oxygen and other electronegative donor atoms. However, there is as yet no comprehensive review of all structures containing the type of secondary bonds briefly covered in this section. A few examples will perhaps show how vast this particular area is likely to be.

In a series of structural determinations of 5-halo-benzfurazan-1-oxide structures, the molecular packing is dictated by C-Br...N secondary bonds for the chloro and bromo complexes, but C-I...O secondary bonds for the iodo compound. Whilst the contact distances are not too accurate [N...Cl 3.20 Å, N...Br 3.14 Å and O...I 3.1 Å] due to the poor quality of the data sets collected,resulting in rigid group refinements, the trend towards shorter distances (I > Br > Cl) and the change from nitrogen to oxygen interactions is quite interesting (attributed to differences in atomic size).[21] In 2,3-dibromo-1,4-naphthoquinone C-Br...O secondary bonding again stabilises the

structure; the Br...O contacts are 3.15 and 3.22 Å with C-Br...O angles of $166-168^{\circ}$ and C-O...Br angles close to 130°. Again these are lateral contacts and the molecules still stack in columns.[27] In 2,4-dibromo-O-cresyl -3', 5'-dinitro salicylate the Br...O contacts are slightly longer at 3.34 and 3.19 Å.[22] Whilst the above examples are examples of linear interactions, it is worth mentioning a rare example of a square planar arrangement of 2 primary and 2 secondary bonds at this point. This occurs in 4,5-dicyano-2-imidazolyl(phenyl)bromonium ylide where the two Br...N secondary bonded distances are 2.912(6) Å and 3.094(6) Å [C-Br...N angles are 175.5° and 159.9°] whilst the (Ph)CBrC(imidazolyl) angle is only $99.3(3)^{\circ}$.[23] Some other examples of linear C-Br...N interactions are compared in ref. 24.

A linear C-S...Br[S...Br 3.49 Å; C-S...Br 171°] secondary bond between a bromide ion which is almost in the same plane as a thiazolium ring is again an important component of the crystal packing of thiamine bromide hydrobromide hemihydrate $(HThiBr_2 \cdot \frac{1}{2}H_2O)$. In comparison, the same S atom in the related $HThiCl_2 \cdot H_2O$ and $HThiI_2$ structures forms totally different contacts; to a water molecule in the hydrochloride and to the β-hydroxy ethyl OH group in the hydroiodide.[25] The difference in these packing arrangements are presumably a consequence of the size of the halogen atom and the number of water molecules present (and hence the number of hydrogen bonds).

In compound (III) there are no secondary bonds because the molecular packing appears to be determined by the volumes occupied by the phenyl rings. This 'herringbone' arrangement which can be seen in Fig. IV.7 is a common feature of aromatic hydrocarbons and other simple organic molecules such as ethylene. The importance of this particular arrangement is that it minimises H...H repulsions.[38]

IV.6. References

1. 'Free Nitroxyl Radicals', E.G. Rosantsev, Plenum Press, London (1970). 'Organic Chemistry of Stable Free Radicals', A.R. Forrester, J.M. Hay and R.H. Thomson, Academic Press, London (1968). Chap. 5.

Table 1

TABLE IV.1

Atomic co-ordinates (x 10^4) and anisotropic temperature factors* (x 10^3) with standard deviations in parentheses.

*In the form exp $\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$

(a) 3,5-dibromo-4-oxo-2,2,6,6-tetramethylpiperidin-1-yloxy (1)

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	2127.1(3)	736.0(2)	-961.5(6)	40.6(2)	59.3(3)	6.8(2)	8.8(2)	-4.5(2)	
O(1)	-776(3)	2500(0)	3776(7)	43(2)	45(2)	45(2)	0(0)	24(2)	0(0)
O(2)	1998(3)	2500(0)	-2817(6)	52(2)	38(2)	34(2)	0(0)	14(2)	0(0)
N	106(3)	2500(0)	2499(7)	23(2)	28(2)	28(2)	0(0)	1(2)	0(0)
C(1)	1821(3)	2500(0)	-835(10)	21(2)	28(2)	42(3)	0(0)	0(2)	0(0)
C(2)	1654(3)	1735(2)	627(6)	25(1)	25(1)	33(2)	2(1)	-2(1)	-3(1)
C(3)	405(3)	1666(2)	1484(5)	28(2)	26(1)	28(2)	-1(1)	2(1)	0(0)
C(4)	337(4)	1027(2)	3390(7)	28(2)	32(2)	36(2)	8(2)	8(2)	6(2)
C(5)	-450(3)	1463(3)	-371(7)	44(2)	44(2)	40(3)	-1(2)	-1(2)	-8(2)

Atom	X	Y	Z	U
H(1)	2169(29)	1777(20)	2009(56)	26(8)
H(41)	583(36)	502(30)	2745(76)	63(13)
H(42)	841(38)	1181(28)	4709(79)	61(13)
H(43)	-479(41)	924(27)	3985(69)	62(12)

Atom	X	Y	Z	U
H(51)	-393(36)	943(31)	-743(67)	52(12)
H(52)	-315(37)	1774(29)	-1642(73)	53(13)
H(53)	-1213(37)	1575(23)	253(60)	44(11)

TABLE IV.1 (continued)

(b) The ester (2) derived from (1)

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	2182.9(13)	761.1(5)	1120.8(11)	83.4(11)	43.1(9)	78.1(11)	12.1(11)	3.5(12)	19.8(10)
Br(2)	1733.2(17)	1967.8(6)	-1660.5(12)	131.1(16)	85.1(13)	50.9(9)	25.9(13)	-5.0(13)	15.5(11)
O(1)	511(9)	2366(3)	1188(8)	76(8)	61(9)	100(10)	30(7)	21(8)	-8(7)
O(2)	7801(7)	209(2)	-1806(6)	21(6)	48(6)	69(6)	14(5)	9(6)	3(5)
O(3)	5067(8)	1325(3)	418(6)	69(8)	99(8)	49(6)	-32(6)	-50(6)	-18(5)
O(4)	3507(7)	1186(3)	-640(6)	30(6)	57(6)	45(6)	22(5)	4(5)	-18(5)
N(1)	1317(10)	2097(4)	859(8)	36(10)	32(9)	52(8)	9(7)	12(7)	17(7)
N(2)	6817(9)	401(3)	-1665(7)	31(7)	37(7)	43(6)	11(6)	9(7)	-8(6)
C(1)	2132(13)	1360(4)	678(11)	42(11)	13(8)	51(9)	16(9)	-8(9)	-6(8)
C(2)	2801(13)	1489(5)	-94(9)	26(10)	54(12)	18(8)	-1(10)	4(9)	-16(8)
C(3)	2651(11)	1956(4)	-462(9)	50(10)	29(9)	54(9)	10(10)	-12(9)	0(8)
C(4)	2441(13)	2260(4)	411(11)	53(13)	20(9)	76(12)	7(8)	17(10)	1(8)
C(5)	1200(11)	1639(4)	1243(9)	62(11)	36(10)	32(9)	5(9)	15(6)	5(6)
C(6)	1444(12)	1637(5)	2413(11)	93(12)	83(12)	58(10)	-23(10)	11(11)	-2(10)
C(7)	-74(11)	1473(4)	1014(11)	42(10)	78(10)	97(12)	17(8)	23(10)	-15(9)
C(8)	3449(12)	2257(5)	1134(12)	77(11)	85(14)	110(15)	-25(10)	-14(12)	-33(11)
C(9)	2209(13)	2727(4)	-45(12)	31(9)	31(9)	150(14)	-11(10)	21(13)	-6(9)
C(10)	-4659(11)	1139(4)	-306(8)	35(10)	40(8)	35(8)	15(8)	-7(6)	-10(7)
C(11)	5306(13)	827(4)	-978(10)	46(12)	32(10)	26(10)	13(9)	9(9)	-7(8)
C(12)	4845(11)	633(4)	-1802(12)	45(11)	24(9)	47(12)	5(8)	17(10)	-10(8)

TABLE IV.1

continued/

Atom	X	Y	Z	U
C(13)	5762(11)	355(4)	-2342(11)	32(10)
C(14)	6612(13)	700(4)	-804(10)	38(10)
C(15)	6036(13)	531(5)	-3424(12)	82(13)
C(16)	5435(10)	-128(4)	2425(12)	11(9)
C(17)	6817(13)	463(4)	199(10)	89(13)
C(18)	7472(12)	1103(5)	-886(10)	60(12)
H(31)	3863(58)	2020(23)	-1073(52)	68(27)
H(61)	1002(54)	1422(21)	2518(54)	-6(19)
H(62)	684(76)	1812(27)	2666(66)	64(30)
H(63)	2044(64)	1797(19)	2664(48)	6(21)
H(71)	-87(65)	1468(23)	312(56)	3(25)
H(72)	-607(58)	1649(22)	1396(50)	15(23)
H(73)	68(75)	1126(30)	1225(65)	28(32)
H(81)	4373(64)	2403(31)	933(79)	74(36)
H(82)	3381(79)	2474(35)	1611(70)	66(31)
H(83)	3599(73)	2124(29)	1498(61)	78(28)
H(91)	1543(101)	2706(34)	-320(93)	108(42)
H(92)	3201(156)	2792(50)	-265(123)	215(73)
H(93)	1846(83)	2888(27)	587(67)	27(31)
H(121)	3909(87)	587(35)	-2029(76)	114(46)

Table 1

Atom	X	Y	Z	U
53(10)	35(11)	0(9)	-16(9)	-10(9)
67(11)	46(10)	8(9)	2(9)	-5(8)
64(11)	55(12)	-4(10)	-10(11)	-1(10)
77(13)	111(11)	7(9)	-4(9)	-23(12)
49(10)	42(9)	26(10)	-15(10)	-4(8)
32(9)	91(12)	5(9)	-4(10)	-28(10)
H(151)	6831(133)	456(52)	-3722(105)	84(64)
H(152)	6369(80)	784(33)	-3307(69)	46(31)
H(153)	5353(68)	444(23)	-3776(55)	5(25)
H(161)	6123(54)	-255(19)	-2631(49)	-5(20)
H(162)	4670(64)	-161(21)	-2724(56)	11(24)
H(163)	5097(57)	-189(20)	-1714(54)	-11(21)
H(171)	6280(111)	-221(41)	356(96)	163(47)
H(172)	6791(81)	680(34)	716(67)	10(33)
H(173)	7804(95)	378(33)	239(73)	103(38)
H(181)	8058(76)	964(27)	-839(62)	20(31)
H(182)	7335(63)	1195(21)	-1611(53)	45(23)
H(183)	7296(83)	1321(30)	-400(70)	48(34)

TABLE IV.1 (continued)

(c) Z-Z 2, 4-Dibromo-1, 5-diphenyl-penta-1, 4-diene-3-one

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(11)	1573 (1)	−1534 (4)	3388 (3)	88 (2)	30 (2)	78 (2)	19 (2)	27 (2)	4 (2)
Br(12)	917 (1)	4886 (5)	5324 (2)	124 (3)	75 (2)	39 (1)	56 (2)	32 (2)	10 (2)
O(1)	1190 (4)	776 (24)	4988 (14)	74 (13)	29 (9)	42 (9)	1 (9)	18 (9)	10 (8)
C(11)	1581 (5)	2553 (34)	2564 (20)	18 (14)	26 (10)	39 (13)	6 (11)	− 5 (11)	− 15 (11)
C(12)	1449 (6)	1279 (39)	3262 (20)	20 (14)	50 (17)	42 (13)	12 (12)	− 12 (11)	10 (13)
C(13)	1223 (6)	1899 (35)	4102 (20)	42 (15)	34 (13)	49 (14)	4 (12)	23 (12)	− 32 (13)
C(14)	1024 (5)	3721 (30)	3849 (18)	23 (13)	20 (12)	28 (11)	16 (10)	8 (10)	− 10 (10)
C(15)	894 (5)	4363 (32)	2773 (16)	40 (16)	31 (14)	11 (10)	0 (11)	14 (10)	14 (9)
C(111)	1825 (5)	2373 (39)	1725 (21)	4 (13)	53 (15)	51 (14)	12 (12)	1 (11)	− 5 (14)
C(112)	2025 (7)	4138 (39)	1561 (21)	40 (18)	64 (16)	37 (14)	− 8 (14)	− 7 (13)	6 (12)
C(113)	2264 (9)	4079 (59)	701 (30)	65 (28)	113 (29)	60 (20)	4 (21)	14 (20)	− 19 (20)
C(114)	2292 (7)	2315 (52)	94 (22)	55 (19)	76 (23)	41 (15)	− 7 (17)	− 1 (13)	− 5 (16)
C(115)	2124 (7)	610 (39)	276 (21)	43 (19)	60 (16)	47 (15)	27 (14)	16 (15)	− 6 (13)
C(116)	1894 (6)	575 (43)	1063 (22)	46 (18)	70 (20)	35 (14)	4 (14)	− 4 (13)	− 10 (14)
C(121)	660 (5)	6054 (33)	2421 (20)	7 (12)	42 (13)	38 (13)	6 (10)	− 8 (10)	21 (11)
C(122)	445 (6)	5732 (40)	1282 (23)	43 (16)	56 (17)	53 (16)	10 (14)	18 (13)	25 (14)
C(123)	201 (8)	7149 (44)	922 (28)	45 (22)	53 (19)	67 (21)	5 (15)	23 (17)	15 (16)
C(124)	169 (6)	8876 (46)	1625 (29)	24 (16)	71 (20)	90 (22)	14 (13)	24 (16)	37 (18)
C(125)	395 (7)	9236 (42)	2716 (27)	57 (20)	61 (18)	66 (20)	13 (16)	28 (17)	23 (15)
C(126)	643 (7)	7840 (41)	3096 (21)	84 (24)	37 (17)	49 (14)	4 (15)	22 (14)	− 10 (13)
Br(21)	4084 (1)	9898 (5)	4436 (2)	119 (3)	70 (2)	28 (1)	− 46 (2)	1 (1)	− 6 (2)
Br(22)	3445 (1)	3329 (4)	1931 (3)	96 (3)	35 (2)	69 (2)	− 16 (2)	− 9 (2)	7 (2)
O(2)	3804 (5)	5763 (24)	3900 (13)	107 (15)	34 (10)	31 (8)	− 15 (9)	15 (9)	6 (7)
C(21)	4112 (6)	9277 (44)	1912 (23)	19 (19)	56 (20)	61 (16)	16 (14)	6 (14)	− 24 (14)
C(22)	3970 (5)	8677 (34)	2892 (20)	10 (12)	48 (14)	37 (13)	13 (11)	1 (10)	− 6 (12)
C(23)	3776 (6)	6793 (36)	2928 (21)	32 (14)	24 (12)	59 (15)	− 4 (11)	13 (12)	− 15 (13)
C(24)	3542 (6)	6133 (30)	1830 (22)	49 (18)	6 (10)	59 (15)	− 9 (10)	26 (14)	− 2 (11)
C(25)	3401 (6)	7260 (35)	1013 (20)	60 (20)	35 (12)	24 (12)	11 (12)	− 4 (12)	− 25 (12)
C(211)	4344 (6)	10955 (31)	1752 (20)	40 (16)	16 (11)	38 (12)	− 22 (11)	− 9 (12)	− 6 (10)
C(212)	4549 (6)	10647 (38)	824 (19)	17 (14)	65 (16)	43 (12)	23 (13)	11 (11)	3 (12)
C(213)	4791 (7)	12076 (42)	697 (22)	39 (19)	68 (19)	46 (16)	− 4 (15)	32 (14)	17 (15)
C(214)	4823 (8)	13850 (38)	1428 (23)	89 (25)	42 (16)	37 (16)	9 (14)	− 14 (16)	24 (14)
C(215)	4593 (7)	14167 (39)	2339 (24)	53 (19)	35 (16)	75 (18)	− 3 (14)	32 (15)	12 (13)
C(216)	4379 (5)	12745 (31)	2455 (18)	2 (12)	29 (13)	37 (12)	− 5 (9)	− 6 (10)	0 (10)
C(221)	3166 (6)	7070 (39)	− 71 (19)	21 (14)	52 (19)	35 (13)	7 (12)	5 (11)	16 (13)
C(222)	2987 (7)	8737 (42)	− 531 (27)	31 (19)	61 (19)	90 (22)	13 (14)	10 (17)	21 (16)
C(223)	2753 (7)	8807 (40)	− 1569 (27)	50 (18)	56 (18)	80 (20)	10 (14)	− 38 (17)	− 9 (16)
C(224)	2701 (7)	6778 (62)	− 2137 (23)	45 (20)	110 (29)	32 (15)	− 16 (22)	− 4 (14)	− 17 (20)
C(225)	2896 (8)	5114 (44)	− 1717 (25)	73 (21)	51 (17)	62 (17)	− 44 (17)	− 4 (16)	14 (17)
C(226)	3115 (8)	5260 (38)	− 663 (28)	49 (22)	36 (15)	60 (22)	− 15 (14)	− 17 (18)	− 2 (16)

Fig. IV.8
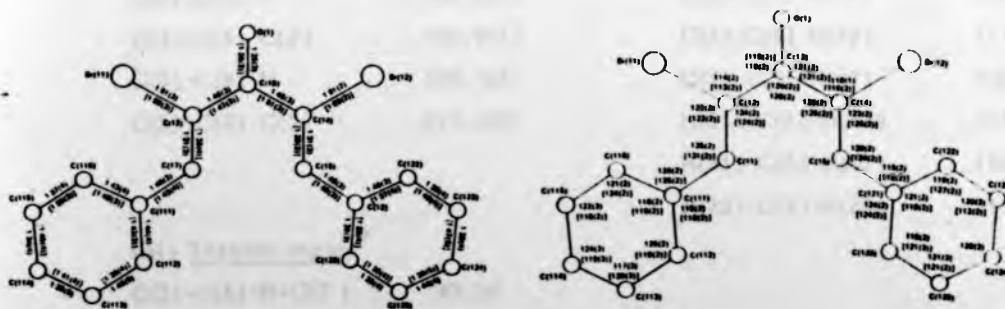
(c) Z-Z 2, 4-Dibromo-1, 5-diphenyl-penta-1, 4-diene-3-one

Atomic numbering, bond lengths and angles (in square
brackets for the second molecule) with standard deviations
in parentheses. For the second molecule, the initial digit in
each atom's number is (2) instead of (1).

TABLE IV.2.

Bond distances (Å), bond and torsion angles (^{o}) with standard deviations in parentheses.

(a) 3, 5-dibromo-4-oxo-2, 2, 6, 6-tetramethyl piperidin-1-yloxy

(i) Distances

Br(1)-C(2)	1.941(3)	C(2)-H(2)	1.02(3)
N-O(1)	1.278(5)	C(4)-H(41)	0.97(5)
N-C(3)	1.510(4)	C(4)-H(42)	1.01(5)
O(2)-C(1)	1.195(7)	C(4)-H(43)	1.03(5)
C(1)-C(2)	1.518(5)	C(5)-H(51)	0.87(5)
C(2)-C(3)	1.548(5)	C(5)-H(52)	0.92(4)
C(3)-C(4)	1.529(5)	C(5)-H(53)	0.98(4)
C(3)-C(5)	1.522(5)		

(ii) Angles

Br(1)-C(2)-C(1)	110.8(3)	Br(1)-C(2)-H(2)	106.2(18)
Br(1)-C(2)-C(3)	111.6(2)	C(1)-C(2)-H(2)	109.3(18)
O(1)-N-C(3)	115.0(2)	C(3)-C(2)-H(2)	107.1(19)
C(3)-N-C(3')	125.1(3)	C(3)-C(4)-H(41)	106.1(27)
O(2)-C(1)-C(2)	125.8(2)	C(3)-C(4)-H(42)	112.2(26)
C(2)-C(1)-C(2')	108.2(4)	C(3)-C(4)-H(43)	114.2(24)
C(1)-C(2)-C(3)	111.5(3)	H(41)-C(4)-H(42)	110.3(36)
C(2)-C(3)-N	106.6(3)	H(41)-C(4)-H(43)	105.6(35)
C(4)-C(3)-C(5)	111.0(3)	H(42)-C(4)-H(43)	108.2(35)
C(4)-C(3)-N	106.8(3)	C(3)-C(5)-H(51)	109.9(28)
C(4)-C(3)-C(2)	109.9(3)	C(3)-C(5)-H(52)	111.5(27)
C(5)-C(3)-N	109.1(3)	C(3)-C(5)-H(53)	106.3(22)
C(5)-C(3)-C(2)	113.1(3)	H(51)-C(5)-H(52)	107.6(39)
		H(51)-C(5)-H(53)	110.0(36)
		H(52)-C(5)-H(53)	111.5(35)

(iii) Torsion angles[†]

C(2)-C(3)-N-C(3')	42.58
C(1)-C(2)-C(3)-N	-50.53
C(3)-C(2)-C(1)-C(2')	65.51

[†]Primed numbers refer to the atom related by the mirror plane.

TABLE IV. 2 (continued)

b. The Ester |2| Derived From |1|.

(i) Distances

Ring 1		Ring 2	
Br(1)-C(1)	1.916(11)	N(2)-O(2)	1.252(13)
Br(2)-C(2)	1.988(12)	N(2)-C(13)	1.468(16)
N(1)-O(1)	1.286(15)	N(2)-C(14)	1.461(16)
N(1)-C(4)	1.462(18)	C(11)-C(12)	1.325(20)
N(1)-C(5)	1.489(17)	C(11)-C(14)	1.517(20)
C(1)-C(2)	1.306(19)	C(12)-C(13)	1.496(19)
C(1)-C(5)	1.525(18)	C(13)-C(15)	1.533(21)
C(2)-C(3)	1.502(20)	C(13)-C(16)	1.519(18)
C(3)-C(4)	1.532(18)	C(14)-C(17)	1.505(18)
C(4)-C(8)	1.461(20)	C(14)-C(18)	1.560(19)
C(4)-C(9)	1.562(17)	**Ester linkage**	
C(5)-C(6)	1.541(16)	C(2)-O(4)	1.403(16)
C(5)-C(7)	1.529(18)	C(10)-O(3)	1.188(14)
		C(10)-O(4)	1.356(14)
		C(10)-C(11)	1.476(18)

Hydrogen atoms			
C(3)-H(31)	1.39(6)		
C(6)-H(61)	0.83(6)	C(15)-H(151)	0.99(15)
C(6)-H(62)	1.05(8)	C(15)-H(152)	0.87(10)
C(6)- H(63)	0.89(7)	C(15)-H(153)	0.92(8)
C(7)-H(71)	0.91(7)	C(16)-H(161)	0.90(6)
C(7)-H(72)	0.94(7)	C(16)-H(162)	0.94(7)
C(7)-H(73)	1.10(9)	C(16)-H(163)	1.01(7)
C(8)-H(81)	1.11(10)	C(17)-H(171)	0.97(12)
C(8)-H(82)	0.84(10)	C(17)-H(172)	0.94(10)
C(8)-H(83)	0.71(8)	C(17)-H(173)	1.13(11)
C(9)-H(91)	0.82(11)	C(18)-H(181)	0.78(9)
C(9)-H(92)	1.15(17)	C(18)-H(182)	0.99(7)
C(9)-H(93)	1.04(9)	C(18)-H(183)	0.94(9)
C(12)-H(121)	1.08(9)		

TABLE IV.2 (continued)

(ii) Angles

Ring 1		Ring 2	
Br(1)-C(1)-C(2)	120.0(10)	O(2)-N(2)-C(13)	124.3(10)
Br(1)-C(1)-C(5)	114.0(9)	O(2)-N(2)-C(14)	122.6(10)
Br(2)-C(3)-C(2)	104.0(9)	C(13)-N(2)-C(14)	113.1(10)
Br(2)-C(3)-C(4)	112.5(9)	C(12)-C(11)-C(14)	112.0(12)
O(1)-N(1)-C(4)	120.5(11)	C(11)-C(12)-C(13)	111.6(12)
O(1)-N(1)-C(5)	115.3(10)	C(12)-C(13)-N(2)	102.0(11)
C(4)-N(1)-C(5)	121.7(10)	C(11)-C(14)-N(2)	101.2(10)
C(5)-C(1)-C(2)	125.9(11)	C(15)-C(13)-C(16)	108.7(12)
C(1)-C(2)-C(3)	123.3(12)	C(17)-C(14)-C(18)	110.2(11)
C(2)-C(3)-C(4)	109.1(10)	C(15)-C(13)-N(2)	110.8(10)
C(3)-C(4)-N(1)	109.9(10)	C(15)-C(13)-C(12)	111.5(11)
C(1)-C(5)-N(1)	107.6(10)	C(16)-C(13)-N(2)	108.9(10)
C(8)-C(4)-C(9)	108.6(11)	C(16)-C(13)-C(12)	114.8(11)
C(6)-C(5)-C(7)	110.6(10)	C(17)-C(14)-N(2)	109.8(11)
C(6)-C(5)-N(1)	108.5(10)	C(17)-C(14)-C(11)	113.3(11)
C(6)-C(5)-C(1)	110.6(11)	C(18)-C(14)-N(2)	110.2(10)
C(7)-C(5)-N(1)	109.0(10)	C(18)-C(14)-C(11)	111.8(11)
C(7)-C(5)-C(1)	110.4(10)	**Ester linkage**	
C(8)-C(4)-N(1)	114.6(12)	O(3)-C(10)-O(4)	124.1(11)
C(8)-C(4)-C(3)	106.3(11)	O(3)-C(10)-C(11)	126.1(12)
C(9)-C(4)-N(1)	108.6(11)	O(4)-C(10)-C(11)	109.7(10)
C(9)-C(4)-C(3)	108.6(11)	C(2)-O(4)-C(10)	115.7(9)
		C(1)-C(2)-O(4)	120.3(12)
		C(3)-C(2)-O(4)	116.3(10)
		C(10)-C(11)-C(12)	125.2(13)
		C(10)-C(11)-C(14)	122.8(11)

TABLE IV.2 (continued)

Methyl groups

H(61)-C(6)-H(62)	83(6)	H(151)-C(15)-H(152)	84(11)
H(61)-C(6)-H(63)	145(6)	H(151)-C(15)-H(153)	118(10)
H(62)-C(6)-H(63)	102(6)	H(152)-C(15)-H(153)	134(8)
H(71)-C(7)-H(72)	122(6)	H(161)-C(16)-H(162)	127(6)
H(71)-C(7)-H(73)	104(6)	H(161)-C(16)-H(163)	120(6)
H(72)-C(7)-H(73)	120(6)	H(162)-C(16)-H(163)	91(6)
H(81)-C(8)-H(82)	92(8)	H(171)-C(17)-H(172)	112(9)
H(81)-C(8)-H(83)	99(8)	H(171)-C(17)-H(173)	114(9)
H(82)-C(8)-H(83)	90(10)	H(172)-C(17)-H(173)	99(7)
H(91)-C(9)-H(92)	140(12)	H(181)-C(18)-H(182)	111(7)
H(91)-C(9)-H(93)	92(10)	H(181)-C(18)-H(183)	121(8)
H(92)-C(9)-H(93)	104(7)	H(182)-C(18)-H(183)	114(7)
H(121)-C(12)-C(11)	130(5)	Br(2)-C(3)-H(31)	93(3)
H(121)-C(12)-C(13)	117(6)	C(2)-C(3)-H(31)	110(3)
		C(4)-C(3)-H(31)	125(3)

(III) Torsion angles

Ring 1		Ring 2	
C(5)-C(1)-C(2)-C(3)	+7.60	C(14)-C(11)-C(12)-C(13)	+1.88
C(1)-C(2)-C(3)-C(4)	+21.92	C(11)-C(12)-C(13)-N(2)	-2.89
C(2)-C(3)-C(4)-N(1)	-48.33	C(12)-C(13)-N(2)-C(14)	+2.93
C(3)-C(4)-N(1)-C(5)	+53.73	C(13)-N(2)-C(14)-C(11)	-1.93
C(4)-N(1)-C(5)-C(1)	-24.38	N(2)-C(14)-C(11)-C(12)	0.0
N(1)-C(5)-C(1)-C(2)	- 7.99		

‡ As defined by R. Bucourt, "Topics in Stereochemistry", Vol.8, p.159, Interscience-Wiley

TABLE IV.3

Least squares planes for (2)

Equations of the least-squares mean planes are given as $PI + QJ + RK = S$[†] in orthogonal space. Deviations of certain atoms from these planes are shown and atoms defining the plane are marked with an asterisk.

Plane 1	P	Q	R	S
	0.7153	0.1862	0.6736	2.9757

Atom. deviation (Å)

Br(1)	0.167	C(3)*	-0.009
Br(2)	-1.935	C(4)	0.602
O(1)	-0.192	C(5)*	-0.009
O(4)	-0.080	C(6)	1.206
N(1)*	0.009	C(7)	-1.313
C(1)	0.079	C(8)	2.049
C(2)*	0.008	C(9)	0.284

Plane 2	P	Q	R	S
	0.2974	0.7482	-0.5931	4.3751

Atom. deviation (Å)

O(3)*	-0.003	C(10)*	-0.005
O(4)*	-0.022	C(11)*	0.013
C(2)*	0.017	C(12)	0.052
N(2)	0.068	C(13)	0.136
O(2)	0.063	C(14)	0.020

Plane 3	P	Q	R	S
	0.2947	0.7690	-0.5673	4.3917

Atom. deviation (Å)

O(2)	-0.025	C(14)*	0.000
N(2)*	0.000	C(15)	1.344
C(11)*	0.000	C(16)	-1.131
C(12)*	0.000	C(17)	-1.226
C(13)	0.046	C(18)	1.287

Angles between planes:- (1)-(2) 87.28° (1)-(3) 88.38° (2)-(3) 1.90°

TABLE IV.3

Least squares planes for (3).   Deviations of atoms forming these planes are insignificant and are not shown.

Plane No.	Defining atoms	P	Q	R	S
1.	Br(11), C(11), C(12), C(13)	.6583	.2039	.7246	6.4071
2.	Br(12), C(13), C(14), C(15)	.8072	.5902	.0019	4.3591
3.	Br(21), C(21), C(22), C(23)	.7768	-.5879	.2257	13.6357
4.	Br(22), C(23), C(24), C(25)	.8316	-.1868	-.5230	11.2415
5.	C(12), C(13), C(14), O(1)	.6604	.5265	.5354	5.9584
6.	C(22), C(23), C(24), O(2)	.7835	-.5312	-.3223	11.8726
7.	C(111) - C(116)	.6055	-.2893	.7414	5.3629
8.	C(121) - C(126)	.7137	.4736	-.5161	2.1855
9.	C(211) - C(216)	.5654	-.4721	.6764	10.9384
10.	C(221) - C(226)	.7973	.2218	-.5614	10.0034

(b)
Angles (°) between planes or lines

(1) - (2)	48.7	(3) - (4)	50.4
(1) - (5)	21.6	(3) - (6)	32.0
(1) - (7)	28.7	(3) - (9)	29.6
(2) - (5)	31.8	(4) - (6)	23.2
(2) - (8)	31.8	(4) - (10)	23.8

† With the orthogonal unit vector I parallel to a , K perpendicular to a in the ac plane and J perpendicular to the ac plane.

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CHAPTER V

The X-ray Structure of a novel pseudo-polyhalide Anion

$$[Me_2N(ICl)_2]^-$$
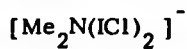
V.1. Introduction

During studies on the halogen-substituted ammonium cations, the reactions of dimethyl chloramine with a series of potential alkylating agents were investigated by workers at the University of Durham. They found that powerful alkylating agents such as methyl fluorosulphate gave salts of the colourless trimethylchloroammonium ion (equation 1).

$$Me_2NCl + MeO \cdot SO_2F \longrightarrow [Me_3NCl]^+[SO_3F]^- \qquad (1)$$
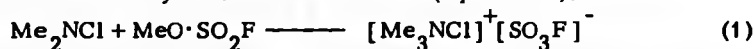
In contrast to this, when dimethylchloramine was dissolved in an excess of iodomethane at room temperature, a fine yellow solid slowly precipitated. The elemental analysis showed this compound to have the empirical formula C_3H_9ClIN and the product was formed quantitatively on the dimethylchloramine taken, with respect to equation (2).[1]
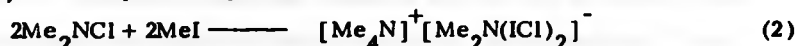
$$2Me_2NCl + 2MeI \longrightarrow [Me_4N]^+[Me_2N(ICl)_2]^- \qquad (2)$$

The compound represented an isomer of the known adduct of trimethyl-amine with iodine monochloride[2] but the i.r. spectrum clearly showed that the compound was of a different structure.[1] Clear demonstration that the compound C_3H_9ClIN was in fact the ionic compound $[Me_4N]^+[Me_2N(ICl)_2]^-$ as indicated in equation (2) only came with the results of a low temperature X-ray analysis at $-60°$ C. Details of this analysis will be described in this chapter. The bonding in the novel pseudo polyhalide anion $[Me_2N(ICl)_2]^-$ will be compared to other polyhalides and to other iodine monochloride adducts which have been described as charge transfer adducts but could be regarded equally well as examples of linear secondary bonds.

V.2. Experimental

Crystals of the compound C_3H_9ClIN were obtained by its slow preparation in tetrahydrofuran at 243 K ($-30°$ C) over a number of months.[1] Crystals are pale yellow chunky plates or rhombs, generally with poorly defined faces.

The crystals decompose in a few hours at 20° C but can be stored indefinitely at lower temperatures. Due to this fact, crystal selection, examination under polarised light and mounting has to be performed in a minimal time and the mounted crystal rapidly transferred to the diffractometer where, with the use of the Syntex LT-1 attachment, the crystal can be cooled to the required temperature. All photographic examination and data collections were performed at -60° C. Several crystals were investigated and although on some crystals the reflections appear to centre well, the autoindexing results indicate twinning.[3] Eventually a block-shaped crystal was found with a monoclinic cell 11.237 x 5.762 x 23.347 Å with a β of 110.20(3)^o and a data collection was started using this crystal. It soon became clear that the chosen cell might be B-centred; there were a significant number of exceptions to this absence, although some of these could be rejected because of their faulty backgrounds.[†] The structure was, however, solved with this data set, but refinement did not proceed below an R-factor of ≈ 15%. Taking the large number of observed systematic absences and the high R-factor it was decided to try and improve the data set using another crystal. The following crystal data and experimental conditions refer to this second data collection.

The crystal for the second data collection was again rapidly selected from a second sample of the compound, mounted using a large amount of hardener in the Araldite glue and was being cooled to -60° C on the diffractometer within ca. 30 min. The reflections from this crystal centre well and 2θ/ω and ω scans of several reflections give no indication of any twinning, although one reflection in the low angle centering did have an h index of 0.95.[3] Using 15 high angle (29 < 2θ < 35°)reflections, a monoclinic B-centred cell 11.233(3) • 5.773(1) • 23.376(5) Å with a β angle of 110.15(2)^o and volume of 1423.2(5) Å^3 was calculated, and the data was collected using an orientation matrix based on this cell. The following crystal data, however, contains the reduced primitive cell based on the angular co-ordinates of the high angle reflections but with transformed hkl indices for each reflection

[†] Preliminary work and initial data set collected by Dr. S. Esperas.

given by

$$h' = h, \ k' = -k \text{ and } l' = -h/2 - l/2 \qquad [4] \qquad\qquad (3)$$

Crystal data:

$C_6H_{18}Cl_2I_2N_2$, M = 442.92, monoclinic, $\underline{a}$ = 11.233(3), $\underline{b}$ = 5.7734(10), $\underline{c}$ = 11.087(2) Å, $\underline{\beta}$ = 98.24(2)$^\circ$, $\underline{U}$ = 711.6(3) Å^3 at -60° C, D_c = 2.067 g/cm^3 for Z = 4, D_m = 2.08 g/cm^3. Mo K$_\alpha$ radiation, λ = 0.71069 Å, μ(Mo K$_\alpha$) = 48.07 cm^{-1}. Space group $\underline{P2}$ or $\underline{P2/c}$ (see below).

Data were collected out to a maximum 2θ of 60° in several shells, using the B-centred cell referred to above.[5] Reflections were measured using θ-2θ scans over a scan range (K$_{\alpha 1}$ - 0.85) to (K$_{\alpha 2}$ + 0.85) and variable scan rate of 1.2 - 29.3 $^\circ$/min depending on the intensity of a preliminary 2 sec count. Background counts were recorded at each end of the scan, each for one quarter of the scan time. The intensities of 3 standard reflections collected every 100 reflections showed a gradual loss of intensity, and collected data were rescaled according to the equation F = F_o(1 + 0.0006655t), t = time in hours. The maximum rescale factor was 1.0626.

Of 2363 collected data (excluding standards and 299 systematically absent reflections due to the B-centering), 1855 were considered observed (I/σ(I) $\geqslant$ 3.0). Lorentz and polarisation factors were applied, and all data were transformed into the primitive cell using the transformation equations (3) above. Absorption corrections were applied at a later stage in the refinement using the program ABSCOR. The crystal was described using measured $d$plane parameters for this calculation, since the use of hkl indices for the crystal faces gives a much inferior description of the crystal.

V.3. Structure Solution and Refinement; Crystal Twinning

The structure of the compound was initially solved by applying Patterson methods to the first data set collected. Using the B-centred cell, the space groups assumed in the analysis were in fact the primitive monoclinic space groups Pm, P2, P2/m. The absence on any large peaks on the Harker plane V = $\frac{1}{2}$ ruled out P2/m. However, there were several large peaks on V = 0 and V = $\frac{1}{2}$ consistent with 8 iodine atoms in P2, such that their y co-ordinates are 0 and $\frac{1}{2}$ with their x and z co-ordinates related by $x' = x + \frac{1}{2}$, $z' = z + \frac{1}{2}$, to give the assumed pseudo-B-centred absence.

In fact, from the Harker peaks (2x, 0, 2z) and those on $V = \frac{1}{4}$, a feasible set of iodine positions appeared to be given by

$$x, \ 0, \ Z$$
$$\tfrac{1}{2} + x, \ 0, \ \tfrac{1}{2} + Z$$
$$\tfrac{1}{4} + x, \ \tfrac{1}{4}, \ \tfrac{1}{4} + Z$$
$$\tfrac{3}{4} + x, \ \tfrac{1}{4}, \ \tfrac{3}{4} + Z$$

with $x \approx 0.07$ and $Z = 0.443$.

Using these positions an R of 0.274 was obtained, and in subsequent Fouriers the missing Cl, C and N atoms were located, enabling the compound to be formulated as $[NMe_4]^+[Me_2N(ICl)_2]^-$. However, refinement with the original data set was not possible below R = 0.15 and the bond distances and angles and some atomic temperature factors were unacceptable.

The second data set, transformed, along with the previous iodine co-ordinates, into the correct primitive cell eventually gave after several refinement cycles an R factor of 6.7% with the iodine and chorine atoms anisotropic. However, even with this low R-factor there were several unsuitable features of the present model. Notably, the temperature factors of the chemically similar atoms N(1) and N(2) had U = 0.014 and U = 0.0988 respectively, the bond lengths and angles between the independent ions were markedly dissimilar and the agreements for certain reflection classes (hOl and OOl) were very poor.[6] In fact, by a suitable origin shift, the co-ordinates of the present solution could be transformed into P2/c so that independent ions become equivalent. When this possibility was tested, the R-factor improved slightly but more importantly the refinement resulting in chemically morereasonable bond distances and angles. Space group P2/c requires the systematic absence hOl , 1 $\neq$ 2n to which there are a significant number of exceptions. However, inspection shows that the groups of reflections hOl, lOh, h̄Ol̄ and l̄Oh̄ contains particular inter-relationships very indicative of crystal twinning such that a' $\equiv$ c with b reversed. The effects of this form of twinning are shown in Fig. V.1 where the hOl lattice points associated with each orientation of the twin are shown very nearly superimposed. From an inspection of hOl and the equivalent l̄Oh̄ reflection, a twinning factor of ca. 0.4 is observed for several sets of reflections, although the inconsistencies between equivalent pairs of
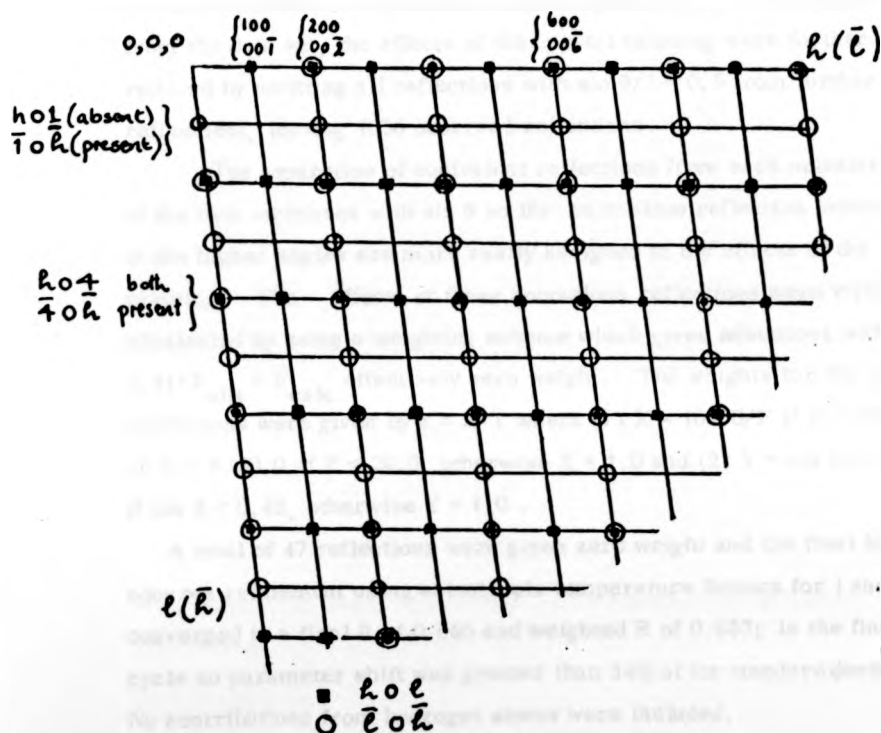
Figure V.1 Diagram showing the twinning of the hOl reciprocal lattice layers in $[Me_4N]^+[Me_2N(ICl)_2]^-$. Some typical indices of reflections for the two componenets ($\blacksquare \equiv hOl$; $O \equiv \overline{h}O\overline{l}$) are shown. The twinning ($h' \equiv \overline{l}$, $l' \equiv \overline{h}$, $k' \equiv \overline{k}$) is perfect as regards angle, but the difference in axial lengths leads to resolution between each pair of lattice points (not shown here) at high angles.

reflections prevented an accurate correction of the twinning effects.[7]

Therefore, it seems certain that space group P2/c is correct, since it gives better bond distances and angles and that the missing hOl absence is due to crystal twinning although no clear signs of twinning were seen in the data collection. Apart from removing all hOl, $l \neq 2n$ reflections from the data set, the effects of the crystal twinning were further reduced by omitting all reflections with $\sin \theta/\lambda < 0.5$ from further refinement, leaving 1056 observed reflections.

The separation of equivalent reflections from each orientation of the twin increases with $\sin \theta$ so that anomalous reflection intensities at the higher angles are more easily assigned to the effects of the twinning. The effects of these anomalous reflections were virtually eliminated by using a weighting scheme which gives reflections with $0.41 * F_{obs} \geq F_{calc}$ effectively zero weight. The weights for the other reflections were given by $\omega = X*Y$ where (1) $X = 100.0/F$ if $F > 100.0$, or $X = F/20.0$ if $F < 20.0$, otherwise $X = 1.0$ and (2) $Y = \sin \theta/0.42$ if $\sin \theta < 0.42$, otherwise $Y = 1.0$.

A total of 47 reflections were given zero weight and the final least squares refinement using anisotropic temperature factors for I and Cl converged to a final R of 0.066 and weighted R of 0.057; in the final cycle no parameter shift was greater than 34% of its standard deviation. No contributions from hydrogen atoms were included.

Final positional parameters and temperature factors for all atoms are listed in Table V.1, bond lengths and angles in Table V.2. Table V.3 contains some equivalent hOl and lOh reflections indicating the twinning factors. The novel $[Me_2N(ICl)_2]^-$ anion is shown in Fig. V.2 and the molecular packing in Fig. V.3. Final structure factors are listed in Appendix V.

V.4. Discussion

The crystal structure analysis of the compound with empirical formula C_3H_9ClIN has shown that it consists of the ions $[NMe_4]^+$ and $[Me_2N(ICl)_2]^-$, each with crystallographic two-fold symmetry

TABLE V.1.

Atomic co-ordinates and temperature factors for $[Me_4N]^+[Me_2N(ICl)_2]^-$ with standard deviations in parentheses

Atom	X	Y	Z	U
I(1)	0.36985(5)	0.11952(9)	0.13486(5)	**
Cl(1)	0.2062(3)	-0.1522(5)	0.0057(3)	**
N(1)	0.5000	0.3452(19)	0.2500	0.043(2)
N(2)	0.0000	-0.4644(19)	0.2500	0.040(2)
C(1)	0.5657(10)	0.4928(18)	0.1718(9)	0.049(2)
C(2)	-0.0737(9)	-0.6114(21)	0.3191(9)	0.052(2)
C(3)	-0.0807(11)	-0.3127(20)	0.1656(11)	0.054(2)

**	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	0.0405(4)	0.0348(4)	0.0411(4)	0.0042(2)	0.0020(1)	0.0015(2)
Cl(1)	0.0628(12)	0.0548(12)	0.0571(11)	-0.0131(10)	-0.0089(9)	-0.0007(9)

TABLE V.2.

Bond lengths (Å) and bond angles (°) with standard deviations in parentheses

Bond lengths (Å)

I(1) - Cl(1)	2.672(3)	N(2) - C(2)	1.475(13)
I(1) - N(1)	2.220(7)	N(2) - C(3)	1.491(13)
N(1) - C(1)	1.486(13)		

Bond angles (°)

N(1)-I(1)-Cl(1)	177.02(7)	C(2)-N(2)-C(2')	109.7(9)
I(1)-N(1)-I(1')	108.1(5)	C(2)-N(2)-C(3)	110.4(6)
I(1)-N(1)-C(1)	110.0(4)	C(2)-N(2)-C(3')	109.1(6)
C(1)-N(1)-C(1')	110.0(9)	C(3)-N(2)-C(3')	108.0(9)
C(1)-N(1)-I(1')	109.3(4)		

126.

TABLE V.3

Twinning Factors for some equivalent h0l and $\overline{1}0\overline{h}$ Reflections

h 0 l	F_1	$\overline{1}0\overline{h}$	F_2	F_1/F_2	h 0 l	F_1	$\overline{1}0\overline{h}$	F_2	F_1/F_2
2 0 $\overline{7}$	26	7 0 $\overline{2}$	56	.47	8 0 $\overline{5}$	9	5 0 $\overline{8}$	20	.42
2 0 $\overline{5}$	33	5 0 $\overline{2}$	78	.42	8 0 $\overline{3}$	22	3 0 $\overline{8}$	60	.36
2 0 $\overline{3}$	15	3 0 $\overline{2}$	34	.43	8 0 $\overline{1}$	5	1 0 $\overline{8}$	15	.31
2 0 $\overline{1}$	58	1 0 $\overline{2}$	139	.42	10 0 $\overline{9}$	13	9 0 $\overline{10}$	32	.41
4 0 $\overline{7}$	28	7 0 $\overline{4}$	70	.40	10 0 $\overline{5}$	15	5 0 $\overline{10}$	42	.37
4 0 $\overline{5}$	16	5 0 $\overline{4}$	14	.92	10 0 $\overline{1}$	8	1 0 $\overline{10}$	65	.12
4 0 $\overline{3}$	58	3 0 $\overline{4}$	142	.41	12 0 $\overline{11}$	7	11 0 $\overline{12}$	13	.53
4 0 $\overline{1}$	30	1 0 $\overline{4}$	87	.35	12 0 $\overline{7}$	10	7 0 $\overline{12}$	25	.40
6 0 $\overline{9}$	20	9 0 $\overline{6}$	53	.38	12 0 $\overline{3}$	8	3 0 $\overline{12}$	41	.20
6 0 $\overline{5}$	43	5 0 $\overline{6}$	105	.41	2 0 5	39	$\overline{5}$ 0 $\overline{2}$	131	.30
6 0 $\overline{3}$	20	3 0 $\overline{6}$	50	.40	$\overline{4}$ 0 $\overline{1}$	6	1 0 4	117	.05
6 0 $\overline{1}$	18	1 0 $\overline{6}$	85	.21	2 0 9	5	$\overline{9}$ 0 $\overline{2}$	49	.10
8 0 $\overline{11}$	10	11 0 $\overline{8}$	31	.33	2 0 7	14	$\overline{7}$ 0 $\overline{2}$	41	.34
8 0 $\overline{7}$	26	7 0 $\overline{8}$	64	.41	$\overline{6}$ 0 $\overline{1}$	4	1 0 6	52	.07

(Fig. V. 2). The only possible analogues to the extremely novel anion are the polyhalide anions, in particular $[I_5]^-$ which exists as a nearly planar V-shaped ion.[8] This latter ion can be regarded as I^- interacting with two iodine molecules with the distances shown in (B). This seems to be a dominant feature in iodine polyatomic anions.[8] In parallel with this, the present anion can be regarded as having the structure (A) with $[Me_2N]^-$ considered as a new pseudohalide. It is perhaps surprising to regard $[Me_2N]^-$ as acting as a pseudohalide in its interactions with iodine monochloride, although conventional pseudohalides have been found to form pseudopolyhalide anion analogues, for example in $(NCS \cdot I_2)^-$.[9]
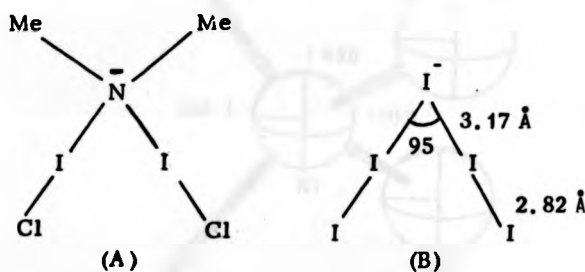
In the anion, the N-I and I-Cl distances are 2.220(7) and 2.672(3) Å respectively, and the N-I-Cl system is very nearly linear [N-I-Cl is 177.02(7)°]. The N-C(Me) distance is 1.486(13) Å compared to N-C distances of 1.475(13) and 1.491(13) Å in the cation. In anion and cation the angles about nitrogen have values close to the tetrahedral value (Table V.2).

The I-Cl bond length in the anion is considerably longer than that in gaseous ICl (2.321 Å)[10] or that found in the two polymorphic forms (α and β) of ICl in the solid state (2.44 and 2.37 (α); 2.440 and 2.351 Å (β)). The differences in these last two values are directly attributable to the different crystal packing arrangements resulting in slightly different inter-molecular contacts. Iodine monochloride has also been characterised in several charge transfer adducts with a variety of bases. The ICl distances in the adducts with pyridine,[12] 2-chloroquinoline[13] and trimethylamine[2] are 2.510, 2.446 and 2.52 Å respectively. The I-Cl distance in the ICl adduct with 1-oxa-4-selenacyclohexane is even longer
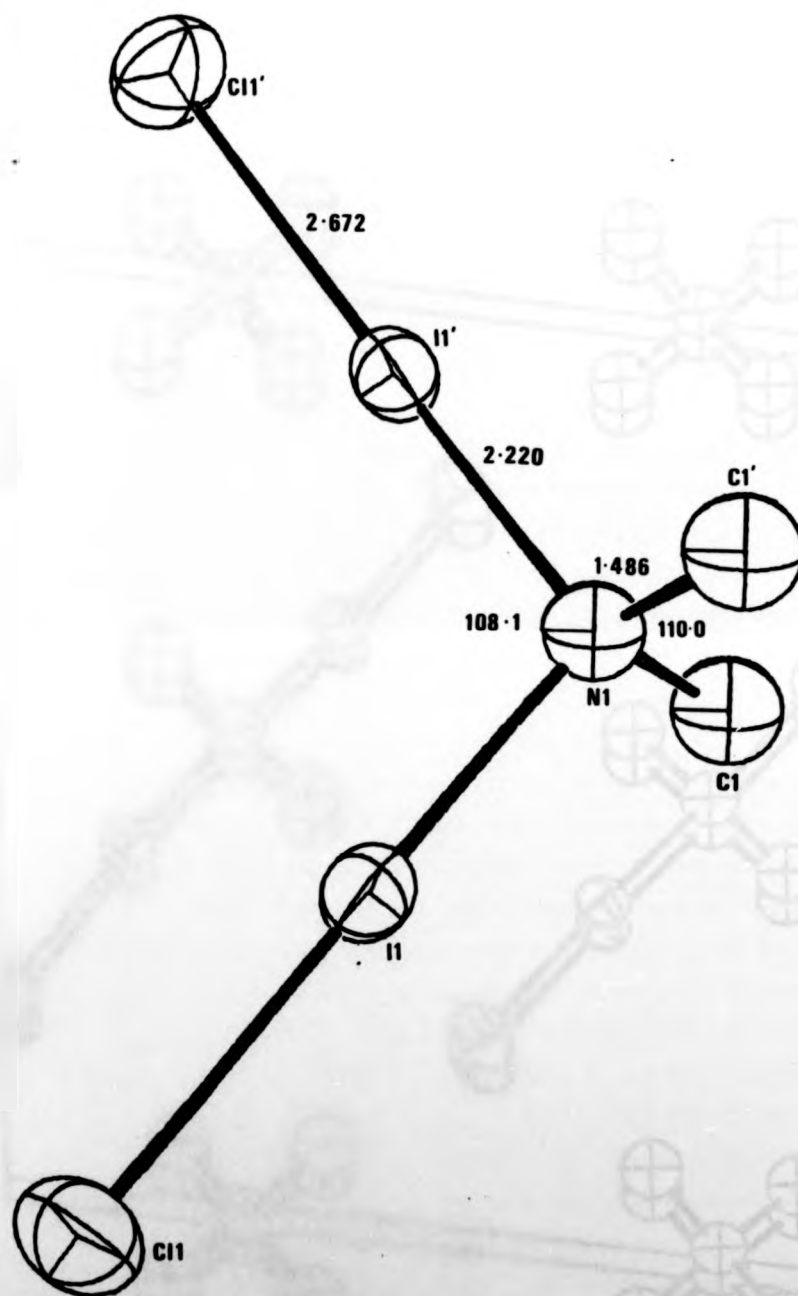
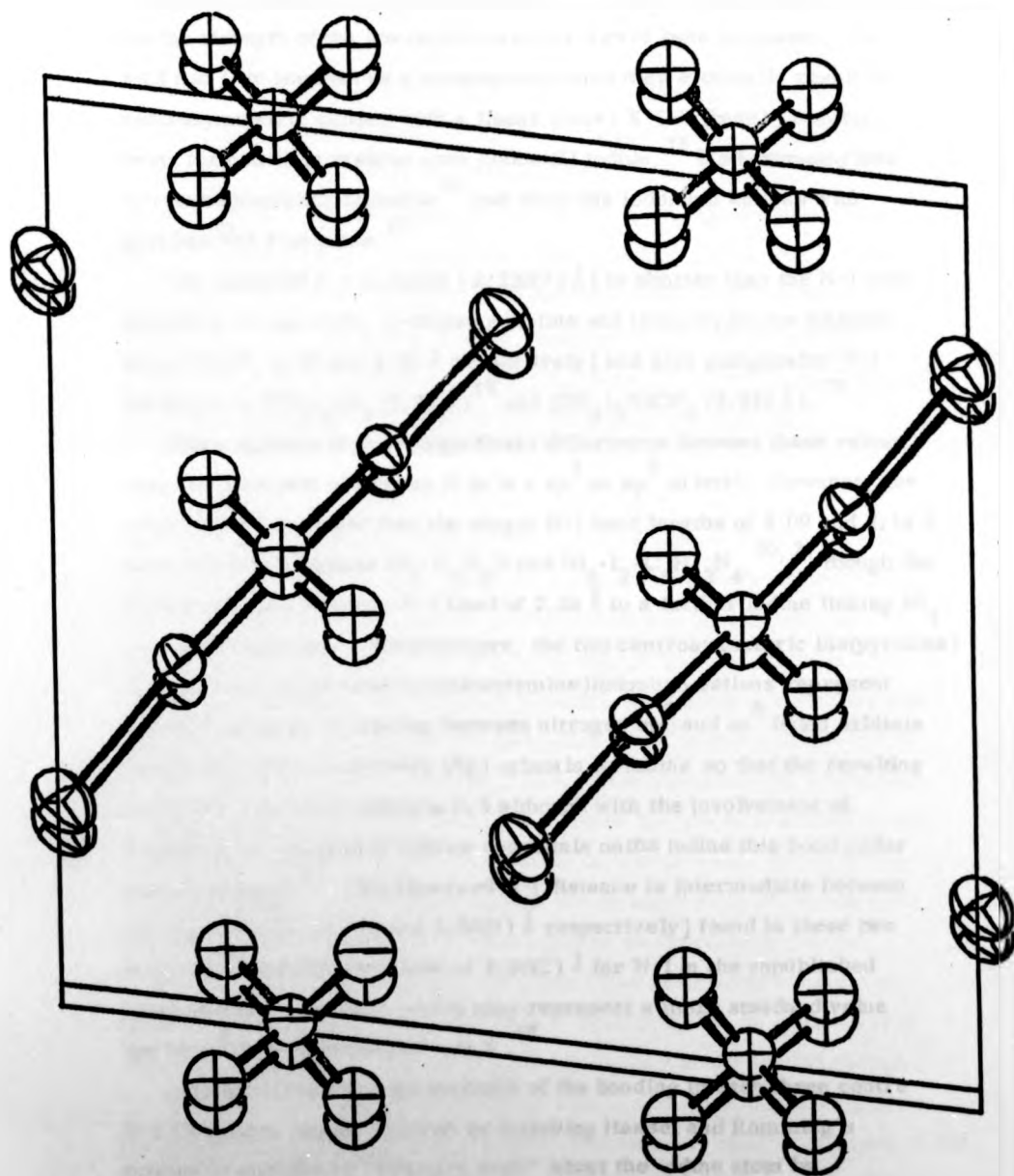Figure V.2   The structure of the anion $[Me_2N(ICl)_2]^-$

Fig. V.3 Packing arrangement in $[Me_4N^+][Me_2N(ICl)_2]^-$ viewed down $\underline{b}$.

(2.73(1) Å)which, with the short Se-I distance (2.630(5) Å), suggests the formation of the selenonium salt $[C_4H_8OSeI]^+Cl^-$.[14] This behaviour is typical of adducts of iodine and the inter-halogen compounds ICl and IBr. As the strength of the interaction with the Lewis base increases, the I-I, I-Cl and I-Br lengthen as a consequence until they eventually result in centrosymmetric cations with a linear (base) X-I-X (base) grouping being formed as in bis(thio urea)iodine(I) iodide,[15] bis(hexamethylene tetramine)iodonium triiodide[16] and other bis iodonium cations with pyridine[16] and 3-picoline.[17]

The observed N-I distance [2.220(7) Å] is shorter than the N-I bond lengths in the pyridine, 2-chloroquinoline and trimethylamine adducts above [2.29, 2.43 and 2.30 Å respectively] and also comparable N-I distances in $(CH_3)_3NI_2$ (2.27 Å)[18] and $(CH_3)_3NICF_3$ (2.932 Å).[19]

There appears to be no significant differences between these values when the lone pair orbital on N is in a sp^2 or sp^3 orbital. However, the observed N-I is longer than the single N-I bond lengths of 2.09 and 2.14 Å observed in the adducts $NI_3 \cdot C_5H_5N$ and $NI_3 \cdot I_2 \cdot C_6H_{12}N_4$.[20,21] though the former also has a longer N-I bond of 2.36 Å to a further iodine linking NI_4 tetrahedra together. Furthermore, the two centrosymmetric bis(pyridine) iodonium and bis(hexamethylenetetramine)iodonium cations represent examples with 3c-4e bonding between nitrogen sp^2 and sp^3 filled orbitals interacting with σ-symmetry (5p) orbitals on iodine so that the resulting N-I bonds have bond orders ≈ 0.5 although with the involvement of π-orbitals on the ligands and/or d-orbitals on the iodine this bond order would increase.[16] The observed N-I distance is intermediate between the distances [2.16(10) and 2.30(1) Å respectively] found in these two compounds although the value of 2.24(2) Å for N-I in the unpublished bis(3-picoline) iodonium cation may represent a more standard value for $N(sp^2)$-I with bond order ≈ 0.5.[17]

Another measure of the strength of the bonding in each three centre N-I-Cl system can be obtained by following Hassel and Romming's method in calculating "effective radii" about the iodine atom by subtracting the covalent radii of the nitrogen [0.70 Å] and chlorine

[0.99 Å] atoms from the evaluated N-I and I-Cl bond lengths.[22] The resultant values for the effective radii R_1 and R_2 in the present anion are 1.52 and 1.68 Å respectively which, if plotted on Hassel and Romming's graph of R_1 versus R_2 values for a series of polyiodide and IX(Y=Cl, Br) complexes, falls very close to the least squares straight line through all these points. The equation for this straight line is, in fact, R_2 = 4.59 - 1.97 R_1 from which the calculated R_2 for R_1 = 1.52 is 1.60 Å compared to an observed value of 1.68 Å. The strongest interactions are, therefore, for those complexes with $R_1 \approx R_2$. A similar attempt to correlate the bond lengths in the linear two-fold co-ordination of iodine which has been found to be an essential structural element in the crystal structures of several $NI_3 : I_2$: base [N, O and I] and NI_3 : base adducts or their analogues is not always obvious for, as yet, undefined reasons.[21]

The bonding in the present anion and the majority of the complexes described above has been described in terms of charge transfer interactions.[22,23] However, as will be further explained in chapter VI, the orbital overlaps already defined in the secondary bonding model can equally well be applied to the present example of a σ-σ charge transfer complex. There are, therefore, two separate 3-centre-4-electron systems formed in the present anion when the two lone pairs in sp^3 orbitals on the Me_2N^- group interact with the σ^*-orbitals of both iodine monochloride molecules. The short N-I and long I-Cl distances indicate that the interactions in the present anion are among the strongest so far observed for iodine mono-chloride adducts. As a consequence of the strength of these interactions, the two chlorine atoms in each anion possess an appreciable partial negative charge which acts to prevent any close inter anion contacts so that the packing is that of discrete ions. Furthermore, no chlorine NQR signal is detected from the anion again as a result of the partial charge.[1] The absence of any inter-anion interactions is somewhat surprising as an essential structural feature of the polyiodide ions and other complexes of the X·I-I (X = base) type, e.g.(iodine adducts of 1-oxa-4-selenacyclohexane and 1,4-diselenacyclohexane) is that the compounds invariably form into polymeric arrangements via several weaker intermolecular contacts

which are possibly described as secondary bonds.[8, 23] Even iodine adducts of such compounds as NI_3,[21] and the transition metal complexes iodo *tris* (N, N-dimethyldithiocarbamato)ruthenium(IV),[24] Pt(phen)I_6 and Pt_2(phen)$_2I_{10}$ (phen = 1, 10 phenanthroline)[25] all form zigzag or helical chains with the iodine molecules bridging the directly bonded iodine atoms. In these latter complexes an adequate picture of the bonding might use semi-metallic bands of delocalised multi-centre orbitals formed by interacting p-orbitals of each iodine along the polymeric chain of iodine atoms.

V.5. References

1. The chemical reactions and physical measurements on the halogen-substituted ammonium cations are part of the research of N.D. Cowan, C.J. Ludman and T.C. Waddington at the University of Durham.

2. O. Hassel and H. Hope, Acta Chem. Scand., 1960, 14, 391.

3. Twinned crystals normally cause problems in either the centering or autoindexing routines or else are visible on axial photographs. Sometimes the reciprocal lattice points from the various members of the twinned crystal do not exactly fall on top of one another, and the centering routine will take many iterations and can often be observed to be oscillating between two close reflections. These will sometimes be clearly seen on plotting the peaks. Sometimes the centering routine behaves normally, but the autoindexing routine produces very few solutions all with very long axial lengths, yet the original rotation photograph may not have had a high density of reflections indicative of a large unit cell. Increasing the integer tolerance for accepting an axial vector will give a larger number of vectors and hence enable the reflections associated with the twin to be identified (normally one or two reflections will be calculated in the least squares routine with bad h, k, l indices). Finally, axial photographs may contain reflections which do not fall on the layer lines which are normally much less intense than the layer line reflections. In all these cases it is advisable to search for a better crystal before continuing with an obvious twin. Source: Syntex Analytical Instruments, Technical Notes, 1974.

4. Alternative transformations such as a' = a/2 - c/2; b' = b; c' = a/2 + c/2 OR a' = a/2 - c_i/2; b' = b; c' = c give larger β-angles. The transformation matrix for the reflection indices is given by Matrix (I) whilst the atom co-ordinates are transformed into the primitive cell by the inverse matrix (II).

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -\tfrac{1}{2} & 0 & -\tfrac{1}{2} \end{pmatrix} (I) \qquad \begin{pmatrix} 1 & 0 & -1 \\ 0 & -1 & 0 \\ 0 & 0 & -2 \end{pmatrix} (II)$$

5. After collecting 613 reflections, of which none with $h + l = 2n + 1$ were observed, the program was coded to exclude systematically absent reflections due to the B-centering condition. As a final check on this absence, after completion of the data collection out to 60°, a shell of data was collected containing only B-centred reflections, none of which were again found to be observed.

6. Marked variation in anion geometry is also the feature of several other complexes where pseudo symmetry and other factors are blamed. See, for example, M. Webster, K.R. Mudd and D.J. Taylor, Inorg. Chim. Acta, 1976, 20, 231.

7. Need to solve the simultaneous equations

$$f_1 = f_a + af_b$$

$$f_2 = f_b + af_a$$ to obtain the true intensities of

reflections 1 and 2 (f_a and f_b) from the observed values f_1 and f_2 (a = twinning factor).

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14. C. Knobler and J.D. McCullough, Inorg. Chem., 1968, 7, 365.

15. G. H-Y. Lin and H. Hope, Acta Cryst., 1972, B28, 643.

16. H. Pritzkow, Acta Cryst., 1975, B31, 1505, 1589 and refs. therein. See also G.A. Bowmaker and R.J. Knappstein, Aust. J. Chem., 1977, 30, 1123.

17. R.S. Osborn, unpublished results, quoted in ref. 16.

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21. J. Jander, Adv. Inorg. Chem. Radiochem., 1976, 19, 1.

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23. 'Selenium', Eds. R.A. Zingaro and W.C. Cooper, Van Nostrand-Reinhold, Chap. 7, esp. p. 361.

24. M. Mattson and L.H. Pignolet, Inorg. Chem., 1977, 16, 488.

25. K.D. Buse, H.J. Keller and H. Pritzkow, Inorg. Chem., 1977, 16, 1072.

CHAPTER VI

A Discussion of Secondary Bonding and Other Intermolecular

Forces

VI.1.   Introduction

In the previous chapters of this section of the thesis the idea of a
secondary bond was introduced and discussed with reference to the
crystal structures determined.   In each chapter the significance of
these structures in relation to other physical measurements made on
these or related compounds was briefly discussed.   It is the purpose
of this chapter to expand these remarks and attempt to draw some
conclusions on the importance of the secondary bonding model in
comparison to other theories of inter-molecular interactions.

VI.2 . Stereochemical Bonding Models

Before discussing this influence of secondary bonds on molecular
geometry, it is important to have a general idea of the factors which
affect the bonding in the unperturbed structures. What follows is
therefore a general summary of a few of the currently accepted stereo-
chemical bonding models.

(VI.2.1) Valence Shell Electron Pair Repulsion (VSEPR)theory

Perhaps the single most important stereochemical model in use in
structural chemistry is the valence shell electron pair repulsion model
of Nyholm and Gillespie[1] in which the molecular stereochemistry is
derived from a simple consideration of lone pair-lone pair (lp-lp), lone pair-
bonded pair (lp-bp) and bonded pair-bonded pair (bp-bp) electron pair
repulsions.   There are two basic principles involved in the application of
this scheme:

(i)   Valence shell electron pairs repel one another so that the system
       adopts a minimum repulsion-energy configuration, and

(ii) lone pair-lone pair (lp-lp) repulsions are greater than lone pair-
       bonded-pair (lp-bp)repulsions which in turn are greater than bonded
       pair-bonded pair (bp-bp) repulsions.

By considering octahedral and trigonal bipyramidal arrangements with two or more lone pairs, Jenkins and Waddington[2] have extended the arguments of Nyholm and Gillespie and formulate two further axioms:

(iii) the lone pair-bonded pair repulsion is less than the arithmetic mean of the lone pair-lone pair and bonded pair-bonded pair repulsions,

and

(iv) in trigonal bipyramidal arrangements, the electron pair interactions at 120° to each other are less than half the corresponding interactions at 90° to each other. (Electron pair interactions at 180° to each other are ignored since they exert no component of force perpendicular to the bond axis).

Together these four rules enable the primary geometries of a vast number of complexes to be rationalised. However, in chapter II it has already been stated that the primary geometry in the solid state may be considerably affected by the varying strengths of any secondary bonds which reflected the fact that in some systems the stereochemical activity of lone pairs may be over-estimated. Due to the weakness and variable lengths of secondary bonds, their inclusion into this stereochemical model is difficult. However, stereotypical arrangements such as those of Brown (Chapter II) are useful in classification.[3]

(VI.2.2.) Galy Model[4]

Secondly, the theoretical model of Galy et al.[4] will be described. Starting from similar basic principles to those of Nyholm and Gillespie, the authors have developed a simple stereochemical model using data on the oxides, fluorides and oxyfluorides of various non-metals in which the distances between the bonded atoms are used to calculate the displacement of the central atom away from the centre of the co-ordination sphere towards the position occupied by a lone pair. The calculation also defines the centroid of the volume occupied by this lone pair. The co-ordination polyhedra resulting from this calculation are very similar to those used by Brown in his bond valence calculations.

(Some of the structures used are common to both models).[3]   Again,
deformation mechanisms for the passage of a structure between polyhedra
are readily predicted from structural results.[5]   Finally, the calculations
enable the lone pair electrons to be defined as an inert pair (i.e. the
electron pair is in a non-hybridised atomic orbital) or a non-bonding
pair (i.e. the lone pair occupies a hybrid orbital) since the calculated
distance between bonded atoms and the lone pair will be greater for the
non-bonding case.[6]

(VI.2.3.)   3c-4e MO's

The 3c-4e MO's used to explain the interactions in hydrogen and
secondary bonded systems are a natural extension of the arguments of
Rundle who proposed delocalised 3c-4e bonds involving only $\underline{s}$ and $\underline{p}$
orbitals to explain the bonding in trihalide ions and related species.[7]
This view was different to that of Gillespie and others who attributed
the stability of the chemical bonds formed between filled shell species
to outer d-orbital participation[8] although other bonding propositions
explaining the stability of these bonds have also been given.[9]   The
theoretical treatment of 3c-4e bonding as related to nitrenes and thio-
thiophthenes has been investigated by Gleiter and Hoffmann.[10]   In
forming the 3c-4e MO's, two cases may be distinguished, depending on
the nature of the central orbital ($\underline{s}$ or $\underline{p}$) participating.
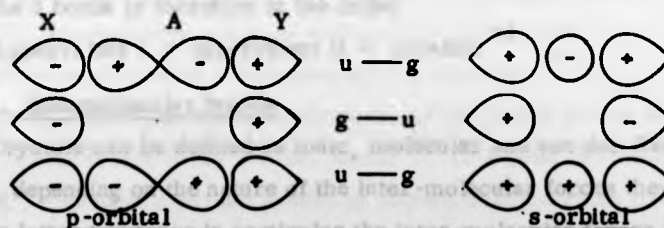
The symmetry designations u (antisymmetric) and g (symmetric) refer to
reflection through the plane bisecting the 3 centre system.   Generally
3c-4e MO's with the middle orbital strictly non-bonding are restricted
the interhalogen and xenon and other rare gas compounds.[10]   In other
cases the system tends to be asymmetric, the distance A-X shortening

as A...Y increases until with very long A...Y distances the orbital overlaps are best described as a lone pair on Y interacting with the σ^* orbital of a 2c-2e A-X bond, i.e. the secondary bonding model. The results of the calculations on the thiothiophenes again do not help to discriminate against the involvement of d-orbitals in the 3c-4e interactions. The potential energy curve produced on displacing the central S from a symmetrical situation show a preference for an unsymmetrical structure when 3d orbitals are not utilised and a nearly symmetrical structure (very flat minimum energy) when 3d orbitals are included.[10] Calculations on other more extended linear arrays of S atoms constrained by π systems favour the viewpoint that the 3d orbitals should be treated as polarising functions only.[11]

In general, therefore, the role of d-orbitals in the bonding of complexes of the non-metals is still ambiguous. According to Musher,[12] however, the bonding in virtually all non-metal compounds should be described without d-orbital participation. Instead, a mixture of "orbitally deficient hypervalent" 3c-3 orbital and covalent (2c-2e) bonds should be used. His 'hypervalent' bonds are virtually identical to 3c-4e MO's above and the bond type is designated hypervalent I and II, depending on whether the central atom of linear L-A-L fragments uses either a p orbital or s and p orbitals in the bonding. The bond strengths for the 3 bonds is therefore in the order

hypervalent I < hypervalent II < covalent [12]

VI.3. Intermolecular forces

Crystals can be defined as ionic, molecular and van der Waals in type, depending on the nature of the inter-molecular forces they contain. In the latter two types in particular the inter-molecular forces can be described using either van der Waals, charge transfer and/or secondary bonding descriptions.

(VI.3.1.) Van der Waals interactions

The definition of a secondary or charge transfer interaction relies on defining a limiting inter- or intra-molecular contact distance (van der Waals) contact. Distances shorter than this value but longer than

single bond distances can then be described as secondary or charge
transfer interactions. Before attempting to discuss any general
factors associated with secondary bonding, it is therefore important to
ask some basic questions. In particular, what are van der Waals forces ?
Associated with this is the very important question: at what point does
an inter- or intra-molecular contact distance cease to be a van der
Waals contact and become a secondary bond ?

(VI.3.1(i))   What are van der Waals forces ?

These forces originate from the quantum mechanical behaviour of
the electrons which are part of an atomic or molecular system. If the
system is considered as positively charged nuclei (or nucleus) each
surrounded by a negatively charged electron cloud which can only have
certain permitted energies, then this electron cloud is not rigidly
distributed around the nuclei but can be deformed by both external and
internal electromagnetic influences. This occurs either when a
permanent dipole exists or when temporary dipoles are induced by either
an external field, a neighbouring dipole or even the mutual interaction of
spherically symmetric non-dipole molecules (when localised fluctuations
in charge density of the electron clouds occur). Such polarisation
effects can, in fact, rapidly propagate through the solid and are known
collectively as London dispersion forces. These localised fluctuations
can be represented as a simple exchange of photons between
neighbouring particles without emission of radiation.[13]

Overall, these forces are known as van der Waals forces after
their initial treatment by van der Waals.[14] Like most inter-molecular
forces, they have a certain sphere of influence inside which the
discussion of these forces involve more directional character - ionic
or MO models - and outside which the influence of the forces steadily
decreases. These effects can be conveniently represented in an
interaction curve called a Morse curve.[15] For each element the radius
of the sphere of influence is represented by a van der Waals radius.

The determination of these radii can be obtained from an analysis of the atomic and molecular packing distances in as many compounds as possible. The most significant values of these radii would be for structures near the close packing limits. The most reliable values are therefore given particularly for the elements of Group VII and neutral spherically symmetrical molecules which can achieve close packing without any of the semi-polar interactions that occur between the dipoles of other asymmetrically shaped molecules being involved.

It is quite common for several values of the van der Waals radius ($r_{v.d.w.}$) of a particular element to appear in the literature, depending on the structures used in the analysis. For example, in Chapter I the van der Waals radius of tin has separately been given as 2.10 and 2.17 Å.

The two values are due to Bondi[16] and Pauling[17] who have both published fairly comprehensive tabulations of $r_{v.d.w.}$ for several atoms. Although Bondi's values are generally similar to Pauling's values, they are based on a more thorough examination of experimental evidence, so that the choice between the two sets of values is somewhat arbitrary. Therefore, the values of $r_{v.d.w.}$ of Bondi have consistently been used in the discussion of the secondary bonded systems in this section of the thesis. In fact, since covalent radii are more accurately known, it has been proposed that neither Pauling's nor Bondi's values should be used, but in fact the van der Waals radii should be obtained by the simple relationship that

$$r_{v.d.w.} \approx r_{covalent} + .75 \text{ Å}$$

since $r_{covalent}$ values are more accurately known.

Irrespective of which van der Waals radii are used, the simple observation that, in an interaction A...X, if the distance A...X for an interaction is shorter than the same interaction with A of lower atomic number, the interaction is stronger. However, once it has been decided that an intra- or inter-molecular contact distance satisfies the criteria for a secondary bond, it is important to have some quantitative measure of the strength of the secondary bond and its effect on the primary geometry. This aspect is relatively complex because, unlike the

TABLE VI.1

Van der Waals and single bond radii, Å after A. Bondi.[16]

	H		He
	1.20		1.40

	C	N	O	F	Ne
r_w	1.70	1.55	1.52	1.47	1.54
r_c	0.77	0.70	0.66	0.64	

	Si	P	S	Cl	Ar
r_w	2.10	1.80	1.80	1.75	1.88
r_c	1.17	1.10	1.04	0.99	

	Ge	As	Se	Br	Kr
r_w	1.95	1.85	1.90	1.85	2.02
r_c	1.22	1.18	1.14	1.11	

	Sn	Sb	Te	I	Xe
r_w	2.10	2.05	2.06	1.98	2.16* [2.00]*
r_c	1.40	1.36	1.32	1.28	1.29

	Bi
r_w	2.15
r_c	1.55

hydrogen bond[18] there are a large number of other factors, steric as well as electronic, which significantly affect the orbitals on the central atom of the secondary bonded system and hence affect any correlations between the distances A-X and A...Y.

(VI.3.2) Charge Transfer Bonding

In the Introduction, it has already been stated that a number of secondary bonded systems have been previously described as examples of charge transfer (C.T.) complexes. The term charge transfer complex is, however, somewhat imprecise unless qualified by some description of the orbital interactions involved. Prout and Wright[19] in reviewing the crystal structures of several electron donor-acceptor (or C.T. complexes) sub-divided the compounds into three classes dependent on the symmetry of the orbitals involved in the charge transfer process. The three types of complex are σ-σ, σ-π and π-π. Secondary bonded complexes can clearly be classified as examples of σ-σ complexes and since the orbital overlaps involved in a secondary bond are more precisely defined, Prout and Wright's observation that, in σ-σ complexes, inter-molecular bonds become shorter and intra-molecular bonds become longer as charge transfer increases, immediately follows from the increased overlap of the donor orbital (on Y) with the σ^{*} orbital of A-X. It is this orbital overlap picture which is perhaps the strength of the secondary bond model.

As regards the σ-π and π-π classes, Prout and Wright also noted some other simple correlations. Thus, for σ-π complexes, the trends in the inter-molecular bond lengths are similar to those in the σ-σ complexes, although there are other factors compromising the situation. Similarly, the π-π complexes were found to contain stacks of alternate plane-to-plane donor and acceptor molecules arranged in 3 characteristic ways, although there is little correlation between the interplanar spacings in these stacks and charge transfer properties.[19,20] This is perhaps not surprising since π-π complexes are again very susceptible to other crystal packing forces, especially H...H repulsions within and between layers preventing maximum orbital overlaps.[13]

In an ideal situation, however, the stacks in the π-π complexes tend
to form with the aromatic rings of the donor and acceptor molecules
displaced by half a ring diameter (maximising C.T. interactions) and
with polar bonds of one molecule overlapping a polarisable region of
another (maximising dipole-induced dipole interactions). [20]

Whether the σ-π and π-π C.T. complexes can be considered to be
formed by similar bonding-antibonding orbital overlaps as in the σ-σ
secondary bonded examples is not at present clear. Certainly, apart
from the secondary bond examples, there are several other theories
which in essence rely on bonding-antibonding orbital interaction to
explain   molecular properties. Notably, the Dewar-Chatt model,
as used to describe the interactions in complexes of the transition
metals with such small molecules as ethylene, CO, NO, etc. involves
donation of electron density from occupied d-orbitals on the metal into
antibonding π^* orbitals with the result that there should be a lengthening
of the C-O distance as this interaction increases in strength. [21] Effects
of this can be observed by other physical measurements (i.r. etc.)
normally. Similarly, the effects of this synergic bonding has been
noted to activate other small molecules, e.g. CS_2 and butadiene, so
that their molecular parameters when co-ordinated are consistent with
those of an excited state. [22]

One of the original theoretical treatments of donor-acceptor or
charge transfer complexes was due to Mulliken who defined the ground
state wave function ψ_N to be a linear combination of the wave functions
of a no-bond structure [$\psi_o(DA)$] with that of a structure with complete
charge transfer [$\psi_1(D^+A^-)$].

$$\psi_N = a\psi_o(DA) + b\psi_1(D^+A^-) \qquad (1)$$

However, this function is only approximate and in systems where three-
centre σ-delocalisation bonding occurs, the wave functions for the
complex should take account of the polarisation of the donor and
acceptor molecule [equation (2)].

$$\psi_N = a\psi_0(N_3X_2) + b\psi_1(N^+XX^-) +$$
$$c\psi_2(N^+X^-X^+) + d\psi_3(NX^+X^-) \qquad (2)$$

Therefore, the difference between the secondary bond examples, the different charge transfer complexes and metal complexes is then the relative significance of each of the wave functions $\psi_{1,2,3...}$ for the excited valence states. These can be treated as perturbation of the neutral separated wave function ψ_N.[23]

(VI.4.) Quantitative Analyses of Secondary Bond Strengths

The treatment of the majority of the structures described in the previous chapters has been only qualitative. The most rigorous treatment of secondary bonds would be to calculate molecular wave functions for the whole system. However, at present there are considerable difficulties in performing accurate calculations for all but the simplest molecules. Part of the difficulty is in obtaining accurately parameters for the d-orbitals. Where calculations have been performed for examples with the 3 centre systems nearly symmetrical, calculations by LCAO and other methods have produced some semi-quantitative correlations.

Apart from such relatively simple ideas as using the difference in A...X differences for bidentate ligands,[24] the ratio $(A-X_{bridge})/A-X_{terminal})$ or differences $(A...X_{observed}) - (A-X_{covalent})$ to quantify the strength of a secondary bond,[25] recourse normally has to be made to semi-qualitative models in an attempt to quantify some of the secondary bond interactions and their effect on the primary geometries. The calculations attempting to model these bonding interactions can be subdivided into two types; (a) those molecular packing models in which the limitation on the interactions of non-bonded atoms is the contact of spheres with radii given by the van der Waals radii or by repulsion energy calculations; (b) those valence models which base the strength of any inter- or intra-molecular interaction on a comparison of the actual distances involved with reference distances, either single bond lengths or single bond radii.

Examples of each type of model are given in the following paragraphs.

Of the former type, the molecular packing model of Zahrobsky has already been mentioned in connection with the diethyl tin dihalides in Chapter I.[26] A criticism of this model and packing models in general is that no allowance is made for the interpenetration of the van der Waals surfaces. From Zahrobsky's model the calculated C-Sn-C angle is significantly lower than the experimental value, and although the calculated inter-molecular distances are of the right order, this is perhaps not surprising since the length of the secondary bonds are near the van der Waals limit. The C-Sn-C angle must be considered as a better indication of whether or not the model is successful. However, in comparison the distortion of the expected _trans_ octahedral stereo-chemistry of several dimethyl tin complexes containing two bidentate ligands to a skew-trapezoidal bipyramidal stereochemistry has been demonstrated to be compatible with the results of simple ligand-ligand repulsion energy calculations. These calculations are based on minimising the repulsion energy $\underline{U}$ given by

$$U = \sum_{ij} u_{ij} = \sum_{ij} a_n d_{ij}^{-n} = a_n X \quad (j > i)$$

where U_{ij} is the repulsive energy between any 2 donor atoms i and j, a_n is a proportionality constant and d_{ij} is the inter-atomic distance between atoms i and j. The usual value of n is $n \sim 6$ where $n = 1$ would represent a purely Coulombic interaction. The calculations are performed as a function of the normalised bite of the bidentate ligands. However, in this type of calculation the predicted angles are again not very meaningful because of the chemical differences between the uni-dentate and bidentate ligands.[27] Again, although the bidentate ligands are predicted to be asymmetric and this asymmetry is a function of the metal-unidentate bond length, no weight can be given to these correlations. An example of this effect and a three-centre secondary bond overlap has already been postulated for related structures in Chapter III with the methyl groups in the structures above replaced by lone pairs (especially $Te(Me_2Xan)_2$).

All the following measures are based simply on inter-molecular

distances. Zefirov and Zorkii* have suggested that a contracted inter-molecular contact radii r_{ij} may be a useful criteria for separating inter-molecular contacts into weak and strong contacts. The contracted inter-molecular contact radii are defined as $r_{ij} < 2(RiRj)^{\frac{1}{2}}-\delta$, where Ri and Rj are the statistical means of van der Waals radii of atoms i and j and δ is 0.15 Å for contacts without H atom participation and 0.30 Å with H particpation. The boundary between weak and strong contacts is defined as $r_{ij} = 2(RiRj)^{\frac{1}{2}}-\delta-0.1$ Å.[28] Zefirov* similarly uses weighted mean van der Waals radii Rij in establishing criteria for the existence of hydrogen bonds as well. The general form of this criterion is that in the contact X-H...Y the distance d(H...Y) must be $< 2.15\sqrt{Rij} -0.35$ Å for a hydrogen bond to exist. For Y = O, N, S and Cl, a hydrogen bond exists, provided d(H...Y) are less than 2.1, 2.3, 2.56 and 2.6 Å respectively.[29] (cf. Table VI.1.)

Finally, there are two closely related valence bond models based solely on inter-atomic distances. Both are completely general in their application with only a few constants being required in their implementation. Pauling's model makes use of equation (1) where the bond order n' is related to bond length D(n') of that bond and D(1), the reference value, is the bond length of a single bond. The best values of D(1) are those from gas-phase measurements.[17] Summation of individual bond orders for the contacts around an atom should be very nearly integral, and it is this principle which is used considerably in the closely related bond valence model of Brown.[3,30] The basis of

$$D(n') = D(1) - 0.71 \log(n') \qquad (1)$$

this empirical model is that the chemical bonding in the crystal can be considered as a sum of two-body interactions. In some cases it has been stated that an a priori prediction of the bond valences and hence the bond lengths in a crystal may be possible by describing a network

* Unfortunately only the abstracts of these papers were available, so no critical appraisal is possible.

of two body contacts or 'bonds'. Then, using an equal valence
principle that the sum of (bond) valences at a node (atom) in the above
network is equal to the atomic valence at that node (atom).[30]

The basic principle of bond valence theory is that for each two-
body interaction/contact/bond a bond valence (S) can be calculated
by either equation (1) or (2) which contain the purely empirical
constants R_o, N and A calculated for each atom pair. R is the contact

$$S = (R/R_o)^{-N} \qquad (1)$$

$$\text{or} \qquad S = \exp(-(R-R_o)/A) \qquad (2)$$

distance and R_o is the length of a bond of 1 valence strength. The
empirical constants are normally determined from a series of curves
based on a known set of compounds, particularly O, F, S and other
halogen complexes, although the use of a pair of values for whole
series of complexes does not significantly affect the resultant bond
valences.[31] There are two criticisms of this approach. Firstly, the
$(S/S_o)^{-N}$ or $\exp(-(R-R_o)/A)$ curves do not go to zero at the van der
Waals limit so that small bond valencies are still calculated for very
long contacts which when summed represents an appreciable valence.
Secondly, the calculated valences are completely non-directional.
However, the model does calculate sums of the bond valencies around
each atom which are very close to the atomic valence in a large number
of crystal structures, and specific bond valencies can be associated
with what had previously been imprecisely defined as strong, weak and
intermediate bonds A-X. Similarly, the correlation between bond
angles X-A-X and the average bond valence <S> of the A-X bond is only
valid for the strong primary bonds. It is notably that when a lone
pair is opposite a primary bond so that the trans bond is replaced by
several weaker bonds, the bond angle correlation breaks down (e.g. $\mathcal{E}$
configuration).[3] A model combining the principles of bond valence
with those of Galy et al. may be of some use.

VI. 5.   Correlations between distances A -X and A...Y

If we accept that the majority of secondary bonded systems contain linear triatomic arrangements in which the bonding can be described using 3c -4e MO's, then there must be some correlation between the interatomic distances A -X and A...Y.   For the ideal arrangement, there would be a linear correlation between A -X and A...Y.   The systems which are very nearly ideal are the simple trihalides (I_3^-, Br_3^-) and the $\sigma - \sigma$ 'charge transfer' adducts of iodine or the iodine mono-halides, ICl or IBr, with other bases.   Using the available data on these complexes, Hassel and Romming have, in fact, arrived at a linear correlation[†], and this has been discussed in Chapter V in relation to the ion $[Me_2N(ICl)_2]^-$.[32]   In these simple examples, second order effects are relatively small.   However, in the majority of secondary bonded sytsems, the second order effects, which are non -linear, act to restrict any linear correlations to large A...Y separations when the effects on A -X distances are likely to be masked by observational errors.   A smooth curve is then likely to be a better fit to the data on any particular system.   A typical correlation between A -X and A...Y distances to be expected is shown for a series of antimony(III) complexes, the majority of which are based on the C (Chapter II) arrangement of 3 primary and 3 secondary bonds.[33]   It should be noted, however, that the correlations found will vary considerably from system to system and from compound to compound due to significantly different second order effects. A large number of different examples of roughly the same type with a large spread of A -X and A...Y distances are required before reasonable accurate conclusions about the correlations can be drawn.

The second order effects which are responsible for the non -linear correlations are both steric and electronic in origin, and may be completely inter -related.   Broadly speaking, the electronic effects can arise from either the involvement of d -orbitals on A (or X and Y) at short distances and/or rehybridisation of the central atom concurrent with a change in the geometry of the surrounding ligands due to steric

[†] Compare, however, the theoretical curve of Wiebenga and Kracht, also shown in Fig. VI. 1.

Fig. VI. 1   Demonstration of an inverse relationship between trans Sb-Cl/Sb...Cl distances in octahedral Sb(III) complexes. (Redrawn from data in ref. 33a and including data in ref. 33b.) When both bonds are equivalent at ca. 2.6 Å, they have formal bond orders of $\frac{1}{2}$.

Inset   A related curve between bond order and bond length minus standard single bond length for polyhalogens. From E.H. Wiebenga and D. Kracht, Inorg. Chem., 1969, 8, 738 (cf. ref. 32).

Sb—Cl Å

Sb···Cl Å

R − R$_{cov}$

Sb—Cl Å

P
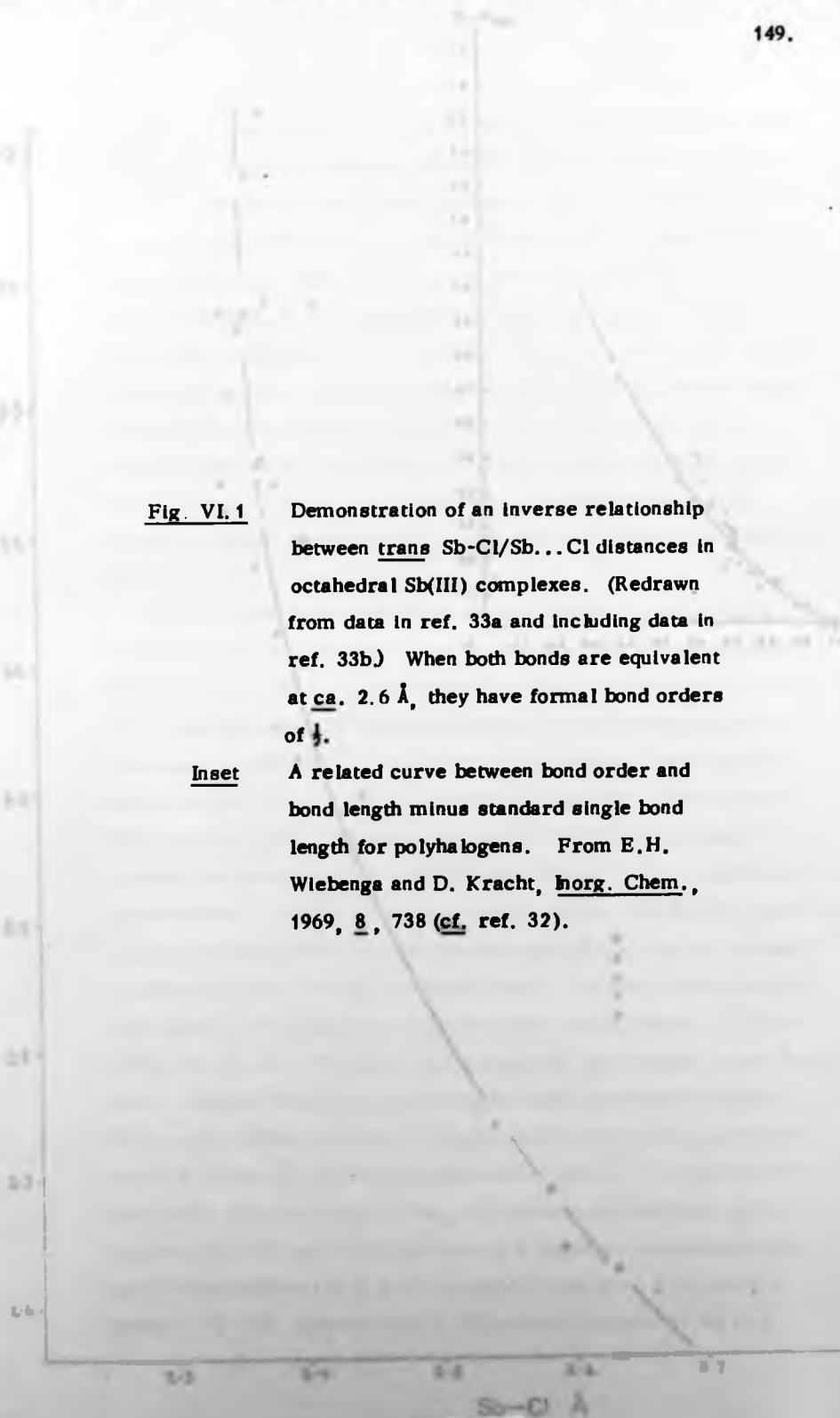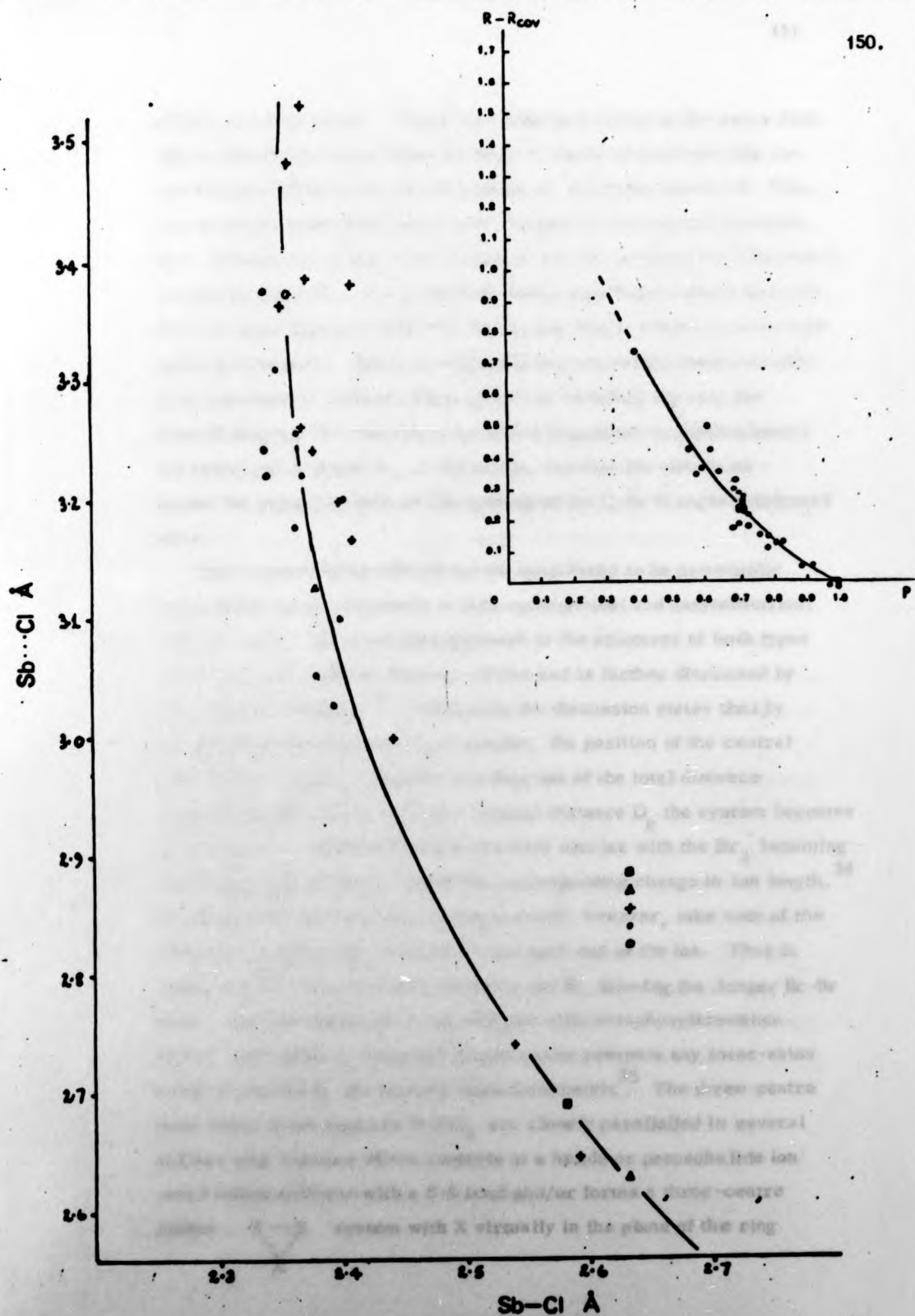
effects and vice versa. These may both be involved at the same time. The steric effects arise when the atom Y begins to penetrate the van der Waals surface of the atomic groups or lone pairs around A. This can be partly relieved by geometric changes in the original molecule (e.g. opening out of the C-Sn-C angle in the tin compounds of Chapter I) or else by the X-A...Y approach deviating significantly from linearity. This is especially true when the interacting atoms Y have to avoid lone pairs (see below). Again in evaluating any secondary bond strengths it is important to consider several factors including not only the overall length of the secondary bonded arrangement or (equivalently) the individual A-X and A...Y distances, but also the effects on molecular geometry such as the opening of the C-Sn-C angle mentioned above.

Again second order effects can be considered to be principally responsible for the existence of both symmetrical and unsymmetrical trihalide ions. An empirical approach to the existence of both types of ion has been given by Mooney-Slater and is further discussed by Breneman and Willett.[34] Principally the discussion states that by analogy with the triatomic $H_2 \cdot H$ system, the position of the central $I(Br)$ atom in $I_3^- (Br_3^-)$ systems is a function of the total distance between the end atoms until at a critical distance D_c the system becomes symmetrical. The two systems are very similar with the Br_3^- becoming more asymmetric than I^- under the corresponding change in ion length.[34] An alternative bond valence approach would, however, take note of the difference in inter-ion contacts around each end of the ion. Thus in $CsBr_3$ the Cs^+ ions are much closer to the Br, forming the longer Br-Br bond. Similar effects occur in CsI_3, but with tetraphenylarsonium Ph_4As^+ tri-iodide I_3^- the much larger cation prevents any inter-anion contacts and the I_3^- are strictly centrosymmetric.[35] The three-centre inter-anion short contacts in CsI_3 are closely parallelled in several sulphur ring systems where contacts to a halide or pseudohalide ion occur either colinear with a S-S bond and/or forms a three-centre planar   S — S   system with X virtually in the plane of the ring

containing the S-S bond. Ref. 36 contains data on several compounds containing these types of interactions.

The stereochemical models discussed in the previous sections have all noted the significant effect lone pairs have on the primary geometry. It follows therefore that the presence of lone pair electrons will also considerably affect the positions of the atoms overlapping with the σ^* orbitals of the primary bonds. In some cases the presence and the angles between secondary bonds which are nearly colinear with primary bonds can be especially useful in demonstrating an inactive lone pair (or pairs) of electrons on the central atom (see Chapter II). However, as has already been noted above, the effects of stereoactive (defined as non-bonding) lone pairs is to split a secondary bonding interaction into several contacts which then adopt positions which avoid the lone pair(s), but still overlap to a lesser extent the σ^* orbital. Obviously in these examples the correlation of A-X and A...Y distances is extremely difficult, and the calculation of bond valencies may be the best approach to correlate particular compounds. The situation in a series of xenon halide ions XeF^+, XeF_3^+, XeF_5^+ and $Xe_2F_3^+$ demonstrates well these effects.[37]

The geometries of the xenon atom in these four ions are described by Gillespie as AXE_3, AX_3E_2, AX_5E and AX_2E_3 respectively.[1] In the crystal, however, all four of these ions possess further inter-ionic contacts which are presumably useful in stabilising the unusual oxidation states of Xe. Furthermore, the directions in which these contacts are formed are dictated by the arrangement of the lone pair orbitals as shown in Fig. VI.3. The actual number and detailed arrangement of the inter-ion contacts is however very variable, which is not unexpected owing to the flexibility with which the contacts can form, avoiding the lone pairs. The xenon atoms in the fourth ion $Xe_2F_3^+$ are, however, completely surrounded by bonding and lone pairs so that the bridging fluorine atom is now unusually charged and becomes involved in several inter-cation contacts.[37]

Fig. VI.2
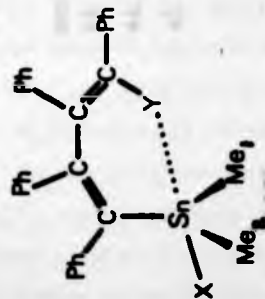
TABLE VI.2 Geometrical parameters for some cis-tetraphenylbutadienyldimethyl tin complexes.

X	Y	Sn...Y	C(Bu)-Sn-C(Me1)	C(Bu)-Sn-C(Me2)	C(Bu)-Sn-X	C(Me)-Sn-C(Me)	X...Sn-Y	X-Sn-C(Me1)	X-Sn-C(Me2)
Br	Br	3.774(5)	129.0	105.9(8)	100.7(5)	112.7	149.5(1)	100.0(7)	105.1(7)
Ph	Br	4.284(3)	117.1(5)	109.5(4)	108.4(5)	104.5(6)	143.4(3)	110.9(5)	105.8(5)
Ph	Cl	4.346(2)	116.5(4)	109.4(5)	109.3(3)	105.5(4)	142.3(2)	110.5(4)	104.9(4)

Fig. VI.3 Shapes of XeF_x^+ ions with arrows indicating directions in which secondary bonding interactions would have to form to avoid the stereoactive lone pairs.

Table VI:3 Correlation of Dihedral Angles with Secondary Bonding in Square Planar Tellurium Compounds[a]
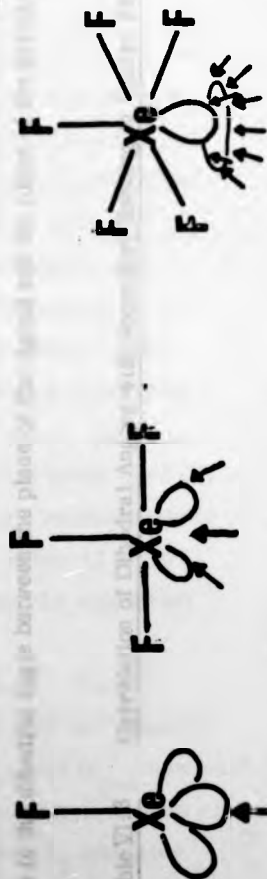
Compound[b]	Dihedral Angle 1 (phenyl)[c]	Dihedral Angle 2 (ligand)[d]	Secondary Bonding
PhTe(etu)I	60-61°	small	None
PhTe(esu)I	60-61°	small	None
PhTe(etu)Br			
form 1 (C2/c)	64.6°	small	None
form 2 (P2$_1$/c)	87.0°	44.1°	Te...Br 3.8313(10)Å C-Te...Br 162.29°
PhTe(etu)Cl	87.24°	44.9°	Te...Cl 3.7401(10)Å C-Te...Cl 162.51(7)°
PhTe(esu)Br	87.25°	45.5°	Te...Br 3.8490(16)Å C-Te...Br 163.31(19)°
PhTe(SCN)$_2$	83.2°	-	No Te...S < 4 Å
PhTe(SeCN)$_2$	85.7°	-	Te...Se 3.965(2)Å C-Te...Se 159.6(2)°
PhTe(tu)$_2^+$Cl$^-$	85°	89° and 46°	Te...Cl 3.606(11)Å C-Te...Cl 163.4(8)°
PhTe(tu)Cl	52°	69°	Te...Cl 3.71(2)Å C-Te...Cl 164.4(10)°
PhTe(tu)Br	55°	70°	Te...Br 3.77(1)Å C-Te...Br 164.2(10)°

[a] System consists of 3 primary bonds forming a T, and a fourth secondary bond trans to the phenyl which completes a square planar arrangement of bonds.

[b] etu = ethyleneurea; esu = ethylenethiourea; tu = thiourea

[c] This is the dihedral angle between the phenyl ring and the plane of the primary bonds.

[d] Similarly, this is the dihedral angle between the plane of the ligand and the plane of the primary bonds.

Finally, the presence of phenyl rings in compounds has both steric as well as electronic effects on secondary bonds. These effects have been already noted in Chapter I in regard to cis cis tetraphenylbutadienyl dimethyl tin X (X = Ph, Cl) compounds,and the results are summarised in Table VI. 2.[38] The difference in Sn-Br distances when X = Br is replaced by phenyl is 0.57 Å. In the series of phenyltellurium(II) compounds in Table VI.3 the phenyl ring appears to be again partly responsible for the presence of the secondary bond completing the square planar arrangement as can be seen from the dihedral angles when no 4th bond forms. This appears to be due to the phenyl ring at certain orientations being able to engage any available trans orbitals on the tellurium in mesomeric interactions as well as influence a steric effect. A cis effect of the other ligands can possibly be observed from the other dihedral angles in that Table.[39] A quantitative measure of related cis-trans effects on primary geometry has been made by Shusterorovich and Buslaev, using LCAO calculations based on hyper-valent orbital structures. Among their conclusions are: in complexes AXL_m where the central atom preserves the ns^2 "lone pair", the influence of the σ-bonded ligand X is trans, hypervalent I bonds (X-A-X) of Musher are stable only if the ligands X are of greater electronegativity than the central atom and in C_{4v} complexes AL_5, with either 12 or 10 valence σ-electrons, the axial bond must be shorter than the equatorial ones.[40]

In concluding this section, it appears that approximately linear correlations between the distances A-X and A...Y will hold for systems where the central atom, A, is surrounded only by lone pairs ($D_{\infty h}$ systems), octahedral systems of type C or AX_3Y_3E where the lone pair,E,is inert or very nearly so,and square planar and trigonal planar AX_3E_2 examples where the linear arrangements are relatively free from steric influences and the likelihood of any rehybridisation effects.

(VI.6.)   Application of Secondary Bonds

Identification of the important areas in which the inclusion of secondary bonding interactions can greatly help in the understanding of chemical properties of compounds is not always clear cut. However, there appear to be five main areas .

(1)   Secondary bonds are useful in predicting chemical reactions and the likely transition state(s) through which the reaction will proceed.

(2)   Somewhat similarly, the photochemical behaviour of several systems is explained using secondary bonds.

(3)   Some systems which include secondary bonds are good models of the short range ordered arrangements likely to occur in the liquid state or in solutions.

(4)   They may also be of significance in stabilising unusual valence states of the central atom.

(5)   They are useful in explaining other physical properties of the system in the solid state.

Of these five areas, (2) has already been discussed in relation to the behaviour of the benziodoxole compounds in Chapter III, and further information may be obtained from the work of Gougoutas and Etter.[41] Similarly (4) was mentioned in Chapter II with regard to the solid solvate of Me_3NCl with $SeOCl_2$ in which a centrosymmetric cluster $(Cl \cdot 5SeOCl_2)_2^{2-}$ occurs.[42]   Again, this area will not be discussed further.

(VI.6.1.)   Reaction Routes

Although chemical reactions are dictated by both kinetic and thermo-dynamical factors, the extent of reaction is normally measured in terms of relatively few parameters in the molecular structure(s) under consideration. Clearly some of the short inter-.and intra-molecular contacts observed in some of the secondary bonded systems must represent very likely reaction co-ordinates along which reactions, notably decomposition or rearrangement reactions, can proceed although actual reaction will require external stimulus (heat, radiation, etc.) A few varied examples will serve to illustrate this point.

The crystal structures of both aluminium iodate nitrate $\{Al[NO_3]_2 \cdot [NO_3] \cdot 6H_2O\}$ and the acid salt aluminium iodate-hydrogen iodate-water $\{[Al(OH_2)_6]^{3+}][IO_3^-] \cdot [HIO_3]\}$ have recently been published. The decomposition patterns of these two salts are markedly different. The acid salt in particular loses six water molecules at 135° C and a seventh, resulting from the decomposition of $2HIO_3$ to H_2O and I_2O_5, at 195° C. This decomposition reaction appears to be related to short I...O contacts in the crystal structure of the latter compound.[43]

Similarly, both 2-biphenyl tellurium halides and the analagous selenium compounds on heating to the melting (decomposition) point eliminate hydrogen halides in forming a dibenzotellurophene or dibenzo-selenophene derivative, and this chemical reaction can be related to short Te...C(12) [Se...C(12)] contacts.[44] In the iodide this contact has a distance of 3.37 Å [compared with values of > 3.83 Å for other Te...C (aromatic) contacts] and is ~ 0.7 Å above the equatorial plane and, if included, would give a roughly octahedral geometry for the tellurium. The corresponding bromide has considerably fewer inter-molecular Te...Br and Br...Br contacts, but the Te...C(12) contact is much stronger than the iodide . [2.945 Å] and is virtually in the equatorial plane [deviates by 0.035 Å]. In both these compounds the C(1)-Te...C(12) angles of 68.1^o (iodide) and 71.5^o (bromide) should be compared to C(1)-Te - C(12) bond angles of 81.7^o and 81.8^o in dibenzotellurophene and dibenzotelluorphene di-iodide respectively.[44]

(VI.6.2.) Stabilisation of unusual valence states

Whilst the above reaction routes can be related to kinetic factors, it may also be tentatively argued that in the majority of cases secondary bonds are more important to the thermodynamics of a system in that they stabilise unusual higher valence states of the central atom. For example, both I^+ and Br^+ species are quite reactive. In the structure of 4,5-dicyano-2-imidazolyl(phenyl) bromonium ylide, however, the bromine atom (Br^+) has a square planar arrangement of two primary bonds and two secondary bonds to the nitrogen atoms of an imidazolyl ring and a cyano group, both

of which are negatively charged and could be expected to stabilise the charge on the bromine.[45] Similarly, the fact that all trivalent iodine compounds (formally I^{3+}) have square planar or pentagonal planar arrangements of primary and secondary bonds, unless strongly electro-negative groups are bonded to iodine (Chapter III) can be related to the stabilising influence of the secondary bonds. Even when lone pairs prevent a secondary bonding interaction colinear with a primary bond, it is still noticeable that this interaction is then split into several weaker contacts which avoid the lone pair(s). The xenon fluorides (see above), again with an unusual valence state of the central atom, are examples of this. Similarly, the structure of the diaryl dialkoxysulfurane $Ph_2S(OC(CF_3)_2Ph)_2$ is based on a trigonal bipyramidal arrangement with the two phenyl rings and a lone pair in the equatorial plane. The unusual sulfur valence state is then stabilised by 3 short intra-molecular S...F contacts of 2.87, 2.93 and 3.09 Å.[46] It is noticeable that in the analagous compounds $(p\text{-}ClC_6H_4)_2SCl_2$ the S-Cl axial bonds are considerably longer than single bond lengths and are involved in S-Cl...Cl-S-Cl...Cl contacts. Presumably the use of $p\text{-}Cl\text{-}C_6H_4$ groups and the lengthening of the S-Cl bonds all help stabilise the sulfur valency.[47]

Finally, in 1-acetonyl-1-thionia-5-thia cyclooctane a transannular S...S contact of 3.12 Å (C-S...S = 179°) is important in the transition state for reactions of this compound. Similarly, it can also be viewed as stabilising the charge on the sulfur atom (along with a short intra-molecular S...O contact of 2.81Å [C'-S...O = 156°]).[48]

The influence of short inter-molecular contacts is not, however, restricted to secondary bonds, and electrostatic contacts are presumably responsible for stabilising unusual ionic complexes such as the oxo-carbenium ions of ref. 49 and ions such as $Sb_2F_4^{2+}$.[50]

(VI.6.3.) Other physical measurements

In the majority of cases, the secondary bonding is confined to the solid state. In solution for some cases, the effects of molecular association should be observable by spectroscopic (i.r., n.m.r., etc.) or cryoscopic techniques for the stronger inter-molecular and particular intra-molecular

interactions whilst the increased molecular motions associated with the liquid state will prevent the weakest interactions from forming permanently. Any gas phase measurements are unlikely to find any intermolecular interactions other than van der Waals forces. However, gas phase electron diffraction and microwave determinations of molecular structure do serve as good comparisons of the unperturbed structure with that in the solid state involving the secondary bonds.

Since the majority of the effects of charge transfer interactions can be observed by a variety of methods and since secondary bonds are a particular class of σ-σ charge transfer compounds. In making these observations, separation of the complexes into the 3 types σ-σ, σ-π and π-π is readily apparent from their different effects.[51] The presence of secondary bonding can readily be seen from shifts in i.r.,[41,52] n.q.r.,[53] n.m.r.[54] and other physical measurements, made in both liquid and solid phases, as described for some examples in the previous chapters. The conductivity of several semiconductors, however, is especially related to secondary bonds.[55] However, one readily observable property which is indicative of secondary bonded systems is the colour of the crystals.

Although principally only applicable to compounds containing the heavier elements (Te, I, etc.), the colouration of the crystals of a compound can indicate not only the presence but also the type of secondary bonding present in that compound. McCullough has noted that the organotellurium diiodides display a range of colours from red-orange through to dark violet with the red crystals being associated with Te...I secondary bonds, and that the dark violet colour results when I...I inter-molecular secondary bonds are present.[44,56] In other tellurium compounds, inter-molecular Te...Te contacts account for the crystal colour: 1,3-dimethylacetylacetone tellurium(II), for example, is connected into a one dimensional polymeric chain with Te...Te contacts of 4.04 Å and forms bright yellow crystals, although smaller Te...Te separations result in darker colourations.[57]

Similarly, NI_3, diodomethylamine and N, N' -tetraiodoethylene-
diamine are all assumed to have very closely related polymeric
structures based on corner shared nitrogen tetrahedra. All 3 compounds
and some of their base adducts are soluble with difficulty in available
solvents and all have very deep or black colours consistent with
extensive I...I contacts (~ 3.6 Å) between the chains of tetrahedra.
If these contacts are disturbed by adduct formation with N bases, as in
$(NI_3 \cdot 3NH_3)_n$ or in the adducts of diiodomethylamine with pyridine,
trimethylamine or methylamine the colour of the products becomes
lighter. Iododimethylamine by comparison is also lighter in colour
and fairly soluble, so that I...I contacts are unlikely and the proposed
structure is probably monomeric or linked into chains by N...I
contacts only.[58]

Finally α -α' - diselenobisformamidinium dichloride is significantly
different from related sulfur derivatives and forms a secondary bonded
Cl...Se-Se...Cl system [Se...Cl 3.19 Å, C...Se-Se 169.4°] which is
responsible for the yellow colour of the crystals.[59]

A theoretical treatment relating the crystal colour to the intermolecular
interactions and which can also be used to explain the electrical properties
of some of these compounds has been given by Donaldson and Silver.[60]
In this, the compounds are assumed to form energy 'bands' by interactions
between the non -bonding lone pair orbitals. The colouration of the
compounds can then be related to the difference in energy between the
band edges. Clearly, as the interacting atoms come closer, or as larger
halogen and other heavy atoms are introduced into the structure, the
band widths will increase so that the energy separation of the band edges
decreases, and the colour of the compound darkens. This treatment is
thus related to the band theories of metallic bonding and to the inter-
pretation of the interactions in semiconductors.

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SECTION 2

CHAPTER VII

Hypho Boranes

(VII.1.)   Introduction; n centre - m electron bonding

Since the initial discovery of the boranes by Stock in the 1920-1930's,[1] the chemistry and physical properties of these compounds, their anions and the closely related carbaboranes has been extensively investigated. Part of the considerable interest in these compounds is that they were and still are structurally novel.[2] Attempts to describe their structures in terms of normal valence structures with two-centre two-electron bonds met with failure resulting in the introduction of three-centre two electron delocalised bonding and other multi-centre interactions. The term 'electron deficient' was similarly introduced to describe this and other classes of compounds where there are too few valence electrons available to provide a pair of electrons between every pair of atoms close enough to be regarded as covalently bonded.[3]

The hydrogen bridged structure of the first member of the series, diborane, was initially recognised by infra-red vibrational analysis although several workers favoured an ethane-like structure. The results of an electron-diffraction study, however, served as confirmation of the hydrogen bridged structure (Fig.VII.1.[4]This structure is also the first in the borane series with a three-centre hydrogen bridge bond formed when each of the hydrogen 1s orbitals interact with two sp^3 hybrid orbitals from the two borons, so that overall there are two three-centre two electron molecular orbitals above and below the B_2H_4 plane.   This represents a convenient MO picture of the bonding although alternative valence bond structures have been formulated including structures where the hydrogen atoms (as H^+) interact with the π-orbitals of a B-B 'ethylenic type' double bond - the protonated double bond model.[4]

The structures of other members of the borane series (B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, etc.) were established unambiguously by Lipscomb using low temperature X-ray data.[4,5]   Recently this structural work has
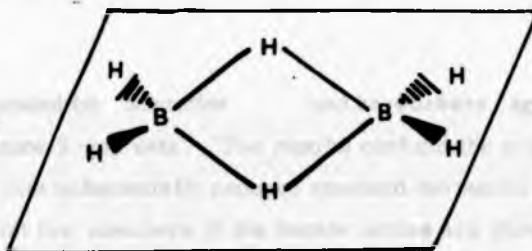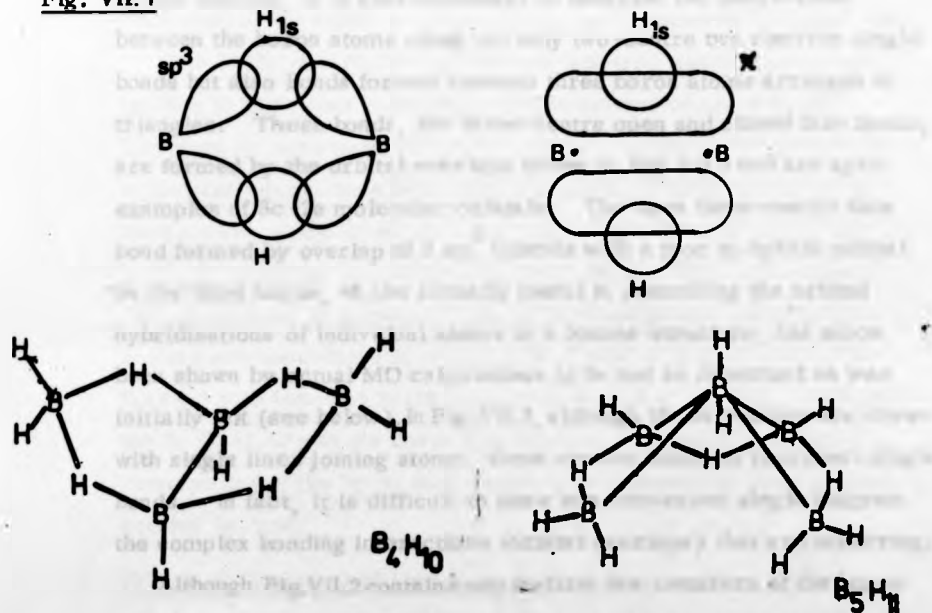
Fig. VII. 1

H_{1s}

sp^3

B

B

H

H_{1s}

X

B •

• B

H

B_4H_{10}

B_5H_{11}

Fig. VII. 2

B_5H_9

B_6H_{10}

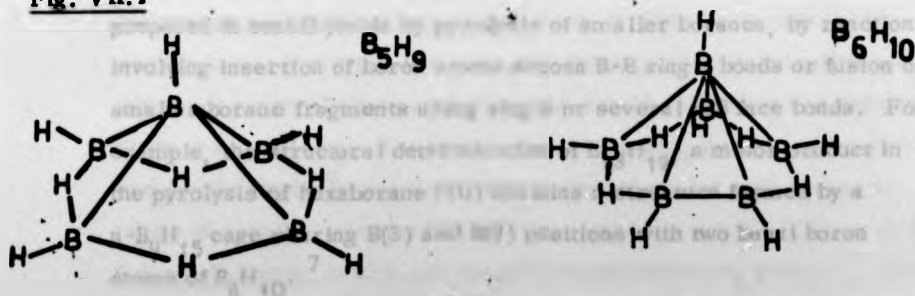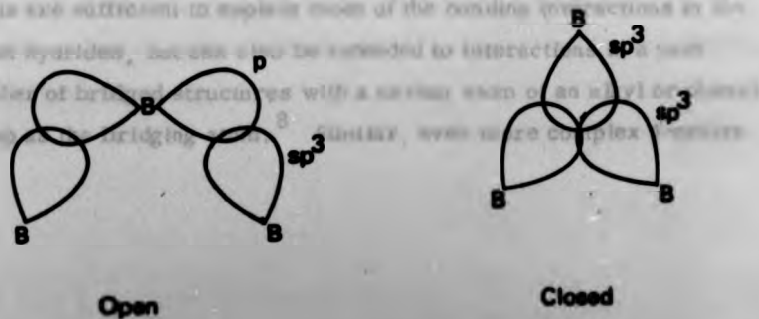Fig. VII. 3

p

B

sp^3

sp^3

sp^3

B

B

B

B

B

Open

Closed

been repeated by Schaeffer and co-workers, again using low temperature X-ray data. The results confirm the original structures but now with substantially reduced standard deviations.[6] The structures of the first few members of the borane series are shown schematically in Fig.VII.2 In these structures, as well as three-centre hydrogen bridge bonding, it is also necessary to describe the interactions between the boron atoms using not only two-centre two electron single bonds but also bonds formed between three boron atoms arranged in triangles. These bonds, the three-centre open and closed face bonds, are formed by the orbital overlaps shown in Fig.VII.3 and are again examples of 3c-2e molecular orbitals. The open three-centre face bond formed by overlap of 2 sp^3 hybrids with a p or sp hybrid orbital on the third boron, whilst initially useful in describing the orbital hybridisations of individual atoms in a borane structure, has since been shown by actual MO calculations to be not as important as was initially felt (see below). In Fig.VII.2, although the structures are drawn with single lines joining atoms, these are not meant to represent single bonds. In fact, it is difficult to show in a convenient single diagram the complex bonding interactions (orbital overlaps) that are occurring.

Although Fig.VII.2 contains only the first few members of the boron hydride series, numerous higher members of the series have been prepared in small yields by pyrolysis of smaller boranes, by reactions involving insertion of boron atoms across B-B single bonds or fusion of smaller borane fragments using single or several BBB face bonds. For example, the structural determination of $B_{13}H_{19}$, a minor product in the pyrolysis of hexaborane (10) contains a structure formed by a n-B_9H_{15} cage sharing B(3) and B(9) positions with two basal boron atoms of B_6H_{10}.[7]

The 3c-2e molecular orbitals of the hydrogen bridge and boron face bonds are sufficient to explain most of the bonding interactions in the boron hydrides, but can also be extended to interactions in a vast number of bridged structures with a carbon atom of an alkyl or phenyl group as the bridging atom.[8] Similar even more complex 4-centre

2 electron M.O. schemes have been postulated in one example of a
carbaborane and in structures from other groups of the Periodic Table,
especially the lithium alkyls.[9] The carbaborane involved is B_5CH_7[10]
which from a microwave study is reported to possess a hydrogen
bridging a BBB face resulting in three long B...B 'bonds' which may be
described using either 4c-2e M.O's or as a protonated BBB face bond.

The 3c-2e (and higher n-centre m-electron where appropriate)
bonding interactions in the boranes and related compounds can
therefore be seen to be related to the multi-centre inter- and intra-
molecular interactions described in Section I where the secondary
bond model   uses 3c-4e M.O's to explain the linearity of systems
X-A...Y where A...Y is the secondary bond.   Also in the case of
the iodobenzene diacetates (Chap. III) the secondary bonding inter-
actions are considered to parallel the 3-centre face bonding of the
boranes with two lone pairs interacting with a σ^* orbital.   Although
the 3c-2e M.O's in the boron hydrides are well established and in
common usage, the 3c-4e description of the secondary bonding inter-
actions is. not.

(VII . 2.)   Topological Models

From the previous   it can be seen that the bonding in the
boranes and electron-deficient compounds is complex in nature and
description.   However, there are two topological models in particular
which are a great help in describing the structure, bonding and geometries
of these compounds.   The first, Lipscomb's styx notation, describes
various theoretically possible valence structures for each borane in
terms of possible combinations of three - and two-centre BBB face and
B-B single bonds, bridging hydrogens and terminal BH_2 groups.[4]   This
notation cannot, however, describe the spacial distribution of the boron
atoms which is the important feature of Wade's (and Rudolph's)
notation.   These models are described in more detail in the following
sections .

(VII.2.1.) Lipscomb's stvx notation[4]

This is a purely empirical set of simple equations which are based
on the assumption that each boron atom provides four orbitals, and
therefore is involved in precisely four bonds, whether these be two-
centre or three-centre. Thus, in the simplest case of a neutral boron
hydride $B_p H_{p+q}$ it is assumed that in any likely valence structure
there will be s hydrogen bridges (3c-2e), t closed (or open) three-

centre $B\!\!-\!\!\overset{B}{|}\!\!-\!\!B$ bonds (3c-2e), y B-B single bonds and x extra
hydrogen atoms on the p B-H groups, i.e. BH_2 groups.   For each
valence structure the following equations of balance must hold:

$$s + x = q \tag{1}$$

$$s + t = p \tag{2}$$

$$p + q/2 = s + t + y + x \tag{3}$$

Using (1), $p = t + y + q/2$ $\hspace{4em}$ (4)

Equation (1) balances hydrogen atoms, (2) equates the number of
three-centre bonds to the number of boron atoms (p) since each boron
provides four orbitals but only 3 electrons and (3) equates the p + q/2
electron pairs to the s + t + y + x bonds in the structure which reduces
to equation (4).   The equations as derived for a neutral boron
hydride $B_p H_{p+q}$ are readily modified to include anion or cation charges
or the substitution of BH groups by carbon to give the carbaboranes.[11]
Similarly, for the higher boranes it is possible that the basic assumption
that each boron atom forms at least one exoskeletal 2c-2e B-H bond will
be broken.   Again the basic equations are readily modified.[12]

Using the simple equations (1-4) for $B_5 H_9$ gives
$s + x = 4$; $s + t = 5$ and $t + y = 3$, from which three solutions, [4120],
[3211] and [2302], written in styx order, are obtained.
The possible solution with $s = 1$ or 5 are not allowed, as they would
give negative values for y and x respectively.[13]   Clearly, as p and q
increase the number of possible valence structures with sets of styx
values also increases, although only a few of these structures are
actually found and isomeric forms of a particular hydride are not

normally isolable. However, all of these possible structures have to be considered in any MO computations on the orbital structure of a particular hydride. In correlating the observed structure with likely styx values, several simple principles are of use in eliminating the majority of the likely structures. These principles are based on observations of symmetry or restricted inter-orbital angles.[14]

Before discussing Wade's notation which deals with the spatial arrangement of the boron atoms, it is important to discuss how styx structures with localised two- and three-centre bonds can be obtained from the results of accurate self-consistent field (SCF) or other MO calculations. These localised chemical bonds are in fact obtained by mixing together MO's of different symmetries, a process which maximises the sum of the repulsions between electrons within the same MO while at the same time minimising the exchange energy and the inter-orbital electron repulsion energy. Using this procedure, Lipscomb was able to derive a series of localised molecular orbitals (LMO) from accurate SCF-MO calculations which in bonding terms are directly comparable to the elements of the styx notation. A quantity $\underline{d}$ [Equation 5] calculated for each orbital (LMO) is a good indicator of the number of centres over which each bond forms.

$$d = 100[\tfrac{1}{2} \int (\varphi_L - \varphi_T)^2 \, dv]^{\tfrac{1}{2}} \tag{5}$$

The calculation of d therefore defines a percentage delocalisation for each orbital, where φ_L is the calculated LMO and φ_T is a truncated LMO obtained by omitting relatively small contributions (less than about 0.2 electrons) to φ_L from other atoms in the structure and then renormalising the remaining orbital. The value of d can, therefore, vary from zero if the LMO is completely localised on the assumed atomic centres to 100% if φ_L and φ_T are completely orthogonal. The results of this type of analysis enabled a few basic bonding principles to be formulated. These may be summarised as follows:

(1) No open three-centre bonds have been found to be important in the localised molecular orbitals of boranes although carbaboranes may

have open three centre bonds providing a C atom is central. Similarly, carbaboranes may have an adjacent pair of C atoms (or an adjacent boron and carbon) joined by both a single bond and also a central three-centre bond. This is not possible for adjacent borons.

(2) Unique preferred three-centre bonds exist in valence structures of B_2H_6, B_4H_{10}, B_5H_{11}, B_6H_{10} and $1,2-C_2B_4H_6$.

(3) Structures for which three-centre bonds can be drawn are preferred over those which cannot be so expressed.

(4) In comparing isomeric structures, that with the larger number of nearly equivalent three-centre bond structures is preferred. This argument takes precedence over which choice has the more favourable charge distribution.

(5) Unique fractional three-centre bond descriptions exist for $4,5-C_2B_4H_8$ and probably also for $B_{10}H_{14}$, $B_{10}H_{14}^{2-}$ and B_9H_{13} whilst fractional three-centre bonds will replace an open three-centre bond and a single bond from the central atom to a fourth atom, except when C is the central atom.

(6) It is probable that valence structures having a vacant orbital which can easily be incorporated into three-centre bond structures are preferred over those which cannot. [15]

(VII.2.2.) Wade's rules[16] (Hypho systems)

Wade's rules were originally developed for the boron hydrides by considering the number of electrons required to fill all the bonding molecular orbitals (MO's) associated with each boron polyhedron, although their use can also be extended to other metal cluster systems. In the case of the boron hydrides the number of bonding orbitals in each polyhedron is obtained by considering each boron to be sp hybridised. Each exoskeletal BH bond is formed by the overlap of H(1s) with one B(sp) orbital, thus leaving the remaining sp orbital pointing into the polyhedron. A strongly bonding orbital results when all of these sp hybrids have the same phase. The p_x and p_y orbitals on each boron can similarly be combined to produce orbitals delocalised over the

whole polyhedron, half of which will be expected to be bonding and half anti-bonding. Therefore for a closed polyhedron B_nH_n there will be $(n + 1)$ bonding orbitals available, all of which must be filled to produce a stable species. However, for B_nH_n, after the electrons associated with each exoskeletal B-H have been considered, there are only n electron pairs available for polyhedron orbitals so that stability results when the species bears a double negative charge. Theoretical calculations have confirmed that for n = 6 or 12 the stable species is in fact $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$.

Wade's approach then was to consider the effect or removing vertices from the closed structure. The significant finding was that for a structure of $(n - 1)$ boron atoms (based on an n-polyhedron with one vertex missing); stability, i.e. the filling of all bonding MO's, still requires $(n + 1)$ skeletal electron pairs. Similarly for the structure of $(n - 2)$ boron atoms (based on the closed n polyhedron with two vertices missing), $(n + 1)$ skeletal electron pairs are again required to fill all bonding MO's. Some of the missing electrons may be provided either as negative charges on the polyhedra or by the replacement of BH by CH. In the majority of structures the additional electrons are obtained by adding hydrogen atoms along open edges of the incomplete polyhedron as hydrogen bridges or BH_2 (BH_3) groups.[†]

The implementation of Wade's rules for borane and carbaborane systems is achieved by the following procedure:-

(1) The system is written as $[(BH)_m(CH)_xH_y]^{z-}$

(2) The number of skeletal electrons are counted (i.e. excluding the electrons in the exoskeletal B-H bonds). Each B-H unit contributes 2 electrons, each CH unit contributes 3 electrons, the extra hydrogen atoms each contribute 1 electron and finally z electrons are included for the charge. This process is summarised in the following equation:

$\frac{1}{2}(2m+3x+y+z) = n + \frac{1}{2}(x+y+z) = $ no. of skeletal electron pairs where $n = m + x = $ no. of basic (B+C) skeletal atoms.

[†] The absence of open edges means that the closed polyhedral boranes only occur as di-negative species.

(3) The expected geometry of the boron polyhedra and *their* classification
are then assigned on the basis of the above formula for the number of
skeletal electron pairs. The results are summarised below:

No. of skeletal electron pairs	Boron polyhedron	No. of missing vertices	Nomenclature	Examples[‡]
$(n + 1)$	n-polyhedron	0	closo	$B_6H_6^{2-}$-octahedron all vertices occupied.
$(n + 2)$	(n+1)-polyhedron	1	nido	B_5H_9-square pyramid but based on octahedron with 1 vertex missing.
$(n + 3)$	(n+2)-polyhedron	2	arachno	B_4H_{10}-octahedron with 2 missing vertices. B_5H_{11}-pentagonal bipyramid with 2 missing vertices.
$(n + 4)$	(n+3)-polyhedron	3	hypho (Gk. net)	See below.

[‡] See also ref. 16. Table 1.
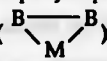
The majority of the boron hydrides, carbaboranes or related
systems can be described as closo, nido or arachno systems. It is
only recently that a fourth system with (n+4) skeletal electron pairs
and which was given the name HYPHO (Greek for net) has been
discussed in the literature. Such systems are even more open than
arachno with the n atoms occupying all but three corners of an (n+3)
polyhedron; they would be expected to be very reactive and have been
postulated to be important reaction intermediates.[13]

Before concentrating on hypho systems, it is worthwhile to review
briefly the other Lewis acid-base adducts of the boron hydrides which
have been structurally characterised. Apart from the simple Lewis
base adducts of the earlier boranes, several attempts were made to
utilise the short B-B bond in hexaborane (10) in nucleophilic and
other reactions where it would then act as a Lewis acid.[17] Such
reactions were eventually realised in 1968 when in a photolytic

reaction the adduct B_6H_{10}: $Fe(CO)_4$ was obtained (eqn.(6))[18]

$$B_6H_{10} + Fe(CO)_5 \xrightarrow{\text{h}\nu} B_6H_{10}:Fe(CO)_4 \qquad (6)$$
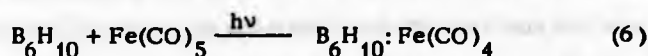
Crystallographic characterisation of this compound and the related adduct $(B_6H_{10})_2PtCl_2$ [19] both show the transition metals forming three-centre bridging interactions with this short bond. Furthermore, the adduct $[\mu Fe(CO)_4 \cdot B_7H_{12}]^-$ was similarly obtained and its structure is related to that of μ-$Fe(CO)_4 \cdot B_6H_{10}$ with one of the basal bridging hydrogens of the B_6H_9 group now replaced by a μ-BH_3 group.[20]

With pentaborane(9) similar μ-bridged structures are likewise known with three-centre $\overset{\text{B}\underline{\qquad}\text{B}}{\underset{\text{M}}{\diagdown\diagup}}$ bonding occurring with the remaining B_5H_8 group. However, although B_5H_9 and B_6H_{10} as well as several boron hydrides are now known to act as ligands to a variety of main group and transition metals, no general principles have yet emerged to predict what type of polyhapto bonding - 2e-2c σ bonding (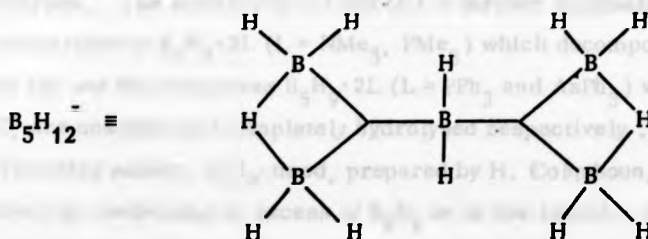B-M), 2e-3c bridge bonding ($\overset{\text{B}\underline{\qquad}\text{B}}{\underset{\text{M}}{\diagdown\diagup}}$) or hydrogen bridged structures (B-H-M) will be formed.[21]

None of these complexes are however known to have hypho structures and in fact very little structural data were known for hypho systems when work began on the crystal structures of the diphenylphosphino complexes of B_5H_9 although the crystal structures of both $B_5H_9 \cdot (PMe_3)_2$ and $B_6H_{10}(PMe_3)_2$ have recently been published by Shore and co-workers.[22] Of the other known examples of hypho species many have been prepared and characterised using proton and [11]B nmr spectra although this method cannot show the very open nature of the skeletal structure. In some cases (e.g. $B_5H_9 \cdot$ tmed) because of poor data or the fluxional behaviour of the open frameworks of these species, several postulated structures could equally well fit the experimental data.[23] One example, fairly well defined by this technique, is $B_5H_{12}^-$ which can be isolated as tetra n-butyl ammonium or triphenylmethylphosphonium salts which are white solids stable at low temperatures. The nmr data are consistent with a structure that has four basal atoms in the form of a pyramid. At

elevated temperatures the structure is again fluxional. The 2205 topological representation is consistent with the nmr data and would be even more open than the structure of nido B_5H_9 or arachno B_5H_{11}.[24]

$$B_5H_{12}^- \equiv$$

Variable temperature nmr data on the two bis triphenylphosphine adducts of B_5H_9 and B_6H_{10} have similarly been measured and reported with their crystal structures.[22] The nmr data on $B_5H_9 \cdot$ dppm (I) and $B_5H_9 \cdot$ dppe (II) were recorded at a single temperature but could still be interpreted in terms of a single apical and four basal boron atoms per molecule.[25] The spectra are very similar to those of $B_5H_9(PMe_3)_2$ containing the same broad featureless signals.[26] Noise decoupling of the ^{11}B nmr spectra of (I) and (II) only sharpened the signals of the basal atoms which would suggest that (I) and (II) are fluxional in solution like $B_5H_9 \cdot (PMe_3)_2$. In both (I) and (II) the ^{31}P nmr contains two separate signals suggesting that co-ordination is at the apex and base. Furthermore, the methylene resonances in the ^1H nmr of (I) is a doublet of doublets and not a triplet showing that the phosphorus atoms are not equivalent.[25]

(VII.3.) Experimental
(VII.3.1.) Preparation

The colourless adducts (I) (m.p. 185-7°), and (II) (m.p. 159-60°) were originally prepared by G. Haran by stirring equimolar ratios B_5H_9/ligand in THF at 25°C for 72 hours. Variations in the conditions can lead to higher m.p. products which were presumed to be cross-linked polymers. Both adducts are stable indefinitely in air, and even in water at 25°C, and are only slowly hydrolysed by hot water or acid, which is remarkable for B_5H_9 derivatives. The corresponding reactions of

elevated temperatures the structure is again fluxional. The 2205
topological representation is consistent with the nmr data and would be
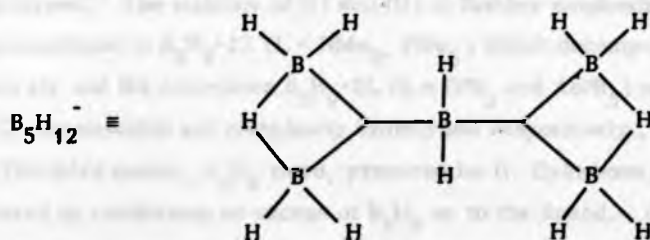even more open than the structure of nido B_5H_9 or arachno B_5H_{11}.[24]

$$B_5H_{12}^- \equiv$$

Variable temperature nmr data on the two bis triphenylphosphine adducts
of B_5H_9 and B_6H_{10} have similarly been measured and reported with their
crystal structures.[22] The nmr data on $B_5H_9 \cdot$dppm (I) and $B_5H_9 \cdot$dppe
(II) were recorded at a single temperature but could still be interpreted
in terms of a single apical and four basal boron atoms per molecule.[25]
The spectra are very similar to those of B_5H_9 $(PMe_3)_2$ containing the same
broad featureless signals.[26]   Noise decoupling of the ^{11}B nmr spectra
of (I) and (II) only sharpened the signals of the basal atoms which would
suggest that (I) and (II) are fluxional in solution like $B_5H_9 \cdot (PMe_3)_2$. In
both (I) and (II) the ^{31}P nmr contains two separate signals suggesting
that co-ordination is at the apex and base.   Furthermore, the methylene
resonances in the ^1H nmr of (I) is a doublet of doublets and not a triplet
showing that the phosphorus atoms are not equivalent.[25]

(VII.3.) Experimental

(VII.3.1.) Preparation

The colourless adducts (I) (m.p. 185-7°) , and (II) (m.p. 159-60°)
were originally prepared by G. Haran by stirring equimolar ratios
B_5H_9/ligand in THF at 25°C for 72 hours.   Variations in the conditions
can lead to higher m.p. products which were presumed to be cross-linked
polymers. Both adducts are stable indefinitely in air, and even in water
at 25°C, and are only slowly hydrolysed by hot water or acid, which is
remarkable for B_5H_9 derivatives. The corresponding reactions of

pentaborane (9) with the arsenic ligands $Ph_2As(CH_2)_nAsPh_2$ (n = 1 or 2)
yielded only high m.p. polymeric materials whilst the anions $B_5H_8 \cdot L^-$
(L = dppm or dppe) are similar to $B_5H_8^-$ itself, and are again readily
hydrolysed.[25] The stability of (I) and (II) is further emphasised
by comparison to $B_5H_9 \cdot 2L$ (L = NMe_3, PMe_3) which decomposes in
moist air and the complexes $B_5H_9 \cdot 2L$ (L = PPh_3 and $AsPh_3$) which, at
$25^{\circ}C$, are unstable and completely hydrolysed respectively .

The third adduct, $B_5H_9 \cdot$ tmed, prepared by H. Colquhoun, was
obtained by condensing an excess of B_5H_9 on to the ligand.   (III) was
found to be air-sensitive and could only be stored or recrystallised
without decomposition if an excess of ligand was present.   Compounds
(I) and (II) are readily recrystallised from tetrahydrofuran, although
very slow recrystallisation of (I) over the weekend resulted in the
incorporation of a half-molecule of disordered solvent into the lattice.

Methanolysis of $B_5H_9 \cdot$ tmed has similarly produced colourless needle
shaped crystals of $B_4H_8 \cdot$ tmed.   Preliminary work on this compound has
shown that contrary to a previous report[23] the crystal class is monoclinic.
A data set has been collected, and the structure solution apparently
shows the structure of this compound to be disordered in a complex
manner although this has yet to be confirmed completely.   Attempts to
recrystallise the original sample by several methods has also failed to
produce better crystals.[27]

(VII.3.2.)   Data collection

Three-dimensional X-ray data for all three compounds were collected
on a Syntex P2$_1$ diffractometer using Mo K$_\alpha$ radiation (λ = 0.71069 Å). In
each case, the cell constants were obtained by least squares refinement
of the diffracting positions of up to 15 high angle reflections.

(VII.3.2(i)) $B_5H_9 \cdot$ dppm

For the data collection, a needle shaped crystal measuring .12 x .20 x
.98 mm was obtained by cleaving a larger crystal perpendicular to its
needle axis.

Crystal data

$C_{25}B_5H_{31}P_2 \cdot \frac{1}{2}C_4H_4O$, M = 481.5, orthorhombic, $\underline{a}$ = 7.931(4), $\underline{b}$ = 16.816(5), $\underline{c}$ = 23.271(8) Å, $\underline{U}$ = 3105(2) Å^3, D_c = 1.03 g/cm^3 for $\underline{Z}$ = 4. Mo K$_\alpha$ radiation (λ = 0.71069 Å), F(000) = 1016.0. Systematic absences $\underline{h}O\underline{l}$, $\underline{h} \neq 2n$, $O\underline{k}O$, $\underline{k} \neq 2n$ and $OO\underline{l}$, $\underline{l} \neq 2n$ indicates space group $\underline{P}2_12_12_1$ (No. 17). Data were collected out to a maximum 2θ of 50°. Reflections were measured using θ - 2θ scans using scan ranges which varied from (K$_{\alpha_1}$ - 0.7) to (K$_{\alpha_2}$ + 0.7) at low sin θ to (K$_{\alpha_1}$ - 0.8) to (K$_{\alpha_2}$ + 0.7) at higher angles. A variable scan rate of 1°/min to 29.3^o/min, depending on the intensity of a preliminary 2 sec count, was used. Background counts were recorded at each end of the scan, each for one quarter of the scan time. The intensities of three standard reflections were monitored every 100 reflections. A large drop in the values of the standards at one point was due to a generator failure and 124 reflections were later edited from the data set (not recollected). Apart from this sudden drop there are only statistical fluctuations in the standards.

Of 3031 data collected 1850 were considered observed (I/σ(I) $\geqslant$ 3.0) and used in refinement.

(VII.3.2(ii)) $\underline{B_5H_9 \cdot dppe}$

For this compound, two data sets were collected. The structure was initially solved and refined using the first data set collected with Cu radiation (λ = 1.5418 Å). However, during this first data collection the crystal moved several times and required frequent re-centring. At a late stage in the refinement (R = 17.6% - all non-hydrogen atoms anisotropic) the listed reflections clearly fell into groups with alternating ΔF positive and negative due to crystal movement and the data set was rejected.

The second data set was collected with the same crystal but this time using Mo radiation (λ = 0.71069 Å). The following crystal data refers to this 2nd data collection.

Crystal data

$C_{26}B_5H_{33}P_2$, M = 461.6, orthorhombic, $\underline{a}$ = 14.297(4), $\underline{b}$ = 16.492(6) and $\underline{c}$ = 22.280(9) Å, $\underline{U}$ = 5253(3) Å^3, D_c = 1.17 g/cm^3 for $\underline{Z}$ = 8. Mo K$_\alpha$ radiation (λ = 0.71069 Å), F(000) = 1952.0. Systematic absences Ok$\underline{l}$, $\underline{k} \neq 2n$, h$\underline{Ol}$, $\underline{l} \neq 2n$ and h$\underline{k}$O, $\underline{h} \neq 2n$ indicates space group $\underline{Pbca}$ (No. 61).

For the second data collection, reflections were measured to a 2θ max of 50°, using θ-2θ scans over a scan range (K$_{\alpha_1}$ - 1.0^o) to (K$_{\alpha_2}$ + 1.0^o) and a variable scan rate of 1 - 29.3^o/min. Three standards were measured after every 75 reflections and showed only statistical fluctuations. In this second data collection the pre-scan count was increased to 8 secs after 284 reflections had been collected, and a reflection was subsequently collected if this count exceeded 50 c.p.s.

Of the total of 3700 data collected using this method 2643 reflections were considered observed ($I/\sigma(I) \geqslant 3.0$).

(VII.3.2(iii)) $B_5H_9 \cdot$ tmed

Crystals of $B_5H_9 \cdot$ tmed are clear colourless platelets when first exposed but which gradually decompose over a period of an hour or two if left in moist air. Preliminary work on the diffractometer using a thin crystal mounted in a Lindemann capillary revealed a possible tetragonal solution. Since the crystal was not scattering too well, further work was by precession photographs. These again showed a ∼ b but fail to show the required tetragonal 4-fold symmetry and the crystal class is orthorhombic.

From a recrystallised sample a larger hexagonal plate was selected and mounted on a fibre in a Lindemann capillary in a period of 15 - 20 min. No decomposition was evident overnight and this crystal was used for the data collection.

Crystal data

$C_6H_{25}B_5N_2$, M = 179.3, orthorhombic, $\underline{a}$ = 12.940(2), $\underline{b}$ = 12.911(3), $\underline{c}$ = 15.046(2) Å, $\underline{U}$ = 2513.9(8) Å^3, D_c = 0.95 g/cm^3 for $\underline{Z}$ = 8 (two independent molecules). Mo K$_\alpha$ radiation (λ = 0.71069 Å), F(000) = 800.0. Systematic absences $\underline{h}$OO, $\underline{h} \neq 2n$; O$\underline{k}$O, $\underline{k} \neq 2n$; and OO$\underline{l}$, $\underline{l} \neq 2n$ indicates space group $\underline{P2_12_12_1}$ (No. 17).

TABLE VII. 1

Starting reflection sets for multisolution direct methods program MULTAN

(a) $B_5H_9 \cdot dppm$

Σ_1	0	0	8	180°	
origin	0	6	17	360°	
	5	0	4	360°	
	5	15	0	90°	
other reflections	0	1	24	90,	270
	1	5	9	45,	315

Enantiomorph fixed by (0, 1, 24)

(b) $B_5H_9 \cdot dppe$

Σ_1	0	0	8	180°
	0	0	14	360°
	0	0	20	360°
	0	0	24	360°
	0	2	14	360°
	0	14	0	180°
	10	0	0	180°
origin	2	15	16	360°
	5	16	16	360°
	4	14	17	360°
other	1	2	8	180° or 360°
	5	18	5	180° or 360°

(c) $B_5H_9 \cdot tmed$

origin fixing	0	3	11	90°
	1	2	0	90°
	2	0	1	90°
other reflections	4	4	2	45°, 135°
	6	3	10	$\pm45^o$, $\pm135^o$
	7	6	5	$\pm45^o$, $\pm135^o$

Enantiomorph fixed by (4, 4, 2)

Data were collected using θ-2θ scans over a scan range (K_{α_1} - 0.9^o) to (K_{α_2} + 0.9^o) to a maximum 2θ of 50°. A variable scan rate of 1 - 29.3^o/min depending on a preliminary 2 sec count was used. Three standards collected every 70 reflections showed only statistical fluctuations. Other conditions were the same as in (VII.3.2.(i)). Of 2858 data collected 1200 were considered observed ($I/\sigma(I) \geqslant 3.0$).

In all three compounds Lorentz and polarisation were applied. All three compounds were eventually solved using direct methods.

(VII.3.3.) Structure Solutions

(VII.3.3(I)) $B_5H_9 \cdot$ dppm

The structure of (I) was solved using NORMAL and MULTAN. Using rigid phenyl groups in the calculation of normalised structure factors for the 3031 data collected, the final statistics and the distribution of the E's clearly showed that the acentric space group $P2_12_12_1$ was correct. In MULTAN, using 295 reflections with E > 1.55, 1500 phase relationships with a minimum abs (E($\underline{h}$)E($\underline{k}$)E($\underline{h}$-$\underline{k}$)) of 7.21 were found. The starting set of reflections after the convergence mapping is shown in Table VII.1. In the case of an acentric space group, the 'hand' or enantiomorph has to be specified by restricting the possible phases of the starting reflections. In $P2_12_12_1$ with two general reflections, the enantiomorph is fixed by giving one reflection values of $\pm \pi/4$ and the other values of $\pm \pi/2$. These two general reflections, therefore, gave four phase sets with absform indices: 0.9295, 0.9302, 1.3255 and 0.9864. The third phase set was given by (1, 5, 9) = 315° and (0, 1, 24) = 90° and 19 atoms of the expected structure were immediately visible in the resulting E-map. These atoms gave R = 34.4% after 2 cycles of least squares refinement and the remaining non-hydrogen atoms were located in the subsequent Fourier. These non-hydrogen atoms were refined for several cycles of least squares, first with isotropic then anisotropic temperature factors, so that the R factor dropped to 15.3%. At this point the difference Fourier contained several peaks attributable to hydrogen atoms and several elongated peaks of sufficient height to be half-weight carbon atoms. These peaks were also found to be present in the initial E-map and the subsequent F_o Fourier. These peaks were attributed to a half-molecule of tetrahydrofuran solvent on a general position, and the best agreement was given when the molecule was
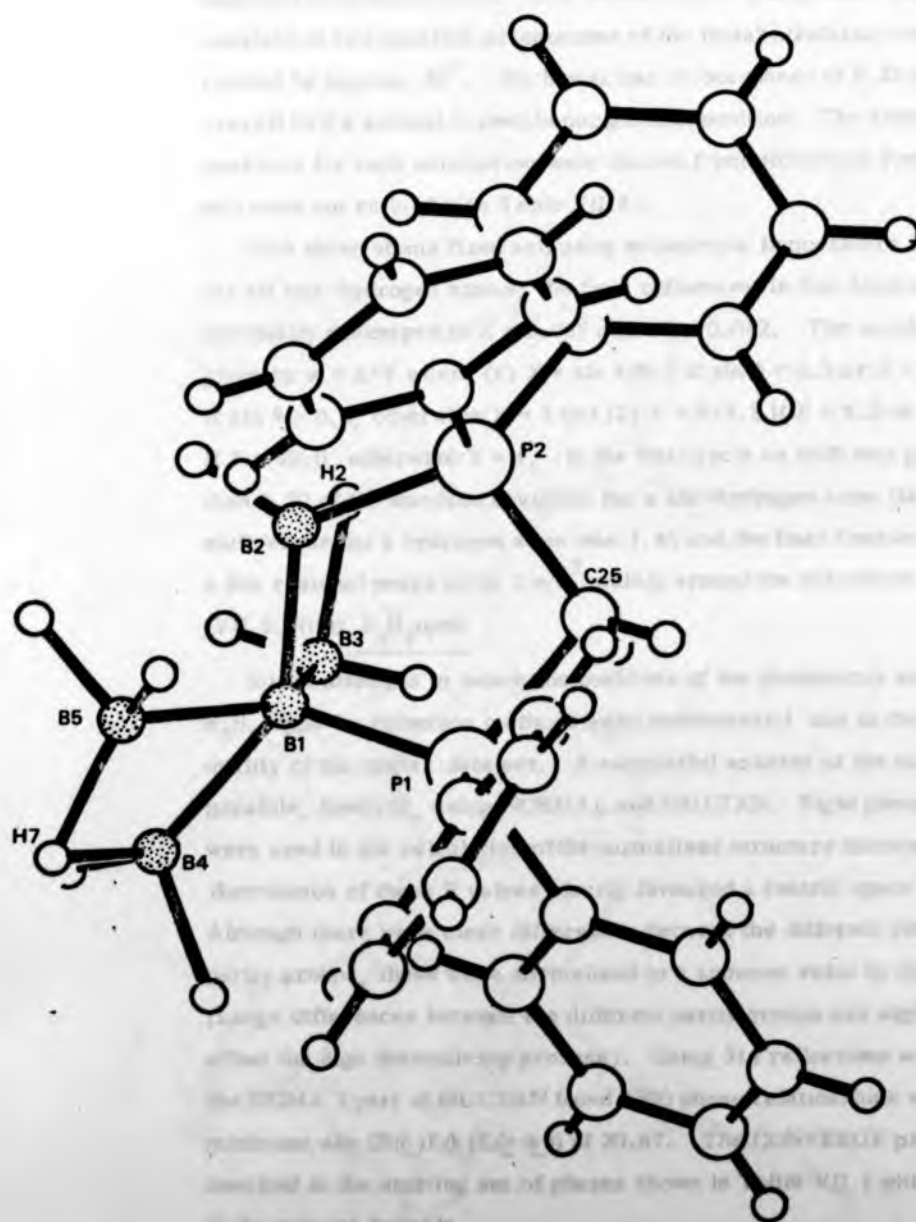
Fig. VII. 4   General view of molecule of $B_5H_9 \cdot dppm$

assumed to be disordered. The model chosen to represent the disorder consists of two separate orientations of the tetrahydrofuran molecule rotated by approx. 36°. Each peak has an occupancy of 0.25 giving overall half a solvent molecule per general position. The atomic positions for each orientation were chosen from difference Fouriers and were not refined (see Table VII. 8).

With these atoms fixed and using anisotropic temperature factors for all non-hydrogen atoms, the final refinement in five blocks eventually converged to R = 0.069 and wR = 0.082. The weights w were given by w = X*Y where (1) X = sin θ/0.3 if sin θ < 0.3 or X = 0.4/sin θ if sin θ > 0.4, otherwise X = 1 and (2) Y = F/9.5 if F < 9.5 or Y = 20.0/F if F > 20.0, otherwise Y = 1. In the final cycle no shift was greater than 0.50 of its standard deviation for a non-hydrogen atom (largest shift/error for a hydrogen atom was 1.4) and the final Fourier contained a few residual peaks up to 1 e/$\mathring{A}^3$ mainly around the disordered solvent.

(VII.3.3(ii)) $\underline{B_5H_9 \cdot dppe}$

Initial attempts to locate the positions of the phosphorus atoms in $B_5H_9 \cdot$ dppe by Patterson methods were unsuccessful due to the poor quality of the initial data set. A successful solution of the structure was possible, however, using NORMAL and MULTAN. Rigid phenyl groups were used in the calculation of the normalised structure factors and the distribution of these E values clearly favoured a centric space group. Although there were clear differences between the different reflection parity groups, these were normalised to a common value by the program. (Large differences between the different parity groups can significantly affect the sign determining process). Using 314 reflections with E > 2.0, the SIGMA 2 part of MULTAN found 1500 phase relationships with a minimum abs $(E(\underline{h})E(\underline{k})E(\underline{h}-\underline{k}))$ of 20.67. The CONVERGE process resulted in the starting set of phases shown in Table VII. 1 which was used in the tangent formula.

The ABSFOM indices of the four resulting phase sets had the values 0.6221, 1.0399, 0.6414 and 0.5034. The second of these phase sets

was given by (5, 9, 9) = w² and (9, 10, 5) = 'w'. The resulting E-map from this phase set had two large peaks but with significantly different heights (559 and 377, arbitrary units). However, least squares resolved to an R-factor of 54.5% for these two phosphorus positions and the following Fourier synthesis revealed several phenyl rings. Eventually, when all the non-hydrogen atoms had been located, several cycles of least squares, even with all atoms anisotropic did not lower R below 17.7%. At this point, the data set was rejected.

Using the synchrotron set collected with Cu-radiation, 66 atoms (including hydrogens) were loaded and two cycles of least squares with all temperature factors isotropic reduced R to 8.5%. Anisotropic temperature factors for all non-hydrogen atoms reduced this further to 6.4%. After repositioning several hydrogen atoms (ring hydrogens in calculated positions, C-H = 0.95 Å), and including corrections for extinction and dispersion effects, the refinement in 5 blocks eventually converged to R = 0.047 and wR = 0.051. The weights used were given by w = √A ... where A = 14.8 and B = 0.0073.

(VII.3.2(iii)) B_5H_9.dppe

... was also solved by direct methods. Normalised structure factors for the 2658 reflections collected were calculated using the X-RAY link NORMSF ... the distribution of the E_{hkl}'s was consistent with the acentric space group $P2_12_1 ...$ direct methods were applied using ...AN on 298 reflections with E > 1.50. 2000 phase sets ... comparison with a figure of merit ... (E(h))B(k)E(h + k)) of 0.42 were found, ... the signs of formula used to fix the signs of any reflections. The ... mapping resulted in a starting set of reflections shown in ... with the enantiomorph being fixed by the (4, 4, 3) reflection. With 3 given 20 reflections, 32 phase sets were calculated. However, the ... time after 32 phase sets were calculated ... the link program was ... necessary code to calculate E-maps ... the ... highest absolute of 1.9985 was given by the ... in agreement ... statistics with (4, 4, 3), (6, 1, 10) and (7, 4, 5) with

Fig.VII.5   General view of molecule of B_5H_9·dppe

was given by (1, 2, 8) = '−' and (5, 18, 5) = '+'. The resulting E-map
from this phase set had two large peaks but with significantly different
heights (559 and 271, arbitrary units). However, least squares
resulted in an R-factor of 54.5% for these two phosphorus positions and
the following Fourier synthesis revealed several phenyl rings.
Eventually, when all the non-hydrogen atoms had been located, several
cycles of least squares, even with all atoms anisotropic did not lower
R below 17.7%. At this point, the data set was rejected.

Using the second data set collected with Mo-radiation, 66 atoms
(including hydrogens) were loaded and two cycles of least squares with
all temperature factors isotropic reduced R to 8.5%. Anisotropic
temperature factors for all non-hydrogen atoms reduced this further
to 5.4%. After repositioning several hydrogen atoms (ring hydrogens in
calculated positions, C-H = 0.95 Å), and including corrections for
extinction and dispersion effects, the refinement in 5 blocks eventually
converged to R = 0.047 and wR = 0.063. The weights used were given
by $w = \sqrt{A + F + B \cdot F^2}$ where A = 14.6 and B = 0.0073.

(VII.3.3(iii)) $\underline{B_5H_9 \cdot tmed}$

Compound (III) was also solved by direct methods. Normalised
structure factors for the 2858 reflections collected were calculated using
the X-RAY link NORMSF. The distribution of the $E_{\underline{hkl}}$'s was consistent
with the acentric space group $P2_12_12_1$. Initially direct methods were
applied using MULTAN on 298 reflections with E > 1.50. 2000 phase
relationships with a minimum abs $(E(\underline{h})E(\underline{k})E(\underline{h}-\underline{k}))$ of 6.42 were found,
but the sigma 1 formula failed to fix the signs of any reflections. The
convergence mapping resulted in the starting set of reflections shown in
Table VII.1 with the enantiomorph being fixed by the (4, 4, 2) reflection.
With 3 general reflections, 32 phase sets were expected. However, the
program ran out of process time after 22 phase sets had been calculated
and was not re-run because it was discovered that at that time the link
FOURR was missing the necessary code to calculate E-maps. Of the
22 phase sets calculated, the highest absform of 1.0988 was given by the
first calculated set of phases with (4, 4, 2), (6, 3, 10) and (7, 6, 5) with

phase angles of 45°. This phase set was investigated further using the direct method links in the program SHELX.[27] For acentric structures this program requires the starting set of reflections to be input by the user from a previously calculated convergence map. In the present case, the origin fixing reflections from MULTAN and the above three values (45°) of the general reflections were input and the other phases of the 230 reflections with $E > 1.55$ were determined. From the resulting E-map, 25 of the expected 26 non-hydrogen atoms were found amongst the most prominent peaks (several peaks spurious). Including all these peaks as carbon atoms and refining for two cycles of least squares on all reflections resulted in an R of 0.333. From the resultant temperature factors and chemical intuition the atoms were correctly re-assigned and the missing carbon atom in one of the tmed ligands was found in the subsequent Fourier.

All subsequent calculations were performed using the XRAY system. After repositioning atoms B13 and B23 and refining with isotropic temperature factors for all atoms, the R-factor decreased to 15.3%. The temperature factors of the second tmed were in general high ($U = 0.06 - 0.13$). After locating and including several hydrogen atoms in the structure factor calculations, the R factor decreased to 12.4%, at which point it became clear that the carbon atoms of the second tmed were disordered, existing in two separate conformations of equal weight. Adopting this model enabled the hydrogen atoms attached to this tmed to be located, some with unit population parameters. Keeping these atoms fixed during the final refinement cycles and allowing anisotropic temperature factors for all atoms except the carbon atoms of the disordered tmed, the least squares refinement in five blocks eventually converged to $R = 0.055$ and $wR = 0.049$. The weights used were given by $w = X \cdot Y \cdot (1/\sigma(F))^{2}$ where (1) $X = \sin\theta/0.245$ if $\sin\theta < 0.245$, otherwise $X = 1$ and (2) $Y = F/5.0$ if $F < 5.0$ or $Y = 18.0/F$ if $F > 18.0$, otherwise $Y = 1$. Six reflections with large $w \cdot (\Delta F)^{2}$ after the application of this scheme were rejected from subsequent refinement cycles. In the final refinement cycle
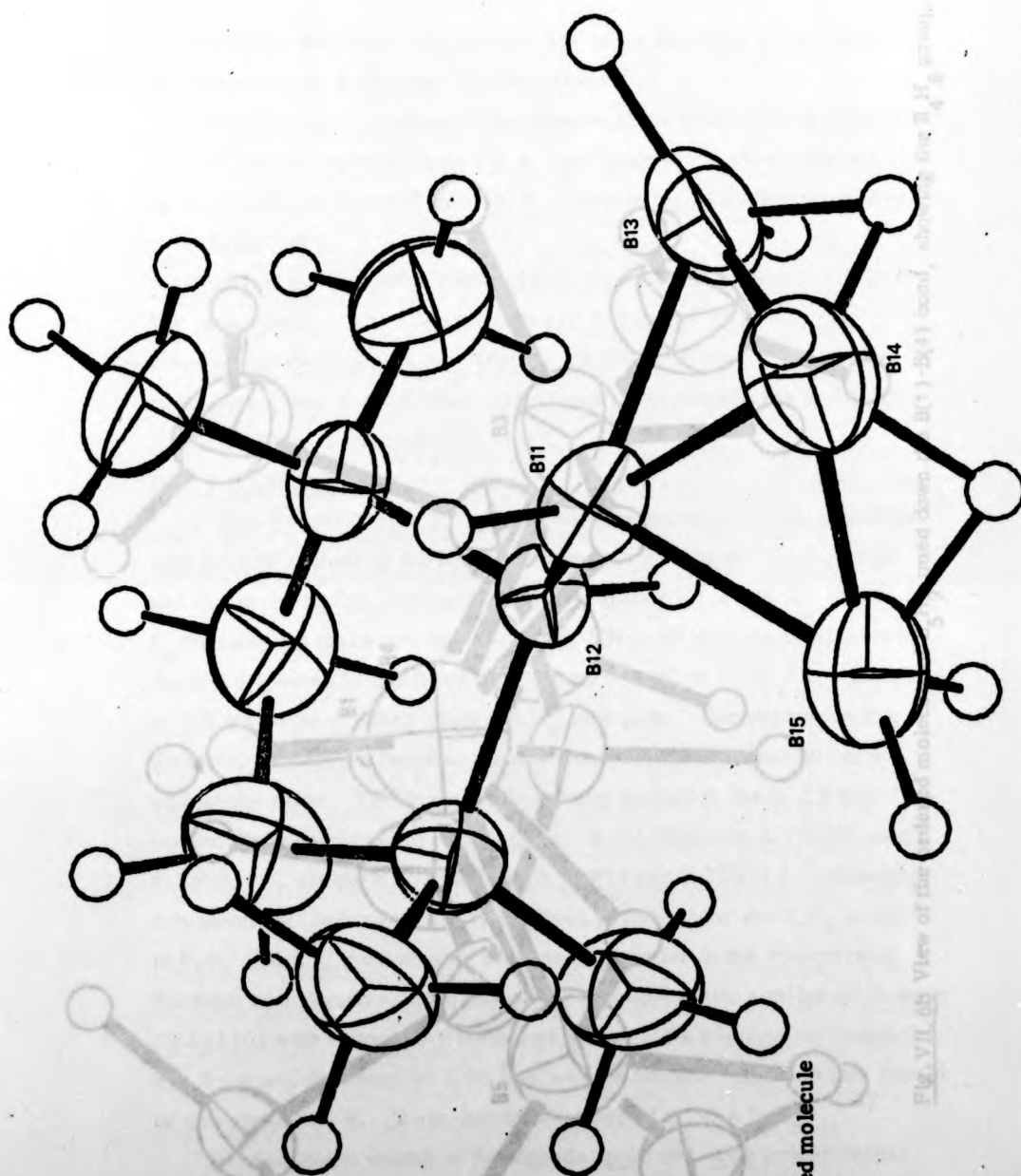
Fig. VII.6a

General view of ordered molecule
of $B_5H_9 \cdot$ tmed.
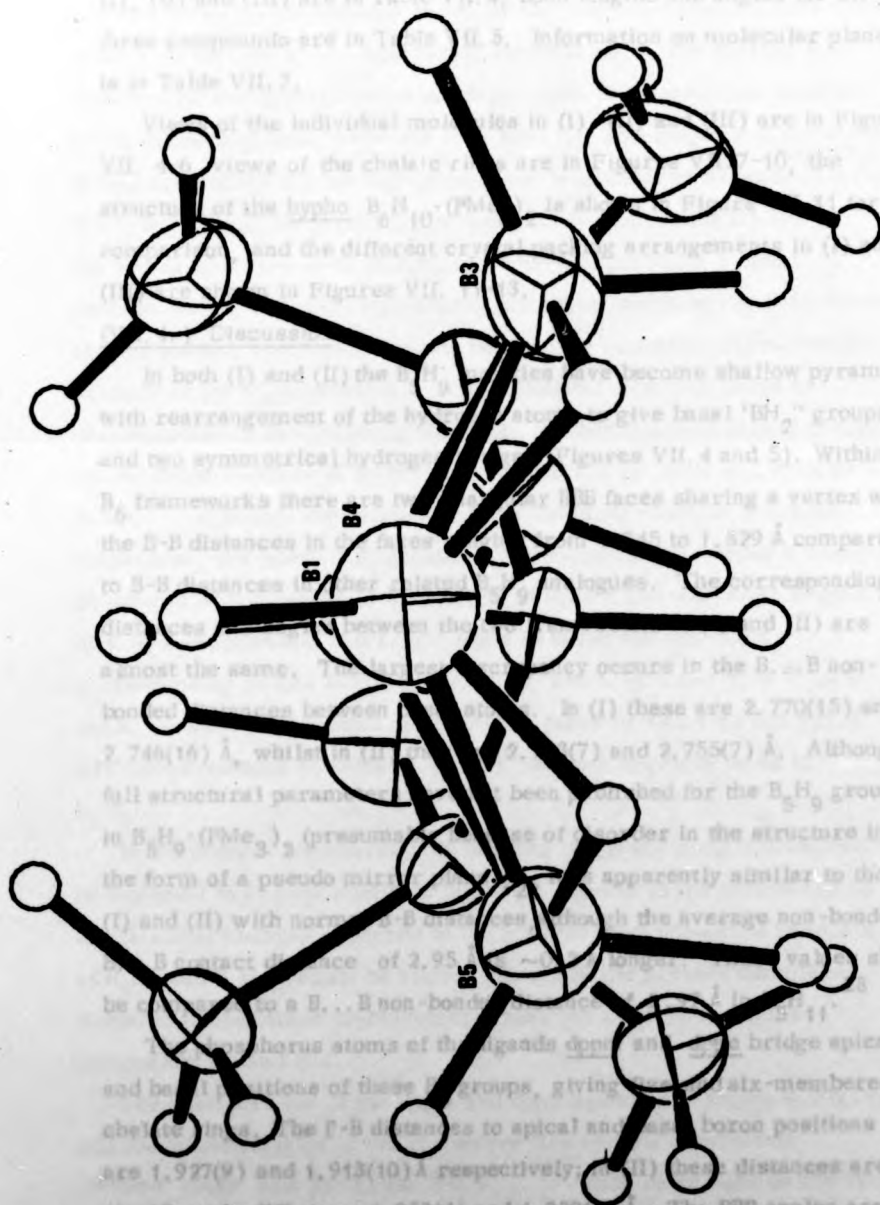
no parameter shift was greater than 33% of its standard deviation and the final difference Fourier was featureless.

Final positional parameters and temperature factors for all atoms in (I), (II) and (III) are in Table VII. 4, bond lengths and angles for all three compounds are in Table VII. 5. Information on molecular planes is in Table VII. 7.

Views of the individual molecules in (I), (II) and (III) are in Figures VII. 4-6, views of the chelate rings are in Figures VII. 7-10, the structure of the hypho $B_6H_{10} \cdot (PMe_3)_2$ is shown in Figure VII. 11 for comparison, and the different crystal packing arrangements in (I) and (III) are shown in Figures VII. 11-13.

(VII. 4.) Discussion

In both (I) and (II) the B_5H_9 moieties have become shallow pyramids with rearrangement of the hydrogen atoms to give basal 'BH$_2$" groups and two symmetrical hydrogen bridges (Figures VII. 4 and 5). Within the B_5 frameworks there are two triangular BBB faces sharing a vertex with the B-B distances in the faces ranging from 1.745 to 1.879 Å comparable to B-B distances in other related B_5H_9 analogues. The corresponding distances and angles between the two frameworks in (I) and (II) are almost the same. The largest discrepancy occurs in the B...B non-bonded distances between basal atoms. In (I) these are 2.770(15) and 2.746(16) Å, whilst in (II) they are 2.723(7) and 2.755(7) Å. Although full structural parameters have not been published for the B_5H_9 group in $B_5H_9 \cdot (PMe_3)_2$ (presumably because of disorder in the structure in the form of a pseudo mirror plane),[22] it is apparently similar to those in (I) and (II) with normal B-B distances, although the average non-bonded B...B contact distance of 2.95 Å is ~0.2 Å longer. These values should be compared to a B...B non-bonded distance of 2.97 Å in B_5H_{11}.[28]

The phosphorus atoms of the ligands dppm and dppe bridge apical and basal positions of these B_5 groups, giving five- and six-membered chelate rings. The P-B distances to apical and basal boron positions in (I) are 1.927(9) and 1.913(10) Å respectively; in (II) these distances are significantly different, 1.953(4) and 1.939(4) Å. The BBP angles are within the range 107-117°. The difference in distances in (II) was

similarly found in $B_5H_9 \cdot (PMe_3)_2$ where the P-B distances to apical and basal positions are 1.90(1) and 1.98(1) Å.[22a] In $B_6H_{10} \cdot (PMe_3)_2$, however, the P-B distances are the same (1.887 Å ave.).[22b] In other adducts involving phosphorus-boron bonds, the P-B distances have varied from 1.83 to 1.96 Å.[29] Apart from steric factors, the shorter P-B distance for the apical bond presumably reflects the electron densities at the apical and basal positions (see later). The longer P-B distances in (II) are needed for the formation of the 6-membered as opposed to the 5-/membered ring in (I). In forming the skeletal arrangements in compounds (I) and (II), the apical hydrogen atom of B_5H_9 must have migrated to a basal position during the rearrangement of the boron atoms on the introduction of four bonding electrons from the phosphorus atoms into the molecular orbitals of the B_5 polyhedron. With 9 skeletal electron pairs to accommodate in the hypho-B_5 skeleton, the boron atoms should occupy all but three vertices of an 8-vertex polyhedron by Wade and Rudolph's rules.[16] Although the dodecahedron is the most common 8-vertex polyhedron, the present B_5 geometry more closely resembles a hexagonal bipyramid with a centre to apex height of 0.64 Å and with edge lengths of 1.81 Å (equatorial) and 1.77 Å (apex to base) for (I); the corresponding values in (II) are 0.645 Å, and 1.82 Å and 1.78 Å. The angle between the opposite triangular B_3 faces is 130.4° (I) and 126.5° (II) compared with an angle of $90 - 91^{\circ}$ between opposite faces in B_5H_9.

In the present structures, the bridging dppm and dppe ligands would be expected to impose a certain degree of rigidity to the structures so that the fluxional changes observed in the bis(trimethyl phosphine) adducts of B_5H_9 and B_6H_{10} would be slightly slower in the present complexes. Variable temperature measurements have yet to be made on the compounds (I) and (II).

The configuration of the dppm and dppe ligands are shown in Fig. VII. 10 and the torsion angles in the respective five and six membered chelate rings are in Table VII. 5. Both these ligands are very
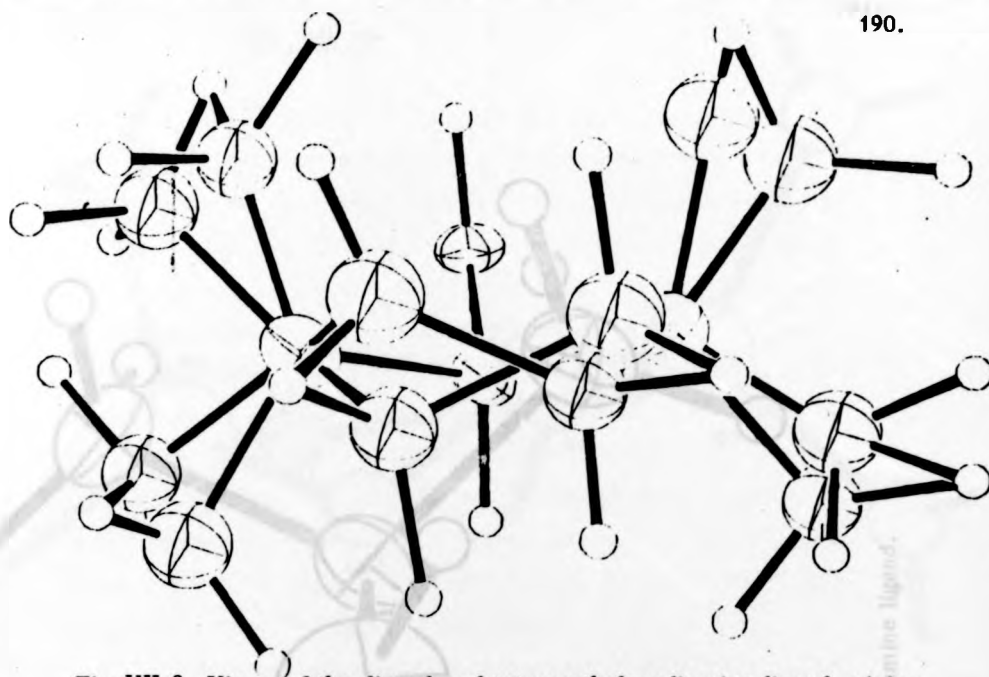
Fig. VII. 8   View   of the disordered tetramethylenediamine ligand, giving the arrangement of hydrogen atoms.
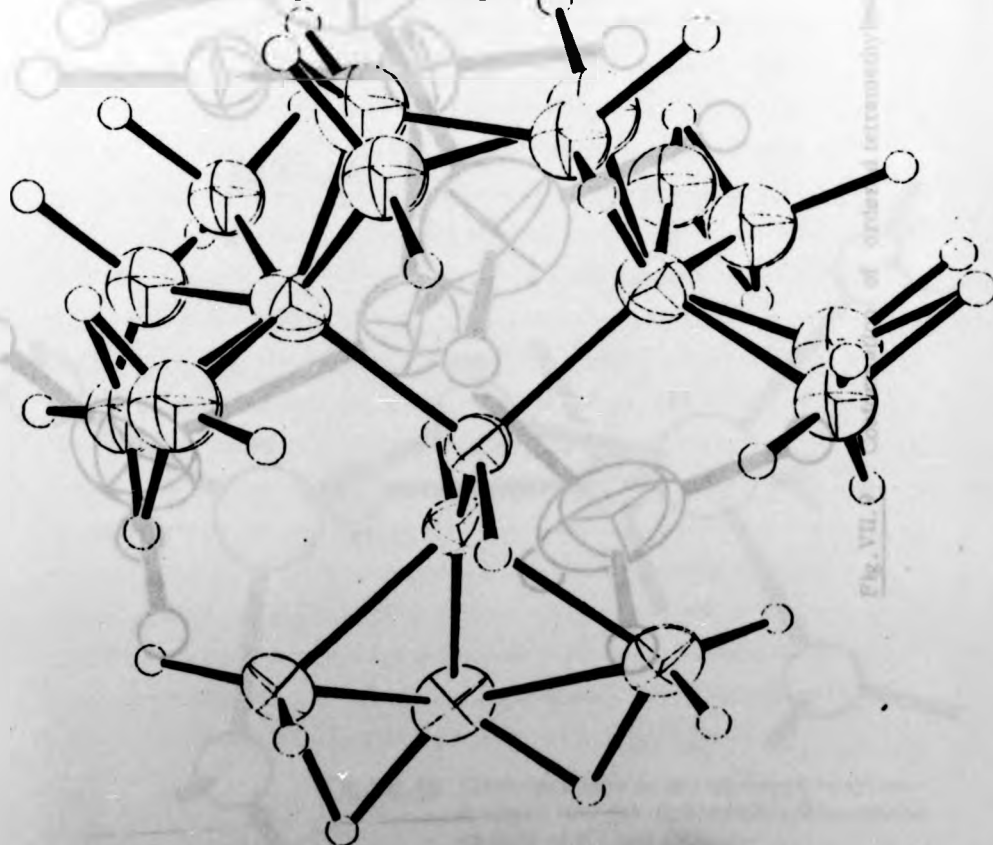

Fig. VII. 7   View of the disordered molecule of $B_5H_9 \cdot$ tmed
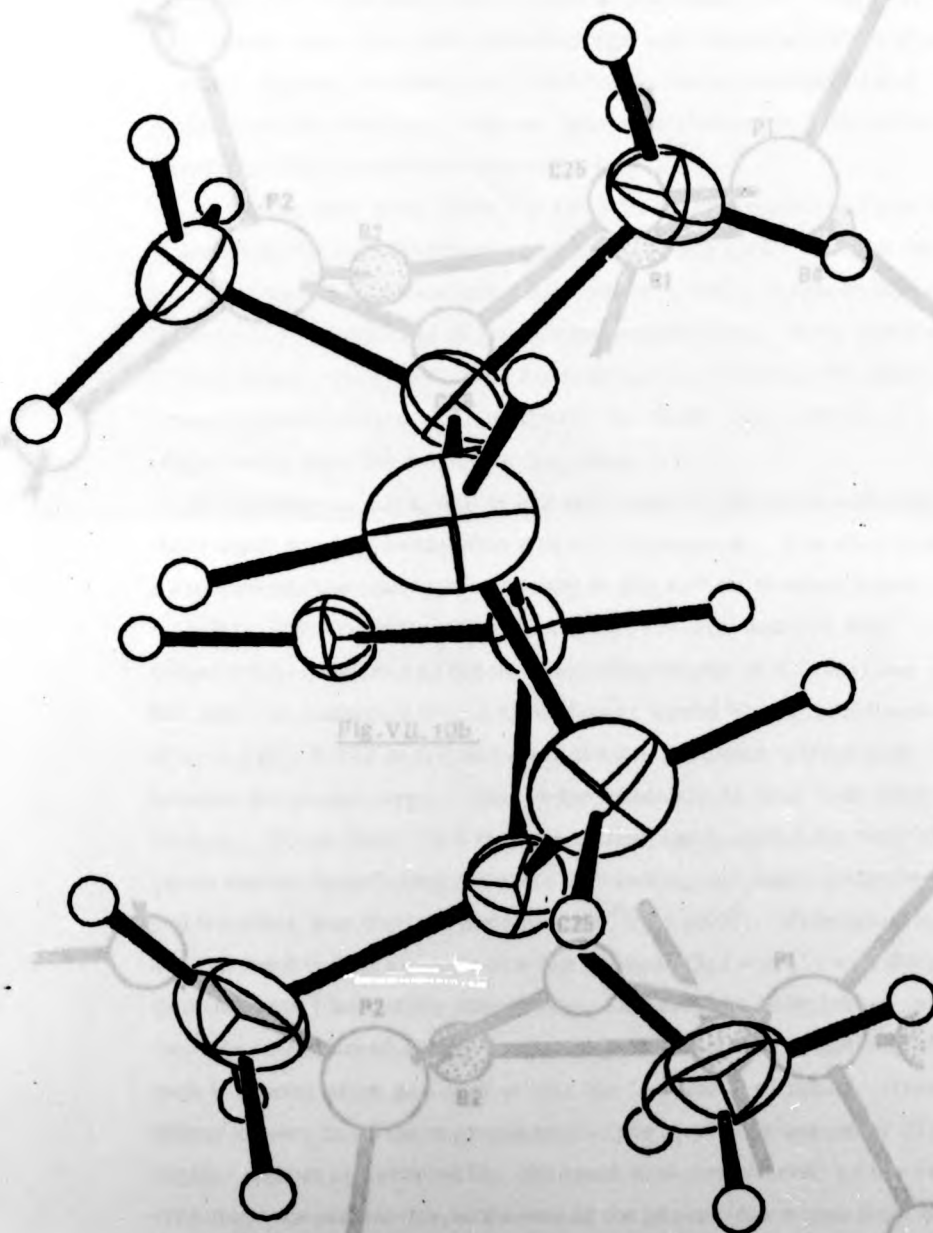
Fig. VII. 9   Conformation of ordered tetramethylene diamine ligand.
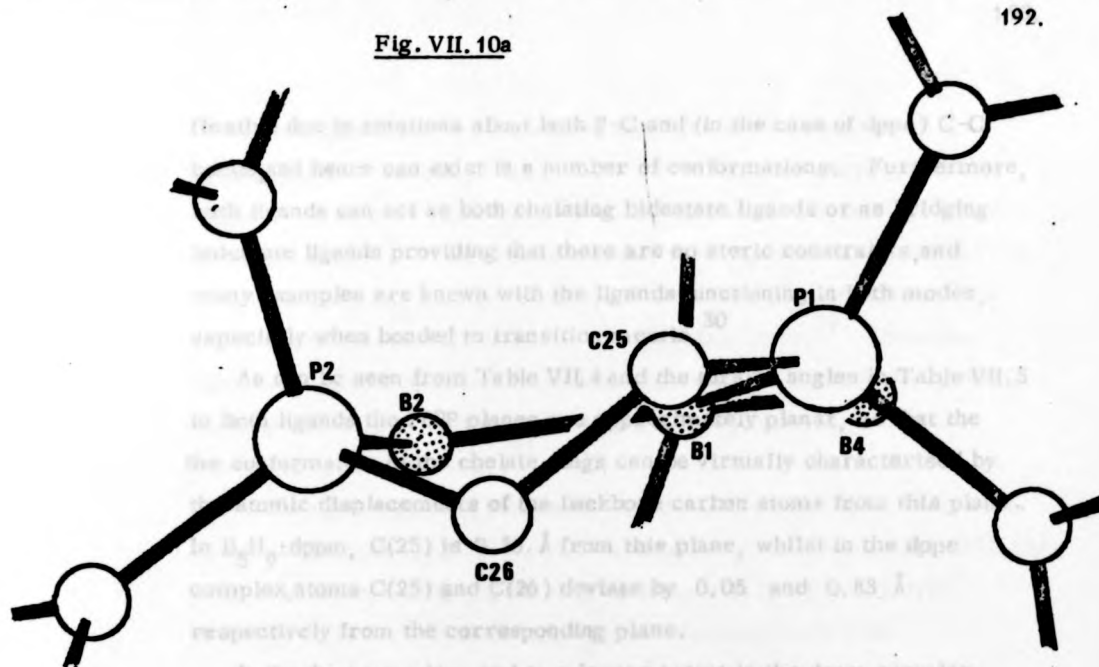
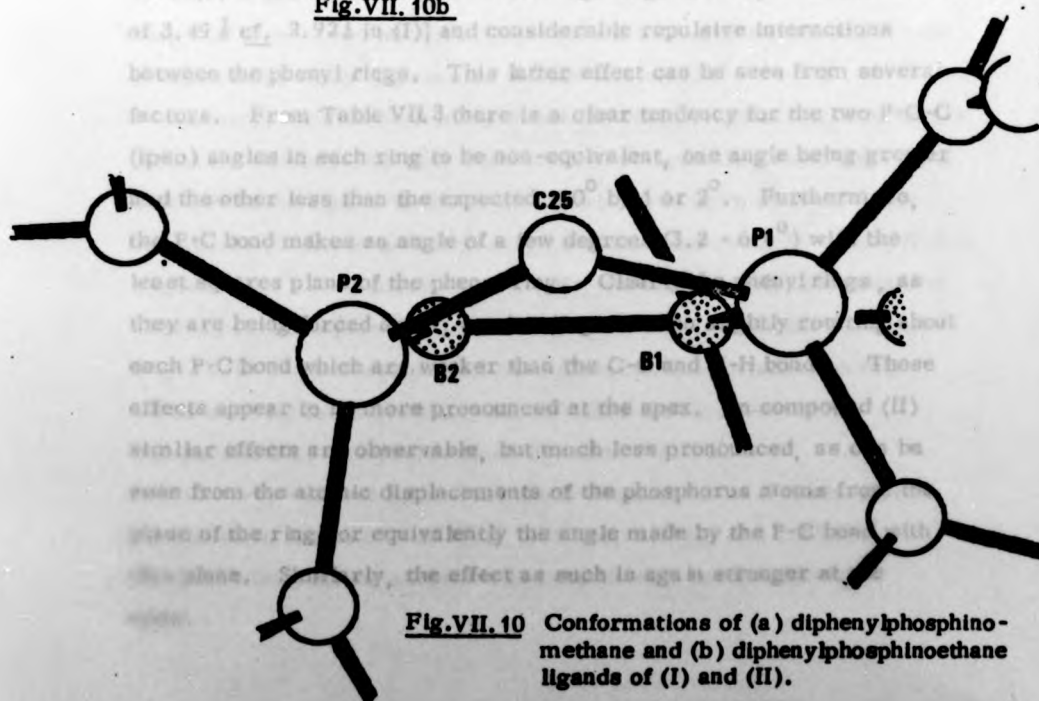**Fig. VII. 10a**

Fig.VII. 10b

Fig.VII. 10 Conformations of (a) diphenylphosphino-
methane and (b) diphenylphosphinoethane
ligands of (I) and (II).

flexible due to rotations about both P-C and (in the case of dppe) C-C bonds,and hence can exist in a number of conformations. Furthermore, both ligands can act as both chelating bidentate ligands or as bridging bidentate ligands providing that there are no steric constraints,and many examples are known with the ligands functioning in both modes, especially when bonded to transition metals.[30]

As can be seen from Table VII. 4 and the torsion angles in Table VII. 5 in both ligands the PBBP planes are approximately planar, so that the the conformation in the chelate rings can be virtually characterised by the atomic displacements of the backbone carbon atoms from this plane . In $B_5H_9 \cdot$dppm, C(25) is 0.56 Å from this plane, whilst in the dppe complex,atoms C(25) and C(26) deviate by 0.05 and 0.83 Å respectively from the corresponding plane.

In the dppe complex, and to a lesser extent in the dppm complex, there appears to be considerable strain in the ligands. The need to form a strained six membered chelate ring in (II) results in much larger P(1)-B(1)-B(2) and P(2)-B(2)-B(1) angles [117.2(3) and 115.9(3)$^{\circ}$ respectively compared to the corresponding angles of 107.7(6) and 107.4(6)$^{\circ}$ in compound (I)], a much larger ligand bite [P...P distance of 3.49 Å cf. 2.92Å in (I)] and considerable repulsive interactions between the phenyl rings. This latter effect can be seen from several factors. From Table VII. 3 there is a clear tendency for the two P-C-C (ipso) angles in each ring to be non-equivalent, one angle being greater and the other less than the expected 120° by 1 or 2°. Furthermore, the P-C bond makes an angle of a few degrees (3.2 - 6.6°) with the least squares plane of the phenyl ring. Clearly the phenyl rings, as they are being forced apart, are bending and also slightly rotating about each P-C bond which are weaker than the C-C and C-H bonds. These effects appear to be more pronounced at the apex. In compound (II) similar effects are observable, but much less pronounced, as can be seen from the atomic displacements of the phosphorus atoms from the plane of the rings or equivalently the angle made by the P-C bond with this plane. Similarly, the effect as such is again stronger at the apex.

These effects are not uncommon and have been extensively investigated by Coulson, Domenicano and Vaciago for phenylphosphino ligands and several other examples with second row non-metals attached to phenyl rings.[31]   The results of these investigations show that the use of a rigid body D_{6h} (6/mmm) model for the substituted phenyl rings in these ligand classes will result in systematic errors.[32]   These and similar inductive effects may also be apparent in cyclohexylphosphine ligands resulting in systematic changes in bond angles and bond distances around the rings.[33]

In the dppm ligand of compound (I), the C-C distances in the phenyl rings range from 1.326(18) to 1.408(15) Å (weighted average is 1.375(25)Å) with the corresponding angles varying from 116.7(10) to 122.1(8)$^{\circ}$ (average 119.18).   For the dppe ligand of compound (II) the corresponding C-C distances and CCC angles range from 1.346(8) to 1.407(6) Å (average 1.385(14)Å)and from 117.9(4) to 121.5(5)$^{\circ}$ (average 119.99) respectively.   The corresponding P-C(Ph) distances in (I) average   1.821 Å; in (II) they average 1.828 Å.   These should be compared to the normal range of P-C(sp^2) distances of 1.807(3) to 1.839(6) Å [31] found in phosphines.   Possibly because of the strains in the chelate ring and between the phenyl rings, there is no distinct difference in the P-C(Ph) and P-C(sp^3) distances in both compounds.

In compound (III) both independent molecules contain a B_5 framework which is markedly different from those in compounds (I) and (II).   Both nitrogen atoms donate to the same 'basal' boron atom forming a five membered chelate ring with average B-N distance of 1.673   Å and N-B-N angle of 97.1°.   In molecule 2 of (III), the chelate ring is disordered existing in two separate conformations with equal weight as shown in Fig. VII.7. The arrangement of the hydrogen atoms attached to this disordered ligand is similarly shown with a similar view of the conformation of the ordered tmed ligand in Fig. VII. 8.

The ave. value of 1.673 Å for the B-N distances in (III) should be compared to values of 1.636(4), 1.610(6), 1.60(2) and 1.58(3) Å in the trimethylamine adducts with respectively boron trifluoride

Fig. VII. 11   Two views ((a) and (b)) of the <u>hypho</u> $B_6H_{10} \cdot (PMe_3)_2$
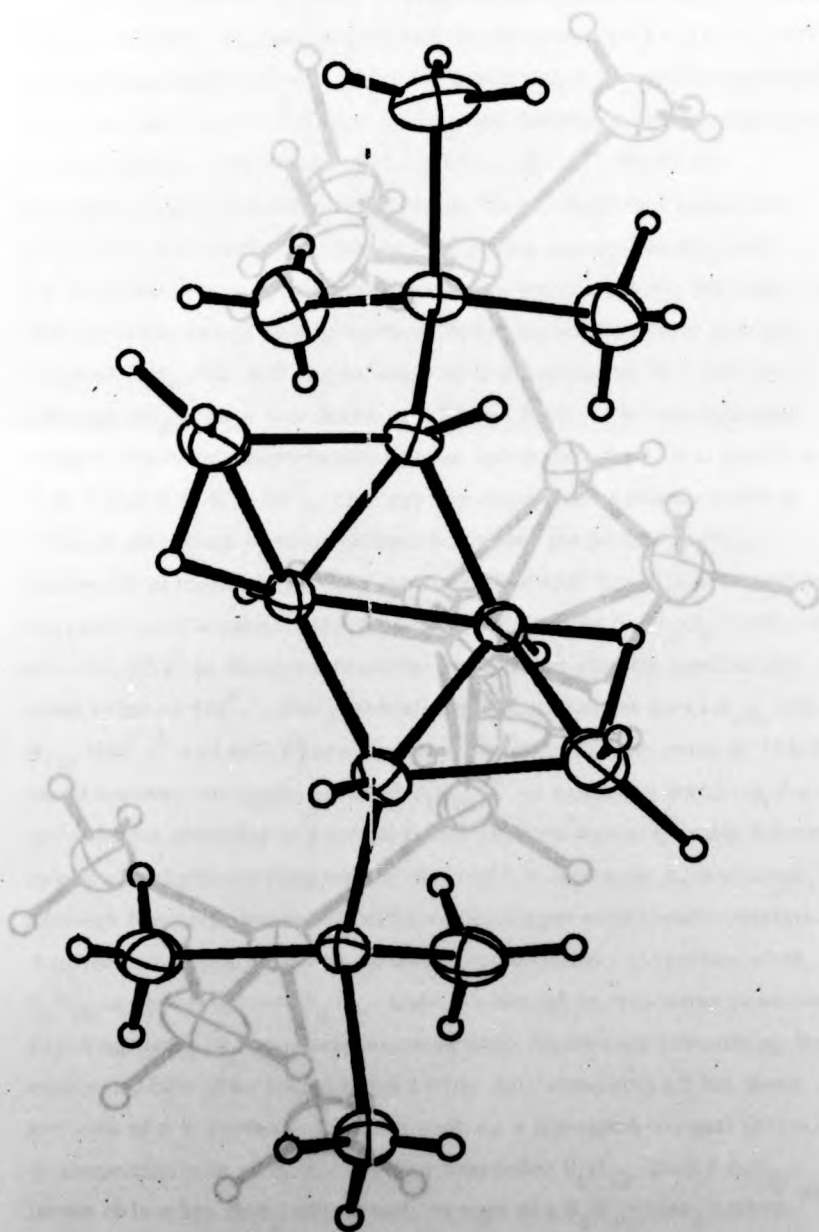adduct.   (Redrawn from co-ordinates in ref. 22b).

Fig. VII. 11a.

Fig. VII.11b

-trichloride, -tribromide and -tri-iodide[34] and values of 1.609 Å and
1.578(8) Å [B-NH$_3$] in BH$_3 \cdot$NMe$_3$ and ammonia-isothiocyanatoborane,
NH$_3 \cdot$BH$_2 \cdot$NCS respectively.[35] Other examples of B-N distances are also in ref.35.

In both molecules of (III) the basal boron atoms bonded to the tmed
ligand becomes, on rearrangement, singly bonded [B(1)-B(2) = 1.699 Å
ave.] to the apical boron atom of the remaining B$_4$H$_8$ and is separated
from the basal atoms B(3) and B(5) by non-bonded contact distances of
2.708 Å [B(2)...B(3)] and 2.721 Å [B(2)...B(5)]. Within the
triangular faces of the two B$_4$H$_8$ group the B-B distances range from
1.699 to 1.835 Å although, interestingly, the shortest is B(1)-B(4)
[1.700 Å ave.] suggesting a possible three-centre system B(2)-B(1)-B(4).
The arrangement of hydrogen atoms bears some similarity with the
original B$_5$H$_9$ with B-H single bonds still occurring at B(1) and B(4)
although BH$_2$ groups now occur at B(3) and B(5). The two hydrogen
bridges are within experimental error symmetric (ave. B-H bridge is
1.32 Å and B-H-B is 84°), although the individual values do seem to
indicate that there is some difference between the bridge to H(5)
compared to that to H(7). The parent polyhedron for (III) can again be
regarded as a hexagonal bipyramid with the angles B$_3$-B$_4$-B$_5$ = 107.9(6)$^\circ$
and 107.5(5)$^\circ$ in the two independent molecules slightly smaller than the
ideal value of 120°. The dihedral angles between the faces B$_{134}$ and
B$_{135}$ (129.4° and 127.4°) are, however, higher than the value of 118.1°
found between analagous faces of B$_4$H$_{10}$.[4] A structure involving the
tmed ligand chelating at a single boron position was previously favoured
over several possibilities on the basis of i.r. and n.m.r. devidence,
although the arrangement of boron and hydrogen atoms was uncertain.[23]
A gross movement of one of the basal boron atoms also occurs when
B$_6$H$_{10}$ is converted into B$_6$H$_{10} \cdot$2PMe$_3$, although in this latter case the
resulting hypho-B$_6$ fragment forms an open framework resembling the
equatorial belt of an icosahedron rather than occupying all but three
vertices of a 9-vertex polyhedron such as a tricapped trigonal prism.[22]
In connection with this, it should be noted that B$_6$H$_{10}$, unlike B$_5$H$_9$,
forms only a bis PMe$_3$ adduct with no sign of a B$_6$H$_{10} \cdot$PMe$_3$ adduct.[22]

A rearrangement compatible with this involves attachment of the two P atoms at the two ends of the basal single bond which is broken. A subsequent diamond-square-diamond arrangement is needed to break an apex-base bond before the boron skeleton flattens out to give the arrangement in Fig. VII.11 with the two PMe_3 groups well separated. What effect the fact that the phosphorus atoms are constrained in dppm and dppe may have on any $B_6H_{10} \cdot$ dppe (or dppm) adducts is open to speculation.

The _overall_ atomic arrangement of the borons in (III) is still believed to be an example of the _hypho_ class, although the structure might be interpreted in several different ways. In particular, zwitterionic canonical forms such as (A) or a valence structure such as (B) probably make significant contributions to the overall molecular orbitals.
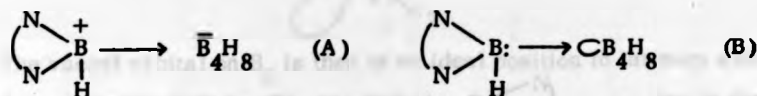
The valence structure (A) in fact shows strong similarities to adducts of the type $L \cdot B_4H_8$ where the $B_4H_8^-$ fragment would then be an _arachno_ species.[35] However, the present arrangement of _tmed_ and hydrogen atom at the 'basal' boron atom B(2) in each molecule appears to be unique amongst the boranes and their ions, so that there may be some justification for putting some weight on the suggestion that a truer representation of the present structure is given by the canonical form (B), especially as the 'B_4H_8' fragment can be written in terms of a 2112 vacant orbital valence structure.[36] Examples of possible vacant orbital valence structures are again given by modification of the rules for calculating normal neutral valence structures.

Using Lipscomb's _styx_ notation for a neutral boron hydride B_pH_{p+q} with v vacant orbitals, the rules become:

$$s + x = q$$
$$s + t = p - v$$
$$t + y = p - q/2$$

where the number of three-centre bonds (s + t) is reduced by the number of vacant orbitals, but the number of

hydrogens $(s + x + p)$ and the number of framework bonds $(t + y)$ remain constant. The normal styx structures for B_4H_8 are [4020], [2202] and [3111]; those for valence structures with one vacant orbital $(v = 1)$ are [3021], [2122] and [1203]. Of these latter structures, the C_s 2112 structure is a resonance hybrid between a structure having a single B_2B_4 bond and a central three-centre $B_1B_2B_3$ bond, and a valence structure with a single B_2B_3 bond and central three-centre $B_1B_2B_4$ bond.[36]
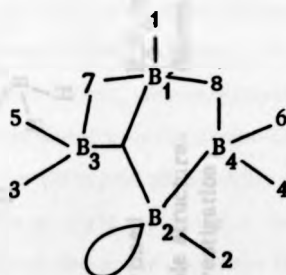
The vacant orbital on B_2 is then in an ideal position to interact with a donor species such as $:BH_3$ to which the $:B$ species is formally equivalent. Assuming that all hypho tmed structures contain the ligand chelating at a single boron position, it is possible to postulate a closed series for these tmed complexes as shown in Table VII.2. Of the structures in this Table, $B_5H_9 \cdot$ tmed and $[BH_4]^- [tmedBH_2]^+$ [37] are well characterised, and $B_4H_8 \cdot$ tmed is currently under investigation. It is assumed that the series is completed with $B_6H_{10} \cdot$ tmed because there are then no more H-atoms remaining on the apical boron atom, although this criterion is somewhat arbitrary and may be incorrect if similar vacant orbital structures to those in $B_5H_9 \cdot$ tmed have some significance for the higher ($>B_6$) boranes. Each structure in the Table can therefore be written as a neutral valence structure analagous to (B) above, and the styx vacant orbital structures for the fragments with which each

$L(\equiv$ $)$ group interacts are shown below each entry in the Table, with the favoured styx structure noted. For $B_6H_{10} \cdot$ tmed, this favoured structure requires a further modification to the equations for calculating

TABLE VII.2

Known or postulated structures for tetramethylene diamine adducts of the boron hydrides.

Formulation	BH₅L	B₂H₆L	B₃H₇L	B₄H₈L	B₅H₉L
Structure	(structural diagram)	(structural diagram)	(structural diagram)	(structural diagram)	(structural diagram)
Full formula	medBH₂⁺BH₄⁻ (known as individual ions)	B₃H₇·tmed	B₄H₈·tmed (probable structure under investigation)	B₅H₉·tmed (known)	B₆H₁₀·tmed (postulated)
No. of H atoms on apical boron	[4]	2 terminal + 1 bridge	2 terminal	1 terminal	0
Vacant orbital valence structure for 'BH' group		$[1003]_{v=1}$	$[1103]_{v=1}$	$[2112]_{v=1}$	$[3122]_{v=1}$
Alternatives			$[2012]_{v=1}$	$[1203]_{v=1}$	$[3021]_{v=1}$

See Table VII.3

styx values to allow the vacant orbital to occur on a bare boron atom, i.e. without an exoskeletal BH bond. In Table VII.3 some of the alternative styx vacant orbital structures not shown in Table VII.6 are depicted.

In comparing compounds (I) and (II) with (III), it could be expected that an open hypho framework would be rather flexible and might not correspond precisely to the rigid geometry of the corresponding closed parent polyhedron. It is somewhat unexpected to find it capable of the gross rearrangements observed here. In discussing some of the reasons for this isomerism, any mechanism for delocalising some of the excess electron density in the boron framework will be of importance. In this respect, the ability of phosphorus to accept electron density into its empty 3d orbitals might account for the preferential co-ordination of a phosphorus atom at the apical position (especially as in B_5H_9 there is a residual negative charge at the apical boron atom[4]) and the bridging mode of the phosphine ligands. Since any electron density removed by the phosphorus atoms can then be effectively further delocalised in phenyl ring orbitals, this process could be very effective. The fact that $B_5H_9 \cdot (PPh_3)_2$ is completely decomposed at $25^{\circ}C$ may be attributed to the fact that electron delocalisation from the hypho structures is so effective that the resultant boron framework is unstable with respect to dissociation into stable products such as $(Ph_3P)_2BH_2$.

Since nitrogen has no low-lying d-orbitals, no π-character can be associated with the B-N bonds. Hence the co-ordination of the ligand tmed into a chelating mode at a basal position could be predicted. The different framework arrangement in (III) then reflects a need to delocalise effectively a greater electron density left on the B_5 skeleton by the ineffective tmed. Part of this electron density is effectively localised in the short B(1)-B(2) bond which is close to a 2c-2e bond rather than the 3c-2e bonds in the triangular faces of the frameworks in (I) and (II). The retention of an integral B_4 unit in (III) may again be fractionally better at delocalising the remaining framework electrons than the two three-centre systems in (I) and (II) connected via the apical atom.
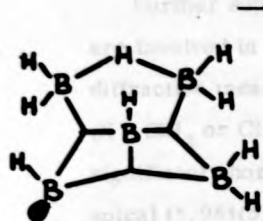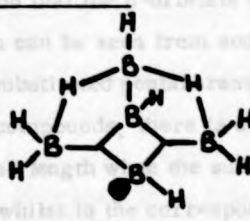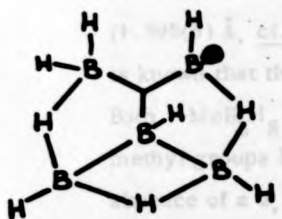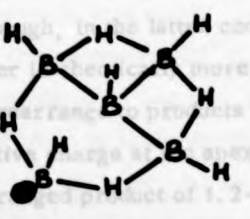
2
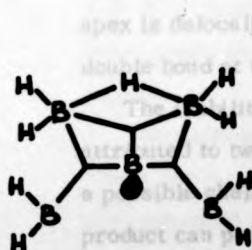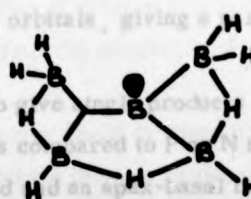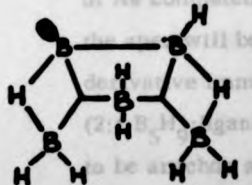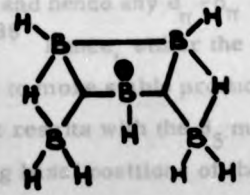
Further support for the suggestion that the d-orbitals on phosphorus are involved in charge delocalisation can be seen from some electron diffraction measurements on mono-substituted pentaboranes, B_5H_8X (X = SiH_3 or CH_3). With the silyl compounds, there is a very significant shortening of the B-Si bond length when the substituent is apical (1.981(5) Å, cf. 2.006(4) Å) whilst in the corresponding methyl substituted derivatives there is no difference in B-C bond lengths (1.595(5) Å, cf. 1.592(5) Å) even though, in the latter compounds, it is known that the 2-substituted isomer is chemically more stable. Both 1-MeB_5H_8 and 1,2-$(Me)_2B_5H_7$ rearrange to products with the methyl groups basal due to the negative charge at the apex. The absence of a 2,4 isomer in the rearranged product of 1,2-$(Me)_2B_5H_7$ is attributable to H(methyl)...H(bridge) repulsions in the likely inter-mediate for the rearrangement.[37] The shortening of the apical B-Si bond is consistent with the suggestion that the negative charge at the apex is delocalised into the empty Si 3d orbitals, giving a partial double bond at the apical position.[6]

The inability of the arsino ligands to give single products can be attributed to two factors; the size of As compared to P or N rules out a possible chelating mode for this ligand and an apex-basal bridged product can possibly be ruled out because the phenyl substituents on the As atom are ineffectual in contracting the more diffuse 4d orbitals of As compated to 3d orbitals on P, and hence any d_π-p_π overlap at the apex will be very small for As.[38] Hence, either the hypho derivative immediately decomposes to more stable products or else a (2:1 B_5H_9:ligand) polymeric product results with the B_5 moieties likely to be arachno and the ligand bridging basal positions of these groups.

The reaction of pentaborane (9) with other ligands and other metal complexes similarly results in basal co-ordination, either via two-centre M-B or three-centre B——B bridging interactions regardless of whether the starting borane had been apical or basal substituted. As noted already in the introduction, there are no rules regarding

whether the result bond is M-B or B $\underset{\displaystyle M}{\overbrace{\qquad}}$ B at present, although the common feature is the co-ordination of the metal at the base. Any rules for these co-ordination modes must take into consideration the excess electron density at the B_5H_9 apical atom, which presumably is forcing poor π-acceptor metals into their basal co-ordination.

Finally, the presence of a chelate effect is apparent in all the adducts, the monodentate ligand species being much less stable, so that, for example, $B_5H_9 \cdot 2PPh_3$ is completely decomposed at 25° C. Of the three compounds, (III) is the least stable (cf. I and II) , presumably decomposing to give $[tmedBH_2]^-$ and other ionic products. Part of the chemical stability of complexes (I) and (II) must also be attributed to the size of the extremely bulky diphos ligands compared to the B_5H_9, preventing any approach from nucleophiles, etc. Furthermore, the three hypho structures must be considered to be electron rich compared with B_5H_9 itself, so that a greater number of valence structures for these hypho derivatives can be formulated with single (2c-2e) bonds present.

The packing of the three compounds are shown in Figs. VII. 12 and 13. There are no close inter-molecular contacts between molecules which are separated by typical van der Waals contacts.

VII.5. References

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2. See for example, E. Wiberg, Ber., 1936, 69B , 2816 and S.H. Bauer and L. Pauling, J. Am. Chem. Soc., 1936, 58 , 1403.

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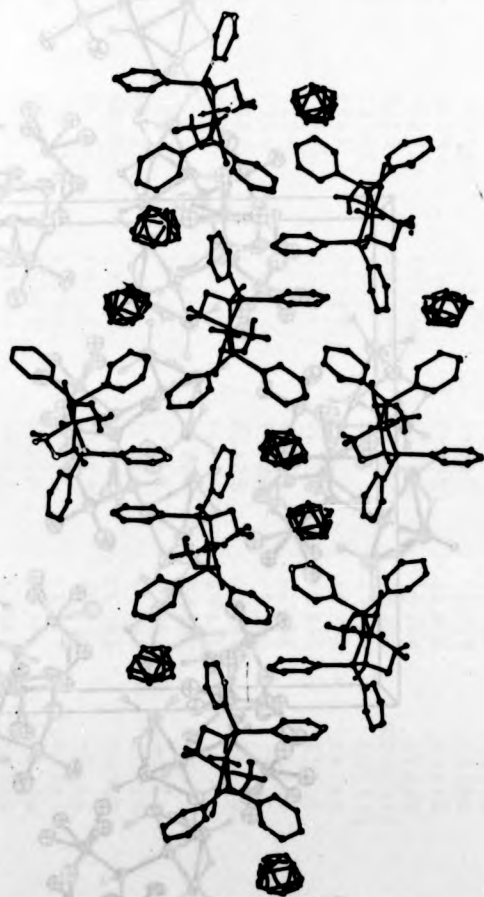
Fig. VII. 12   Packing arrangement in $B_5H_9 \cdot$ dppm viewed down $\underline{a}$.

Fig. VII. 13   Packing diagram for B_5H_9 dppm viewed down $\underline{c}$.
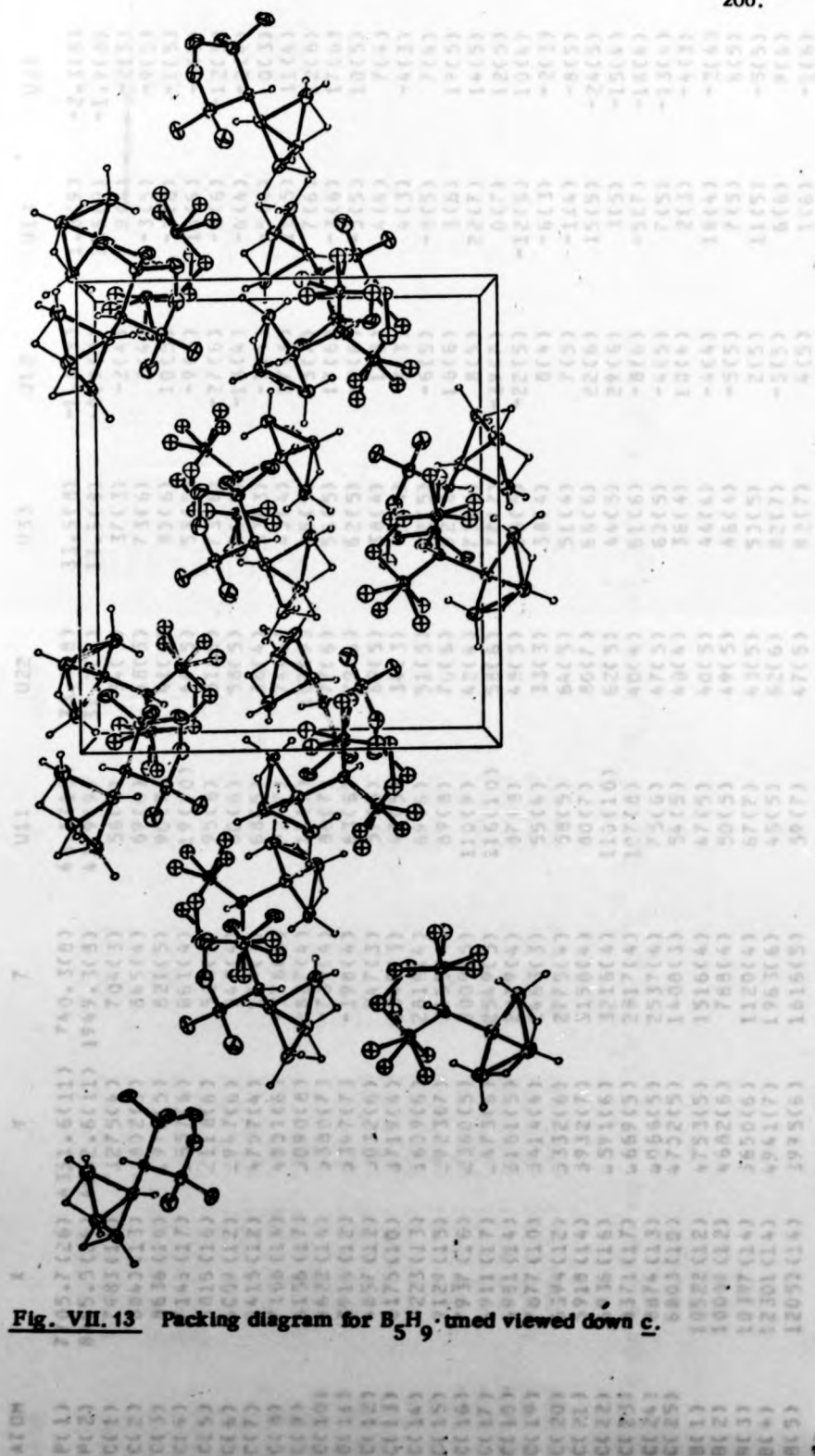
Fig. VII. 13 Packing diagram for $B_5H_9 \cdot$ tmed viewed down $\underline{c}$.

TABLE VII.4

Atomic co-ordinates (* 10 ** 4) and temperature factors (* 10 ** 3), with standard deviations in parentheses.

(a) B₅H₉·dppm

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
P(1)	7705.7(26)	4351.6(11)	740.3(8)	48.1(10)	38.4(8)	33.5(8)	-1.0(9)	1.6(9)	-2.3(8)
P(2)	8665.5(24)	4642.6(11)	1949.3(8)	42.9(9)	31.2(8)	33.5(8)	-0.9(9)	2.5(9)	-1.9(8)
C(1)	7483(11)	5275(4)	704(3)	56(5)	34(3)	37(3)	-2(4)	9(4)	-2(3)
C(2)	8843(13)	5802(5)	865(4)	69(6)	48(5)	73(6)	2(4)	-3(5)	-9(5)
C(3)	8636(16)	4972(5)	821(5)	90(6)	41(4)	80(6)	10(5)	-2(6)	-1(5)
C(4)	7146(17)	-657(6)	661(4)	119(10)	44(5)	55(5)	-9(6)	13(6)	-5(5)
C(5)	5816(16)	2118(6)	528(5)	95(8)	51(6)	73(6)	-27(6)	-6(6)	-12(5)
C(6)	6009(12)	2947(6)	542(4)	60(6)	58(5)	55(5)	-13(4)	-6(4)	-2(4)
C(7)	6415(12)	4757(4)	169(3)	68(5)	38(4)	33(3)	-7(4)	-5(4)	0(3)
C(8)	7168(14)	4801(6)	-376(4)	92(7)	74(6)	40(4)	27(6)	10(5)	11(4)
C(9)	6156(17)	5090(8)	-827(4)	111(9)	107(9)	45(5)	13(7)	7(6)	12(6)
C(10)	4622(14)	5380(7)	-739(4)	88(7)	77(6)	55(5)	17(6)	-3(6)	17(6)
C(11)	3916(12)	5347(7)	-198(4)	63(6)	79(6)	62(5)	-8(6)	-5(5)	10(5)
C(12)	4857(12)	5032(6)	247(3)	59(5)	69(5)	38(4)	1(5)	4(4)	7(4)
C(13)	8175(10)	3719(4)	2349(3)	47(5)	34(3)	45(4)	3(3)	4(3)	-4(3)
C(14)	9223(13)	3609(6)	2818(4)	69(6)	51(5)	52(5)	-6(5)	-8(5)	7(4)
C(15)	9129(15)	2923(7)	3155(4)	89(8)	70(6)	62(6)	16(6)	3(6)	19(5)
C(16)	7937(16)	2360(5)	3009(5)	110(9)	42(4)	73(6)	8(5)	22(7)	14(5)
C(17)	6911(17)	2473(6)	2549(5)	116(10)	58(6)	77(7)	-39(7)	0(7)	12(5)
C(18)	6951(14)	3161(5)	2219(4)	87(8)	49(5)	55(5)	-22(5)	-12(5)	10(4)
C(19)	7877(10)	5414(4)	2463(3)	55(4)	33(3)	38(4)	8(4)	-6(3)	-2(3)
C(20)	6394(12)	5332(6)	2775(4)	58(5)	64(5)	51(4)	7(5)	-1(4)	-8(5)
C(21)	5918(14)	5932(7)	3158(4)	80(7)	80(7)	65(6)	22(6)	15(5)	-24(5)
C(22)	6936(16)	6591(6)	3216(4)	110(10)	62(5)	44(5)	29(6)	3(5)	-15(4)
C(23)	8371(17)	6669(5)	2917(4)	107(8)	40(4)	61(6)	-8(6)	-5(7)	-18(4)
C(24)	8874(13)	6066(5)	2537(4)	75(6)	47(5)	60(5)	-4(5)	7(5)	-13(4)
C(25)	6803(10)	4772(5)	1408(3)	54(5)	40(4)	36(4)	10(4)	2(3)	-4(3)
B(1)	10522(12)	4753(5)	1516(4)	47(5)	40(5)	44(4)	-4(4)	18(4)	-2(4)
B(2)	10009(12)	4682(6)	788(4)	50(5)	49(5)	46(4)	-5(5)	7(5)	6(5)
B(3)	10397(14)	5650(6)	1120(4)	67(7)	43(5)	53(5)	2(5)	11(5)	-5(5)
B(4)	12301(14)	4941(7)	1963(6)	45(5)	62(6)	82(7)	-3(5)	6(6)	9(6)
B(5)	12052(14)	5995(6)	1616(5)	59(7)	47(5)	82(7)	4(5)	1(6)	-1(6)

TABLE VII.4(cont.)

(a) $B_5H_9 \cdot$ dppm

ATOM	X	Y	Z	U
H(1)	9568(88)	5416(45)	593(29)	42(20)
H(2)	10856(115)	4422(58)	529(38)	84(28)
H(3)	9343(75)	6005(37)	1197(25)	21(15)
H(4)	11612(114)	5952(50)	1016(34)	58(23)
H(5)	13063(87)	4269(43)	1968(30)	45(19)
H(6)	11898(95)	5138(46)	2402(33)	50(22)
H(7)	9796(189)	2908(82)	3578(56)	70(15)
H(8)	11672(127)	5500(56)	1694(40)	68(27)
H(9)	13008(131)	5945(65)	1254(45)	93(33)
H(21)	10643(171)	6006(72)	2843(52)	70(35)
H(31)	3226(95)	2317(47)	1771(31)	46(20)
H(41)	7433(125)	-920(53)	3213(36)	70(37)
H(51)	5951(122)	-2242(55)	2565(39)	70(41)
H(61)	6271(122)	2201(54)	1905(39)	70(23)
H(81)	5593(146)	4984(68)	2654(45)	70(38)
H(91)	4801(143)	2887(60)	3332(42)	70(35)
H(101)	6373(146)	6951(64)	3498(43)	70(31)
H(111)	9137(157)	7038(74)	3104(52)	70(45)
H(121)	245(109)	1113(45)	2728(32)	70(37)
H(141)	10673(128)	-930(56)	988(38)	70(26)
H(151)	9555(146)	1727(68)	886(46)	70(23)

ATOM	X	Y	Z	U
H(161)	6970(113)	1224(49)	696(37)	70(35)
H(171)	5148(157)	1736(70)	358(48)	70(31)
H(181)	4984(174)	3138(78)	490(51)	70(44)
H(201)	7723(247)	4293(112)	-474(75)	70(92)
H(211)	6817(129)	5168(611)	-1225(39)	70(40)
H(221)	3514(313)	5533(138)	-867(95)	70(120)
H(231)	2849(132)	5648(60)	-148(42)	70(33)
H(261)	3930(235)	4938(112)	500(71)	70(86)
H(251)	6415(94)	5231(48)	1373(30)	70(26)
H(252)	5875(165)	4368(80)	1520(51)	70(51)

In the form: $U = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$

Table VII. 4(cont.)

(b) $B_5H_9 \cdot (Ph_2PCH_2)_2$, (II)

Atom	X	Y	Z
P(1)	0.35387(6)	0.01975(6)	0.28206(4)
P(2)	0.25323(6)	0.04436(6)	0.41652(4)
C(1)	0.3875(2)	0.0423(2)	0.2168(2)
C(2)	0.3373(3)	0.0346(3)	0.1632(2)
C(3)	0.3539(3)	0.0865(3)	0.1156(2)
C(4)	0.4207(3)	0.1475(3)	0.1212(2)
C(5)	0.4707(3)	0.1559(2)	0.1730(2)
C(6)	0.4556(2)	0.1028(2)	0.2208(2)
C(7)	0.3406(3)	-0.1215(2)	0.2499(2)
C(8)	0.4155(3)	-0.1540(3)	0.2174(2)
C(9)	0.4127(4)	-0.2339(3)	0.1972(2)
C(10)	0.3352(4)	-0.2815(3)	0.2074(2)
C(11)	0.2614(4)	-0.2499(3)	0.2367(2)
C(12)	0.2628(3)	-0.1700(2)	0.2589(2)
C(13)	0.2229(2)	0.1235(2)	0.4703(2)
C(14)	0.1608(3)	0.1857(2)	0.4565(2)
C(15)	0.1439(3)	0.2474(3)	0.4974(2)
C(16)	0.1885(3)	0.2470(3)	0.5520(2)
C(17)	0.2490(3)	0.1858(3)	0.5665(2)
C(18)	0.2673(3)	0.1237(3)	0.5261(2)
C(19)	0.1754(2)	-0.0409(2)	0.4282(2)
C(20)	0.2100(3)	-0.1186(2)	0.4256(2)
C(21)	0.1499(3)	-0.1848(3)	0.4285(3)
C(22)	0.0552(3)	-0.1734(3)	0.4335(2)
C(23)	0.0197(3)	-0.0960(3)	0.4367(2)
C(24)	0.0785(3)	-0.0297(3)	0.4336(2)
C(25)	0.2323(2)	0.0149(2)	0.2951(2)
C(26)	0.2217(2)	0.0816(2)	0.3420(2)
B(1)	0.4350(3)	-0.0159(3)	0.3525(2)
B(2)	0.3846(3)	0.0156(3)	0.4201(2)

Table VII. 4(cont.)

B(3)	0. 4603(3)	0. 0837(3)	0. 3773(2)
B(4)	0. 5502(3)	-0. 0494(3)	0. 3297(3)
B(5)	0. 4763(3)	-0. 1151(3)	0. 3740(2)
H(1)	0. 4173(26)	0. 0859(22)	0. 4296(16)
H(2)	0. 4030(25)	-0. 0125(22)	0. 4615(16)
H(3)	0. 4262(29)	0. 1316(27)	0. 3543(19)
H(4)	0. 5305(31)	0. 0985(25)	0. 3935(18)
H(5)	0. 5493(31)	-0. 1285(28)	0. 3433(20)
H(6)	0. 6127(27)	-0. 0214(22)	0. 3550(17)
H(7)	0. 5585(28)	-0. 0517(24)	0. 2782(18)
H(8)	0. 5003(25)	-0. 1244(23)	0. 4191(17)
H(9)	0. 4299(27)	-0. 1659(23)	0. 3583(16)
H(21)	0. 2878(27)	-0. 0057(22)	0. 1591(18)
H(31)	0. 3232(31)	0. 0741(25)	0. 0768(19)
H(41)	0. 4324(25)	0. 1795(21)	0. 0883(16)
H(51)	0. 5194(28)	0. 1980(24)	0. 1792(17)
H(61)	0. 4871(22)	0. 1071(19)	0. 2555(15)
H(81)	0. 4695(31)	-0. 1222(28)	0. 2078(20)
H(91)	0. 4592(29)	-0. 2557(25)	0. 1735(18)
H(101)	0. 3379(34)	-0. 3390(30)	0. 1898(21)
H(111)	0. 2112(30)	-0. 2724(27)	0. 2438(21)
H(121)	0. 2081(21)	-0. 1460(19)	0. 2818(13)
H(141)	0. 1324(20)	0. 1839(17)	0. 4195(13)
H(151)	0. 1094(24)	0. 2890(20)	0. 4884(16)
H(161)	0. 1777(29)	0. 2869(23)	0. 5811(17)
H(171)	0. 2779(31)	0. 1816(27)	0. 6019(20)
H(181)	0. 3086(26)	0. 0877(22)	0. 5339(16)
H(201)	0. 2772(31)	-0. 1272(28)	0. 4222(19)
H(211)	0. 1753(33)	-0. 2349(28)	0. 4238(21)
H(221)	0. 0117(28)	-0. 2205(25)	0. 4341(17)
H(231)	-0. 0463(34)	-0. 0828(28)	0. 4415(21)
H(241)	0. 0571(29)	0. 0181(25)	0. 4394(19)

Table VII. 4 (cont.)

H(251)	0.1985(22)	-0.0272(20)	0.3113(14)
H(252)	0.2057(25)	0.0305(22)	0.2558(18)
H(261)	0.2573(23)	0.1290(20)	0.3340(14)
H(262)	).1581(26)	0.0988(22)	0.3436(16)

TABLE VII. 4 (cont.)

Anisotropic Temperature Factors (x 10^3)[†] for B_5H_9.dppe

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	28.2(5)	32.0(5)	41.8(5)	-2.3(4)	1.4(4)	1.5(4)
P(2)	29.6(5)	33.7(5)	41.1(5)	1.4(4)	1.0(4)	3.2(4)
C(1)	36.0(19)	34.2(20)	44.2(21)	6.0(16)	9.5(17)	1.3(17)
C(2)	51.6(25)	50.9(26)	51.8(24)	2.6(20)	0.7(20)	4.4(20)
C(3)	59.7(27)	72.9(31)	49.8(26)	10.2(26)	-3.0(22)	9.2(24)
C(4)	64.9(29)	59.7(29)	60.5(30)	20.2(24)	19.7(25)	27.0(24)
C(5)	51.1(24)	39.3(23)	66.9(29)	3.3(19)	17.4(23)	12.1(22)
C(6)	38.7(20)	41.6(22)	49.3(23)	-0.2(17)	6.4(18)	-0.9(18)
C(7)	48.4(22)	33.7(18)	39.7(20)	-2.1(17)	-7.7(18)	3.4(17)
C(8)	59.2(26)	43.8(24)	64.3(29)	4.9(20)	3.9(23)	-3.2(22)
C(9)	94.6(36)	43.2(25)	61.2(29)	9.7(26)	6.5(27)	-4.0(22)
C(10)	106.5(42)	36.4(23)	55.2(28)	-1.5(28)	-16.6(29)	1.7(21)
C(11)	81.4(34)	47.4(27)	72.9(33)	-23.1(29)	-18.1(29)	8.6(23)
C(12)	54.6(25)	42.6(23)	63.4(26)	-11.2(21)	-1.1(22)	0.5(21)
C(13)	35.9(19)	37.2(20)	43.0(21)	-3.7(17)	3.3(16)	0.3(17)
C(14)	36.5(20)	45.5(22)	46.4(22)	3.0(17)	-0.5(17)	-2.2(18)
C(15)	45.7(21)	37.9(20)	68.9(27)	0.5(20)	11.4(21)	0.0(20)
C(16)	60.1(26)	49.7(25)	57.3(27)	-4.6(24)	17.8(23)	-13.1(22)
C(17)	63.0(28)	72.8(33)	49.0(25)	1.6(27)	-2.6(23)	-10.7(22)
C(18)	54.4(26)	54.6(25)	49.3(23)	5.0(21)	0.1(20)	-2.1(21)
C(19)	29.5(17)	39.1(21)	43.6(21)	-1.5(16)	2.5(16)	3.0(17)
C(20)	33.3(20)	38.7(24)	95.6(35)	1.5(16)	5.1(27)	12.2(23)
C(21)	46.2(25)	37.0(23)	127.5(47)	-1.1(21)	6.4(28)	10.6(26)
C(22)	47.2(25)	48.5(26)	81.7(34)	-12.5(22)	3.8(23)	5.5(24)
C(23)	30.9(21)	66.8(32)	92.3(37)	-5.0(21)	9.7(22)	-4.1(27)
C(24)	36.9(21)	43.8(25)	81.8(32)	2.4(19)	13.0(21)	-6.0(22)
C(25)	29.5(18)	49.5(22)	40.9(20)	2.6(17)	-2.6(15)	3.2(18)
C(26)	31.9(18)	41.3(21)	45.3(22)	6.3(16)	0.8(16)	3.1(18)

TABLE VII.4 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
B(1)	27.0(19)	40.0(22)	47.3(25)	-2.4(18)	-1.1(19)	3.2(20)
B(2)	31.1(21)	41.4(24)	48.0(25)	-4.2(19)	-2.4(18)	7.6(21)
B(3)	36.4(24)	51.0(28)	57.7(30)	-15.3(22)	6.0(22)	-3.4(24)
B(4)	30.7(23)	59.8(32)	67.2(34)	5.7(22)	7.9(22)	-3.1(27)
B(5)	40.2(25)	51.3(30)	59.4(31)	9.5(23)	0.2(24)	7.4(25)

Atom	U	Atom	U	Atom	U
H(1)	47(10)	H(41)	41(10)	H(171)	64(14)
H(2)	44(10)	H(51)	58(12)	H(181)	49(11)
H(3)	64(13)	H(61)	37(9)	H(201)	74(14)
H(4)	64(12)	H(81)	73(14)	H(211)	76(15)
H(5)	70(13)	H(91)	77(13)	H(221)	54(12)
H(6)	51(11)	H(101)	84(16)	H(231)	83(15)
H(7)	53(12)	H(111)	81(14)	H(241)	58(13)
H(8)	43(10)	H(121)	26(8)	H(251)	34(9)
H(9)	47(11)	H(141)	19(7)	H(252)	43(10)
H(21)	56(12)	H(151)	41(10)	H(261)	31(8)
H(31)	67(13)	H(161)	53(12)	H(262)	45(11)

† In the form

$$U = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hl\,a^*c^* + 2U_{23}klb^*c^*)\}$$

TABLE VII.4 (cont.)

Atomic co-ordinates (* 10 ** 4) and temperature factors (* 10 ** 3), with standard deviations in parentheses.

(c) $B_5H_9 \cdot$ tmed

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
N(11)	3718(3)	4102(3)	4543(3)	48(3)	39(3)	44(2)	-4(3)	1(2)	8(2)
N(12)	3129(3)	4865(3)	5991(3)	40(3)	41(3)	57(3)	4(2)	1(2)	-2(3)
N(21)	2180(3)	840(3)	-1546(3)	43(3)	47(3)	56(3)	-2(2)	1(2)	8(3)
N(22)	1353(3)	706(3)	-45(3)	44(3)	50(3)	48(3)	2(3)	-3(2)	6(3)
C(11)	3432(6)	3014(5)	4257(4)	69(5)	77(5)	47(4)	-24(4)	-3(4)	-13(4)
C(12)	4553(5)	4471(5)	3941(4)	91(5)	89(5)	42(3)	-42(4)	10(3)	1(3)
N(13)	2766(5)	4769(6)	4456(4)	84(5)	86(5)	63(4)	36(4)	-19(4)	13(4)
C(14)	2767(5)	5472(5)	5213(5)	64(4)	57(4)	86(5)	35(3)	-3(4)	4(4)
C(15)	2295(5)	4199(6)	6371(6)	49(4)	83(5)	82(6)	-3(5)	19(4)	2(5)
C(16)	3477(5)	5618(5)	6687(4)	88(5)	70(5)	96(6)	25(4)	12(4)	-28(4)
B(11)	4384(5)	3053(5)	6106(4)	39(4)	42(4)	52(4)	1(3)	10(4)	-1(4)
B(12)	4119(4)	4200(5)	5599(4)	32(3)	30(3)	41(4)	0(3)	-6(3)	1(3)
B(13)	4860(6)	3475(7)	7173(5)	54(5)	72(6)	61(6)	-9(5)	-18(5)	8(5)
B(14)	5298(6)	2364(7)	6662(5)	65(5)	56(6)	71(6)	6(4)	-14(5)	14(5)
B(15)	5566(5)	2668(6)	5533(5)	54(4)	50(5)	71(5)	8(4)	-2(5)	-4(5)
B(21)	164(5)	1721(5)	-1380(4)	44(4)	32(4)	48(4)	-8(3)	2(3)	-9(3)
B(22)	1339(4)	1515(5)	-913(4)	37(3)	33(4)	43(4)	-7(3)	11(3)	-3(3)
B(23)	509(6)	2694(6)	-2208(5)	66(5)	50(4)	50(5)	7(5)	2(4)	11(4)
B(24)	-608(6)	2661(6)	-1678(5)	44(4)	64(5)	66(5)	-1(4)	-9(4)	-12(4)
B(25)	-454(6)	2506(6)	-513(5)	41(4)	49(4)	67(5)	-14(4)	5(4)	-10(4)

ATOM	X	Y	Z	U	ATOM	X	Y	Z	U
C21A	1715(9)	22(10)	-2049(8)	54(3)	H(123)	5150(67)	3766(69)	3903(57)	207(36)
C22A	2780(10)	1527(10)	-2122(8)	55(4)	H(131)	2677(39)	5063(42)	3883(32)	87(17)
C23A	2900(9)	416(10)	-844(8)	57(3)	H(132)	2105(37)	4081(39)	4644(29)	81(16)
C24A	2145(13)	-63(13)	-112(11)	69(6)	H(141)	2104(27)	5831(30)	5317(21)	34(11)
C25A	1533(10)	1492(11)	807(9)	51(5)	H(142)	3467(43)	6128(43)	4874(34)	105(19)
C26A	400(11)	130(11)	200(10)	71(5)	H(151)	2028(45)	3676(52)	5963(40)	88(25)
C21B	1761(9)	517(11)	-2451(8)	63(4)	H(152)	2516(37)	3904(37)	6912(33)	43(18)
C22B	3103(10)	1592(11)	-1752(9)	68(4)	H(153)	1735(39)	4780(41)	6613(31)	87(17)
C23B	2541(10)	-105(11)	-1072(9)	70(4)	H(161)	3006(33)	6101(31)	6792(25)	51(13)
C24B	2470(11)	185(11)	-129(10)	50(5)	H(162)	3597(50)	5190(54)	7091(39)	128(23)
C25B	1308(12)	1154(13)	781(11)	62(5)	H(163)	4019(38)	6151(36)	6377(32)	74(16)
C26B	528(11)	-128(11)	-164(10)	70(5)	H21AB	1188	49	-2396	80

TABLE VII.4 (cont.)

ATOM	X	Y	Z	U
H22AB(1)	3486	1100	-2044	80
H22AB(2)	2805	2185	-2024	80
H23AB	3362	-175	-1164	80
H24AB	2531	-289	482	80
H25AB	719	1797	768	80
H26AB(1)	-109	438	98	80
H26AB(2)	369	-599	-158	80
H21A(1)	2347	-347	-2394	80
H21A(2)	1256	-640	-1813	80
H22A(3)	2401	1370	-2736	80
H23A(2)	3369	1074	-514	80
H24A(2)	1877	-850	-355	80
H25A(1)	1560	959	1445	80
H25A(2)	2180	1921	593	80
H26A(3)	424	-116	934	80
H21B(1)	2494	137	-2786	80
H21B(3)	1446	1196	-2820	80
H22B(3)	3442	1929	-1187	80
H23B(2)	2342	-724	-1436	80
H24B(1)	2994	667	132	80
H25B(1)	1108	629	1298	80
H25B(3)	1972	1388	960	80

(c) $B_5H_9 \cdot$ tmed

ATOM	X	Y	Z	U
H(11)	3773(33)	2451(35)	6065(28)	47(13)
H(12)	4702(24)	4784(26)	5538(20)	10(9)
H(13)	5182(41)	4175(46)	7090(31)	67(18)
H(14)	4385(41)	3445(41)	7851(36)	74(17)
H(15)	5704(40)	2806(38)	7331(32)	62(15)
H(16)	5198(34)	6116(47)	6854(27)	53(15)
H(17)	6116(47)	2473(43)	6213(40)	86(18)
H(18)	5576(36)	2034(38)	5109(32)	57(15)
H(19)	6071(34)	3505(41)	5326(28)	63(15)
H(21)	-203(33)	1058(36)	-1601(27)	48(14)
H(22)	1757(28)	2225(32)	-720(24)	27(11)
H(23)	1171(30)	3100(30)	-1896(23)	22(11)
H(24)	436(28)	2473(28)	-2934(28)	26(11)
H(25)	-90(38)	3492(42)	-2082(28)	63(15)
H(26)	-1390(37)	2436(35)	-1954(27)	42(13)
H(27)	-851(35)	3221(39)	-1013(32)	58(14)
H(28)	37(42)	2966(38)	-147(33)	74(16)
H(29)	-1126(35)	2185(35)	-85(29)	47(13)
H(111)	3221(24)	3026(25)	3682(20)	18(10)
H(112)	2893(37)	2718(37)	4726(30)	56(17)
H(113)	4138(43)	2650(39)	4266(34)	60(17)
H(121)	4920(37)	5186(38)	4097(30)	80(15)
H(122)	4326(31)	4293(33)	3347(24)	49(12)

In the form: $U = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$

Table VII. 5a

Bond distances ($\mathring{A}$) and bond angles (^{O}) with the standard deviations in parentheses for $B_5H_9 \cdot (Ph_2P)_2CH_2$ (I) and $B_5H_9 \cdot (Ph_2PCH_2)_2$ (II)

(a) Distances

(i) B_5H_9 moiety

	I	II		I	II
P(1)-B(1)	1.927(9)	1.953(4)	B(2)-H(1)	1.36(8)	1.27(4)
P(2)-B(2)	1.913(10)	1.939(4)	B(3)-H(1)	1.45(7)	1.32(4)
B(1)-B(2)	1.745(13)	1.747(6)	B(2)-H(2)	0.11(9)	1.06(4)
B(1)-B(3)	1.769(14)	1.768(6)	B(3)-H(3)	1.04(6)	1.06(4)
B(1)-B(4)	1.781(15)	1.810(6)	B(3)-H(4)	1.12(9)	1.09(4)
B(1)-B(5)	1.774(14)	1.804(6)	B(4)-H(5)	1.28(7)	1.34(5)
B(2)-B(3)	1.827(14)	1.829(7)	B(5)-H(5)	1.24(7)	1.27(4)
B(4)-B(5)	1.794(16)	1.806(7)	B(4)-H(6)	1.29(8)	1.15(4)
B(2)...B(5)	2.770(15)	2.723(7)	B(4)-H(7)	1.07(8)	1.16(4)
B(3)...B(4)	2.746(16)	2.755(7)	B(5)-H(8)	0.90(10)	1.07(4)
			B(5)-H(9)	1.14(11)	1.12(4)

(ii) Ligand

	I	II		I	II
P(1)-C(1)	1.825(7)	1.841(4)	C(25)-C(26)	-	1.525(5)
P(1)-C(7)	1.826(8)	1.834(4)	C(25)-H(251)	0.94	0.92(3)
P(2)-C(13)	1.821(7)	1.824(4)	C(25)-H(252)	0.96	0.99(4)
P(2)-C(19)	1.811(8)	1.812(4)	C(26)-H(261)	-	0.95(3)
P(1)-C(25)	1.827(8)	1.853(4)	C(26)-H(262)	-	0.95(4)
P(2)-C(25)	1.809(8)	-			
P(2)-C(26)	-	1.827(4)			

(iii) Phenyl rings   I $B_5H_9 \cdot$ dppm

	Ring 1			Ring 2
C(1)-C(2)	1.384(13)		C(7)-C(8)	1.389(12)
C(2)-C(3)	1.398(14)		C(8)-C(9)	1.397(14)
C(3)-C(4)	1.381(16)		C(9)-C(10)	1.378(16)
C(4)-C(5)	1.358(17)		C(10)-C(11)	1.340(17)
C(5)-C(6)	1.390(14)		C(11)-C(12)	1.403(13)
C(6)-C(1)	1.367(12)		C(12)-C(7)	1.362(12)

Table VII.5a (cont.)

Ring 3		Ring 4	
C(13)-C(14)	1.378(13)	C(19)-C(20)	1.404(12)
C(14)-C(15)	1.406(13)	C(20)-C(21)	1.408(15)
C(15)-C(16)	1.347(17)	C(21)-C(22)	1.326(18)
C(16)-C(17)	1.346(17)	C(22)-C(23)	1.377(14)
C(17)-C(18)	1.402(14)	C(23)-C(24)	1.383(13)
C(18)-C(13)	1.346(13)	C(24)-C(19)	1.332(13)

II $B_5H_9 \cdot$ dppe

Ring 1		Ring 2	
C(1)-C(2)	1.399(5)	C(7)-C(8)	1.399(6)
C(2)-C(3)	1.384(6)	C(8)-C(9)-	1.394(6)
C(3)-C(4)	1.392(7)	C(9)-C(10)	1.377(8)
C(4)-C(5)	1.366(7)	C(10)-C(11)	1.346(8)
C(5)-C(6)	1.396(6)	C(11)-C(12)	1.407(6)
C(6)-C(1)	1.397(5)	C(12)-C(7)	1.386(6)

Ring 3		Ring 4	
C(13)-C(14)	1.392(5)	C(19)-C(20)	1.374(6)
C(14)-C(15)	1.387(6)	C(20)-C(21)	1.390(5)
C(15)-C(16)	1.374(6)	C(21)-C(22)	1.372(6)
C(16)-C(17)	1.368(6)	C(22)-C(23)	1.376(7)
C(17)-C(18)	1.388(6)	C(23)-C(24)	1.380(6)
C(18)-C(13)	1.395(6)	C(24)-C(19)	1.402(5)

(b)   Angles

(i) B_5H_9 moiety

	I	II
P(1)-B(1)-B(2)	107.7(6)	117.2(3)
P(1)-B(1)-B(3)	107.9(6)	113.7(3)
P(1)-B(1)-B(4)	112.4(6)	107.8(3)
P(1)-B(1)-B(5)	116.1(6)	112.2(3)
P(2)-B(2)-B(1)	107.4(6)	115.9(3)
P(2)-B(2)-B(3)	116.4(6)	113.7(3)
B(2)-B(1)-B(3)	62.6(6)	62.7(3)
B(4)-B(1)-B(5)	60.6(6)	60.0(3)

Table VII.5a (cont.)

B(2)-B(1)-B(5)	103.8(7)	100.1(3)
B(3)-B(1)-B(4)	101.3(7)	100.6(3)
B(2)-B(1)-B(4)	139.7(8)	135.0(3)
B(3)-B(1)-B(5)	136.0(8)	133.8(3)
B(1)-B(2)-B(3)	59.3(5)	59.2(3)
B(1)-B(3)-B(2)	58.0(5)	58.1(3)
B(1)-B(4)-B(5)	59.5(6)	59.9(3)
B(1)-B(5)-B(4)	59.9(6)	60.2(3)
P(2)-B(2)-H(1)	89.9(30)	98.0(17)
P(2)-B(2)-H(2)	118.5(54)	112.4(19)
B(1)-B(2)-H(1)	108.8(30)	105.3(17)
B(1)-B(2)-H(2)	117.2(52)	121.1(20)
B(3)-B(2)-H(1)	51.5(30)	46.2(17)
B(3)-B(2)-H(2)	122.0(55)	125.0(19)
H(1)-B(2)-H(2)	111.5(62)	99.3(26)
B(1)-B(3)-H(1)	103.6(30)	101.8(16)
B(1)-B(3)-H(3)	116.3(34)	116.6(24)
B(1)-B(3)-H(4)	117.0(44)	119.8(22)
B(2)-B(3)-H(1)	47.4(30)	43.9(16)
B(2)-B(3)-H(3)	116.6(34)	115.9(23)
B(2)-B(3)-H(4)	117.4(43)	120.4(22)
H(1)-B(3)-H(3)	86.4(44)	100.9(28)
H(1)-B(3)-H(4)	109.4(50)	97.3(27)
H(3)-B(3)-H(4)	117.9(56)	114.6(32)
B(2)-H(1)-B(3)	81.1(38)	89.9(23)
B(1)-B(4)-H(5)	102.9(32)	103.1(19)
B(1)-B(4)-H(6)	113.3(34)	116.5(19)
B(1)-B(4)-H(7)	114.0(41)	112.4(20)
B(5)-B(4)-H(5)	43.6(32)	44.6(19)

Table VII.5a (cont.)

B(5)-B(4)-H(6)	128.3(35)	115.2(19)
B(5)-B(4)-H(7)	114.5(42)	125.7(20)
H(5)-B(4)-H(6)	109.5(47)	106.7(27)
H(5)-B(4)-H(7)	101.7(53)	101.1(27)
H(6)-B(4)-H(7)	114.1(53)	114.8(28)
B(1)-B(5)-H(5)	105.3(34)	106.5(21)
B(1)-B(5)-H(8)	117.5(64)	118.9(20)
B(1)-B(5)-H(9)	114.3(54)	113.5(20)
B(4)-B(5)-H(5)	45.6(33)	47.8(21)
B(4)-B(5)-H(8)	139.8(61)	114.3(20)
B(4)-B(5)-H(9)	108.9(55)	128.4(19)
H(5)-B(5)-H(8)	115.3(70)	102.6(28)
H(5)-B(5)-H(9)	94.9(62)	100.8(28)
H(8)-B(5)-H(9)	107.6(83)	112.0(28)
B(4)-H(5)-B(5)	90.9(46)	87.7(28)

(ii) **Ligand**

B(1)-P(1)-C(1)	117.1(4)	117.4(2)
B(1)-P(1)-C(7)	119.4(4)	113.9(2)
B(1)-P(1)-C(25)	104.1(4)	114.9(2)
C(1)-P(1)-C(7)	103.8(3)	103.1(2)
C(1)-P(1)-C(25)	107.9(4)	101.4(2)
C(7)-P(1)-C(25)	103.2(4)	104.2(2)
B(2)-P(2)-C(13)	112.6(4)	112.3(2)
B(2)-P(2)-C(19)	118.2(4)	113.5(2)
B(2)-P(2)-C(25)	103.5(4)	-
B(2)-P(2)-C(26)	-	111.0(2)
C(13)-P(2)-C(19)	106.6(4)	108.3(2)
C(13)-P(2) C(25)	109.0(4)	-
C(13)-P(2)-C(26)	-	107.4(2)

Table VII.5a (cont.)

C(19)-P(2)-C(25)	106.5(4)	-
C(19)-P(2)-C(26)	-	103.9(2)
P(1)-C(1)-C(2)	116.1(6)	119.3(3)
P(1)-C(1)-C(6)	123.9(6)	121.9(3)
P(1)-C(7)-C(8)	119.2(6)	118.3(3)
P(1)-C(7)-C(12)	120.4(6)	123.7(3)
P(2)-C(13)-C(14)	119.2(7)	122.2(3)
P(2)-C(13)-C(18)	120.3(7)	118.6(3)
P(2)-C(19)-C(20)	116.3(7)	119.7(3)
P(2)-C(19)-C(24)	123.7(6)	121.1(3)
P(1)-C(25)-P(2)	106.8(4)	-
P(1)-C(25)-C(26)	-	115.0(2)
P(2)-C(26)-C(25)	-	110.9(3)
P(1)-C(25)-H(251)	110.2	108.8(20)
P(1)-C(25)-H(252)	109.4	107.6(21)
P(2)-C(25)-H(251)	111.2	-
P(2)-C(25)-H(252)	110.2	-
H(251)-C(25)-H(252)	108.9	110.1(29)
P(2)-C(26)-H(261)	-	108.4(19)
P(2)-C(26)-H(262)	-	107.6(22)
C(26)-C(25)-H(251)	-	102.8(20)
C(26)-C(25)-H(252)	-	112.4(21)
C(25)-C(26)-H(261)	-	114.3(19)
C(25)-C(26)-H(262)	-	109.5(22)
H(261)-C(26)-H(262)	-	105.8(30)

Table VII.5a (cont.)

(iii) Phenyl rings

(I) $B_5H_9 \cdot dppm$

Ring 1		Ring 2	
C(6)-C(1)-C(2)	120.0(8)	C(12)-C(7)-C(8)	120.4(8)
C(1)-C(2)-C(3)	121.4(9)	C(7)-C(8)-C(9)	119.3(9)
C(2)-C(3)-C(4)	117.7(10)	C(8)-C(9)-C(10)	119.0(10)
C(3)-C(4)-C(5)	120.6(9)	C(9)-C(10)-C(11)	121.7(9)
C(4)-C(5)-C(6)	121.9(10)	C(10)-C(11)-C(12)	119.8(10)
C(5)-C(6)-C(1)	118.5(9)	C(11)-C(12)-C(7)	119.8(9)
Ring 3		Ring 4	
C(18)-C(13)-C(14)	120.5(8)	C(24)-C(19)-C(20)	120.0(8)
C(13)-C(14)-C(15)	118.3(9)	C(19)-C(20)-C(21)	116.7(10)
C(14)-C(15)-C(16)	120.1(10)	C(20)-C(21)-C(22)	122.3(10)
C(15)-C(16)-C(17)	121.6(9)	C(21)-C(22)-C(23)	120.0(10)
C(16)-C(17)-C(18)	118.8(11)	C(22)-C(23)-C(24)	118.7(9)
C(17)-C(18)-C(13)	120.6(9)	C(23)-C(24)-C(19)	122.1(8)

(II) $B_5H_9 \cdot dppe$

Ring 1		Ring 2	
C(6)-C(1)-C(2)	118.5(3)	C(12)-C(7)-C(8)	117.9(4)
C(1)-C(2)-C(3)	120.7(4)	C(7)-C(8)-C(9)	120.5(4)
C(2)-C(3)-C(4)	119.7(4)	C(8)-C(9)-C(10)	120.6(5)
C(3)-C(4)-C(5)	120.5(4)	C(9)-C(10)-C(11)	119.3(4)
C(4)-C(5)-C(6)	120.1(4)	C(10)-C(11)-C(12)	121.5(5)
C(5)-C(6)-C(1)	120.5(4)	C(11)-C(12)-C(7)	120.1(4)
Ring 3		Ring 4	
C(18)-C(13)-C(14)	119.1(4)	C(24)-C(19)-C(20)	118.8(3)
C(13)-C(14)-C(15)	120.4(4)	C(19)-C(20)-C(21)	120.5(4)
C(14)-C(15)-C(16)	119.8(4)	C(20)-C(21)-C(22)	120.4(4)
C(15)-C(16)-C(17)	120.4(4)	C(21)-C(22)-C(23)	119.7(4)
V(16)-C(17)-C(18)	120.7(4)	C(22)-C(23)-C(24)	120.4(4)
C(17)-C(18)-C(18)	119.6(4)	C(23)-C(24)-C(19)	120.1(4)

TABLE VII.5b

Bond distances (Å) and bond angles ($^\circ$) with standard deviations in parentheses for $B_5H_9 \cdot$ tmed

(a) **Distances**

(i) B_5H_9 moiety

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
N(11)-B(12)	1.677(7)	1.689(7)	B(1)-H(1)	1.111(45)	1.033(46)
N(2)-B(2)	1.651(7)	16.73(7)	B(2)-H(2)	1.071(33)	1.102(40)
B(1)-B(2)	1.700(9)	1.697(8)	B(3)-H(3)	1.003(59)	1.109(39)
B(1)-B(3)	1.804(10)	1.824(10)	B(3)-H(4)	1.192(54)	1.133(42)
B(1)-B(4)	1.701(10)	1.699(10)	B(3)-H(5)	1.418(51)	1.303(53)
B(1)-B(5)	1.825(10)	1.835(10)	B(4)-H(5)	1.271(50)	1.456(51)
B(3)-B(4)	1.723(13)	1.742(11)	B(4)-H(6)	1.026(56)	1.040(47)
B(4)-B(5)	1.778(11)	1.789(11)	B(4)-H(7)	1.264(61)	1.252(49)
B(2)...B(3)	2.720(10)	2.696(10)	B(5)-H(7)	1.272(60)	1.297(49)
B(2)...B(5)	2.726(10)	2.716(9)	B(5)-H(8)	1.038(49)	1.029(52)
B(3)...B(5)	2.830(12)	2.848(11)	B(5)-H(9)	1.301(51)	1.160(45)

(ii) **Ligand**

	Molecule 1		
N(11)-C(11)	1.515(8)	C(13)-H(131)	0.95(5)
N(11)-C(12)	1.488(7)	C(13)-H(132)	1.27(5)
N(11)-C(13)	1.508(8)	C(14)-H(141)	0.99(4)
N(12)-C(14)	1.485(8)	C(14)-H(142)	1.34(6)
N(12)-C(15)	1.494(9)	C(15)-H(151)	0.97(16)
N(12)-C(16)	1.499(8)	C(15)-H(152)	0.94(5)
C(13)-C(14)	1.457(9)	C(15)-H(153)	1.10(5)
C(11)-H(111)	1.06(5)	C(16)-H(161)	0.89(4)
C(11)-H(112)	1.03(5)	C(16)-H(162)	0.84(6)
C(11)-H(113)	0.91(3)	C(16)-H(163)	1.09(5)
C(12)-H(121)	1.06(5)		
C(12)-H(122)	0.97(4)		
C(12)-H(123)	1.19(9)		

TABLE VII.5b   continued

(ii)   Ligand (cont.)

Molecule 2

N(21)-C921a)	1.432(13)	N(21)-C(21b)	1.524(13)
N(21)-C(22a)	1.464(13)	N(21)-C(22b)	1.570(14)
N(21)-C(23a)	1.511(13)	N(21)-C(23b)	1.488(15)
N(22)-C(24a)	1.430(17)	N(22)-C(24b)	1.599(15)
N(22)-C(25a)	1.652(15)	N(22)-C(25b)	1.372(17)
N(22)-C(26a)	1.486(15)	N(22)-C(26b)	1.526(15)
C(23a)-C(24a)	1.596(20)		
C(21a)...C(21b)	0.882(18)	C(23b)-C(24b)	1.471(20)
C(21a)...C(23b)	1.825(17)	C(24a)...C(23b)	1.534(21)
C(22a)...C(21b)	1.919(18)	C(24a)...C(24b)	0.529(22)
C(22a)...C(22b)	0.701(19)	C(25a)...C(25b)	0.526(21)
C(23a)...C(23b)	0.887(19)	C(26a)...C(25b)	1.973(22)
C(23a)...C(24b)	1.247(19)	C(26a)...C(26b)	0.662(21)

(b)   Angles

(i) B_5H_9 moiety

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
N(1)-B(2)-N(2)	97.9(4)	96.3(4)	H(3)-B(3)-H(5)	104.5(37)	91.4(30)
N(1)-B(2)-N(1)	115.0(4)	115.1(4)	H(4)-B(3)-H(5)	103.5(33)	106.8(27)
N(2)-B(2)-B(1)	116.7(4)	115.5(4)	B(1)-B(4)-H(5)	116.3(23)	107.0(20)
B(2)-B(1)-B(3)	101.8(5)	99.9(4)	B(1)-B(4)-H(6)	123.2(25)	118.2(22)
B(2)-B(1)-B(4)	144.7(5)	143.3(5)	B(1)-B(4)-H(7)	105.2(27)	108.2(22)
B(2)-B(1)-B(5)	101.2(4)	100.5(4)	B(3)-B(4)-H(5)	53.8(23)	47.1(20)
B(3)-B(1)-B(4)	58.8(4)	59.1(4)	B(3)-B(4)-H(6)	128.7(25)	126.8(24)
B(3)-B(1)-B(5)	102.5(5)	102.2(5)	B(3)-B(4)-H(7)	115.0(26)	120.1(22)
B(4)-B(1)-B(5)	60.4(4)	60.7(4)	B(5)-B(4)-H(5)	125.3(23)	113.7(18)
B(1)-B(3)-B(4)	57.6(4)	56.9(4)	B(5)-B(4)-H(6)	120.2(25)	120.5(24)
B(1)-B(4)-B(3)	63.6(5)	64.0(4)	B(5)-B(4)-H(7)	45.7(27)	46.5(22)
B(1)-B(4)-B(5)	63.2(4)	63.4(4)	H(5)-B(4)-H(6)	104.9(33)	120.1(30)
B(1)-B(5)-B(4)	56.3(4)	55.9(4)	H(5)-B(4)-H(7)	91.6(36)	89.9(29)
B(3)-B(4)-B(5)	107.9(6)	107.5(5)	H(6)-B(4)-H(7)	111.2(36)	109.4(32)

TABLE VII.5b continued

B(2)-B(1)-H(1)	116.2(23)	114.5(25)
B(3)-B(1)-H(1)	120.3(22)	117.6(23)	B(3)-H(5)-B(4)	79.7(28)	78.1(29)
B(4)-B(1)-H(1)	99.0(23)	102.1(25)
B(5)-B(1)-H(1)	112.4(23)	119.1(24)	B(1)-B(5)-H(7)	98.2(28)	98.9(22)
N(1)-B(2)-H(2)	100.9(17)	105.2(19)	B(1)-B(5)-H(8)	121.1(26)	115.5(30)
N(2)-B(2)-H(2)	102.2(18)	108.0(20)	B(1)-B(5)-H(9)	107.9(21)	121.6(22)
B(1)-B(2)-H(2)	120.7(18)	114.8(20)	B(4)-B(5)-H(7)	45.3(28)	44.4(22)
B(1)-B(3)-H(3)	107.7(28)	103.0(20)	B(4)-B(5)-H(8)	114.6(27)	124.4(28)
B(1)-B(3)-H(4)	125.2(26)	117.7(19)	B(4)-B(5)-H(9)	120.6(20)	117.2(23)
B(1)-B(3)-H(5)	103.3(20)	107.5(21)	H(7)-B(5)-H(8)	109.3(37)	98.3(35)
B(4)-B(3)-H(3)	123.9(30)	120.3(20)	H(7)-B(5)-H(9)	94.4(32)	106.2(30)
B(4)-B(3)-H(4)	121.6(26)	111.2(19)	H(8)-B(5)-H(9)	120.1(33)	111.8(36)
B(4)-B(3)-H(5)	46.5(20)	54.9(22)
H(3)-B(3)-H(4)	110.4(39)	126.2(27)	B(4)-H(7)-B(5)	89.1(39)	89.1(31)

(ii) Ligand

Molecule 1

B(12)-N(11)-C(11)	114.5(4)	H(121)-C(12)-H(123)	112.5(50)
B(12)-N(11)-C(12)	101.1(4)	H(122)-C(12)-H(123)	88.4(48)
B(12)-N(11)-C(13)	107.0(4)	N(11)-C(13)-H(131)	114.0(31)
C(11)-N(11)-C(12)	107.5(4)	N(11)-C(13)-H(132)	97.6(23)
C(11)-N(11)-C(13)	107.8(5)	C(14)-C(13)-H(131)	117.4(32)
C(12)-N(11)-C(13)	111.0(4)	C(14)-C(13)-H(132)	105.2(21)
B(12)-N(12)-C(14)	103.8(4)	H(131)-C(13)-H(132)	113.7(37)
B(12)-N(12)-C(15)	113.5(5)	N(12)-C(14)-H(141)	113.4(20)
B(12)-N(12)-C(16)	110.8(4)	N(12)-C(14)-H(142)	114.8(23)
C(14)-N(12)-C(15)	112.2(5)	C(13)-C(14)-H(141)	114.5(21)
C(14)-N(12)-C(16)	107.6(4)	C(13)-C(14)-H(142)	95.6(23)
C(15)-N(12)-C(16)	108.8(5)	H(141)-C(14)-H(142)	110.6(33)
N(11)-C(13)-C(14)	106.7(5)	N(12)-C(15)-H(151)	114.4(36)
N(12)-C(14)-C(13)	106.7(5)	N(12)-C(15)-H(152)	110.1(30)

TABLE VII.5c continued

(ii) Ligand: Molecule 1 cont.

N(11)-C(11)-H(111)	109.2(21)	N(12)-C(15)-H(153)	102.1(27)
N(11)-C(11)-H(112)	101.8(29)	H(151)-C(15)-H(152)	111.8(48)
N(11)-C(11)-H(113)	107.8(26)	H(151)-C(15)-H(153)	116.5(44)
H(111)-C(11)-H(112)	116.1(33)	H(152)-C(15)-H(153)	100.9(39)
H(111)-C(11)-H(113)	106.7(35)	N(12)-C(16)-H(161)	112.0(27)
H(112)-C(11)-H(113)	114.2(39)	N(12)-C(16)-H(162)	97.7(45)
N(11)-C(12)-H(121)	117.9(26)	N(12)-C(16)-H(163)	107.7(25)
N(11)-C(12)-H(122)	105.4(24)	H(161)-C(16)-H(162)	117.6(51)
N(11)-C(12)-H(123)	104.8(42)	H(161)-C(16)-H(163)	94.4(37)
H(121)-C(12)-H(122)	122.9(35)	H(162)-C(16)-H(163)	127.6(52)

Molecule 2

	Conformation			Conformation	
	a	b		a	b
B(22)-N(21)-C(21)	114.1(5)	114.6(6)	B(22)-N(22)-C(25)	102.9(6)	116.3(8)
B(22)-N(21)-C(21)	111.3(6)	106.4(6)	B(22)-N(22)-C(26)	119.8(6)	110.0(6)
B(22)-N(21)-C(23)	101.0(5)	110.8(6)	C(24)-N(22)-C(25)	112.3(8)	106.7(9)
C(21)-N(21)-C(22)	110.9(7)	105.3(7)	C(24)-N(22)-C(26)	105.4(9)	109.0(8)
C(21)-N(21)-C(23)	111.2(7)	108.4(8)	C(25)-N(22)-C(26)	103.4(8)	111.9(9)
C(22)-N(21)-C(23)	107.8(7)	111.3(8)	N(21)-C(23)-C(24)	104.2(9)	103.5(10)
B(22)-N(22)-C(24)	112.8(7)	102.2(6)	N(22)-C(24)-C(23)	102.6(11)	103.9(10)

C(21a)-N(21)-C(21b)	34.5(7)	C(25a)-N(22)-C(24b)	101.1(7)
C(21a)-N(21)-C(22b)	132.1(7)	C(25a)-N(22)-C(25b)	17.0(8)
C(21a)-N(21)-C(23b)	177.3(7)	C(25a)-N(22)-C(26b)	128.5(8)
C(22a)-N(21)-C(21b)	79.9(7)	C(26a)-N(22)-C(24b)	124.0(8)
C(22a)-N(21)-C(22b)	26.4(7)	C(26a)-N(22)-C(25b)	87.2(9)
C(22a)-N(21)-C(23b)	127.9(8)	C(26a)-N(22)-C(26b)	25.3(8)
C(23a)-N(21)-C(21b)	138.2(7)	N(21)-C(23a)-C(24b)	114.5(11)
C(23a)-N(21)-C(22b)	83.9(7)	N(21)-C(23b)-C(24a)	108.5(11)
C(23a)-N(22)-C(23b)	34.4(7)	N(22)-C(24a)-C(23b)	109.3(12)
C(24a)-N(22)-C(24b)	19.1(8)	N(22)-C(24b)-C(23a)	111.7(11)
C(24a)-N(22)-C(25b)	112.7(10)		
C(24a)-N(22)-C(26b)	90.2(9)		

TABLE VII.6

Equations of the least squares mean planes $PI + QJ + RK = S^{\dagger}$, interplanar angles and some significant atomic displacements from these planes.

(a) $B_5H_9 \cdot dppm$

Plane	Defining atoms	P	Q	R	S
1	B(1) B(2) B(3)	0.9708	-0.0754	-0.2279	6.6940
2	B(1) B(4) B(5)	-0.5084	-0.3378	0.7921	-4.1488
3	B(1) B(2) B(5)	0.7268	0.6508	-0.2199	10.4894
4	B(1) B(3) B(4)	-0.6020	0.3866	0.6987	0.5307
5	B(2) B(3) B(4) B(5)	-0.8123	-0.1486	0.5639	-6-6117
6	P(1) P(2) B(1) B(2)	-0.2311	0.9687	-0.0907	5.5597
7	C(1 - 6)	-0.6649	0.4496	0.5965	1.7744
8	C(7 - 12)	0.4995	-0.4586	0.7350	3.1659
9	C(13 - 18)	-0.2955	-0.0028	0.9553	-0.2077
10	C(19 - 24)	0.3640	0.9107	0.1954	9.2242

Lines

11. P(1)-C(1) 12. P(1) - C(7) 13. P(2) - C(13) 14. P(2) - C(19)

Angles (^{o}) between planes or lines:-

(1) - (2) 130.43 (2) - (3) 40.23 (3) - (5) 35.80 (7) - (8) 84.27

(1) - (3) 45.05 (2)- (4) 43.21 (3) - (6) 61.16 (9) - (10) 85.61

(1) - (4) 39.40 (2) - (5) 24.51 (4) - (5) 34.35 (7) - (11) 0.31

(1) - (5) 25.06 (2) - (6) 73.64 (4) - (6) 63.24 (8) - (12) 1.59

(1) - (6) 73.94 (3) - (4) 109.85 (5) - (6) 89.58 (9) - (13) 0.75

(10) - (14) 0.35

Significant atomic displacements from plane above:-

Plane 5:	B(1) by 0.635 $\mathring{A}$	Plane 7:	P(1) by -0.022 $\mathring{A}$
	P(1) by 1.532 $\mathring{A}$	Plane 8:	P(1) by -0.059 $\mathring{A}$
	P(2) by 2.902 $\mathring{A}$	Plane 9:	P(2) by -0.027 $\mathring{A}$
Plane 6:	C(25) by 0·556 $\mathring{A}$	Plane 10:	P(2) by 0.001 $\mathring{A}$

(b) $B_5H_9 \cdot dppe$

Plane	Defining atoms	P	Q	R	S
1	B(1) B(2) B(3)	0.7692	-0.3426	0.4988	8.9581
2	B(1) B(4) B(5)	0.3873	0.3854	0.8375	8.8858
3	B(1) B(2) B(5)	0.8734	0.3978	0.2809	7.5339
4	B(1) B(3) B(4)	0.1678	-0.3462	0.9230	8.3836
5	B(2) B(3) B(4) B(5)	0.6551	0.0295	0.7550	10.6862
6	P(1) P(2) B(1) B(2)	0.2443	0.9456	-0.2149	-0.4200
7	C(1) - C(6)	-0.6943	0.6251	0.3567	-1.6957
8	C(7) - C(12)	0.3965	-0.3198	0.8606	7.3501
9	C(13) - C(18)	0.7537	0.5299	-0.3888	-0.5953
10	C(19) - C(24)	0.0867	-0.0121	0.9962	9.7295

Lines

11.   P(1) - C(1)   12.   P(1) - C(7)   13.   P(2) - C(13)   14.   P(2) - C(19)

Angles (^{o}) between planes or lines:-

(1) - (2)	126.45	(2) - (3)	43.38	(3) - (5)	37.25	(7) - (8)	80.32
(1) - (3)	45.64	(2) - (4)	45.20	(3) - (6)	58.05	(9) -(10)	70.83
(1) - (4)	44.55	(2) - (5)	26.18	(4) - (5)	37.19	(7) - (11)	6.65
(1) - (5)	27.38	(2) - (6)	73.79	(4) - (6)	61.01	(8) - (12)	4.86
(1) - (6)	76.31	(3) - (4)	105.55	(5) - (6)	88.52	(9) - (13)	3.19

(10) - (14)   5.67^o

Significant atomic displacements from planes above:-

Plane 5:	B(1) by -0.690 Å	Plane 7:	P(1) by 0.221 Å
	P(1) by -2.637 Å	Plane 8:	P(1) by 0.168 Å
	P(2) by -1.287 Å	Plane 9:	P(2) by 0.104 Å
Plane 6:	C(25) by 0.050 Å	Plane 10:	P(2) by -0.180 Å
	C(26) by 0.829 Å		

(c) $B_5H_9 \cdot$ tmed

No.	Defining atoms	P	Q	R	S
1	N(1) B(2) N(2)	0.4706	0.8542	-0.2212	5.2767
		[0.7605	0.5120	0.3994	1.7711]
2	B(1) B(2) B(4)	-0.3369	0.3681	0.8666	7.5010
		[-0.4271	-0.0551	0.9025	-2.0874]
3	B(1) B(3) B(4)	0.7178	0.5273	-0.4546	1.9746
		[0.3569	0.5908	0.7236	-0.1147]
4	B(1) B(4) B(5)	0.4380	0.8524	0.2858	8.4696
		[0.7492	0.6601	0.0544	1.7385]
5	B(1) B(3) B(5)	0.1023	0.9294	-0.3548	0.9840
		[0.8866	0.1263	0.4449	-0.4554]
6	B(2) B(3) B(4)	0.8779	0.4437	-0.1801	5.5679
		[0.2409	0.8251	0.5111	1.3299]
7	B(2) B(4) B(5)	0.7017	0.6495	0.2928	9.7291
		[0.4859	0.8739	0.0155	2.5307]
8	B(3) B(4) B(5)	0.9390	0.2395	0.2467	9.6423
		[0.0286	0.9937	0.1083	3.1152]

Angles (^{o}) between planes:-

(1)-(2) 87.9[89.6] (2)-(7) 75.1[76.0] (3)-(8) 46.5[47.5] (5)-(7) 55.1[56.8]

(2)-(3) 63.8[62.1] (2)-(8) 89.2[88.2] (4)-(5) 42.6[43.7] (5)-(8) 76.6[78.5]

(2)-(4) 65.6[66.1] (3)-(4)129.3[128.2] (4)-(7) 19.2[19.9] (6)-(7)148.4[147.8]

(2)-(5) 90.0[89.1] (3)-(5) 43.6[44.5] (4)-(8) 46.7[47.8] (6)-(8) 27.6[28.1]

(2)-(6) 73.2[71.8] (3)-(6) 18.9[19.4] (5)-(6) 55.5[57.0] (7)-(8) 27.5[27.9]

Significant atomic displacements from planes above:-

Plane 1: C(3) 0.18 Å [a, 0.85;b, 0.02 Å] Plane 2: B(3) 1.38Å[-1.38Å]

          C(4) 0.71 Å[a, 0.23;b, 0.70 Å]   B(5) -1.45 Å[1.46 Å]

Plane 2: N(1) -1.26 Å [-1.28 Å]   Plane 5: B(2) 1.61Å[1.63Å]

          N(2) 1.26 Å [1.23 Å]   B(4) -1.00Å[-1.02Å]

          C(3) -0.63Å[a, -0.69;b, -0.77Å]Plane 8: B(1) -1.11Å[-1.13Å]

          C(4) 0.69 Å[a, 0.75;b, 0.53 Å]   B(2) -1.26Å[-1.27Å]

† With the orthogonal unit vector I parallel to $\underline{a}$, K perpendicular to

$\underline{a}$ in the $\underline{ac}$ plane and J perpendicular to the $\underline{ac}$ plane.

TABLE VII.7

Torsion angles * in the Chelate Rings (^{o})

(a) $B_5H_9 \cdot$ dppm

P(1)-C(25)-P(2)-B(2)	+32.98
C(25)-P(2)-B(2)-B(1)	-26.23
P(2)-B(2)-B(1)-P(1)	-9.46
B(2)-B(1)-P(1)-C(25)	-10.51
B(1)-P(1)-C(25)-P(2)	+27.42

(b) $B_5H_9 \cdot$ dppe

P(1)-C(25)-C(26)-P(2)	-66.10
C(25)-C(26)-P(2)-B(2)	+64.74
C(26)-P(2)-B(2)-B(1)	-28.48
P(2)-B(2)-B(1)-P(1)	-0.76
B(2)-B(1)-P(1)-C(25)	-2.34
B(1)-P(1)-C(25)-C(26)	+56.70

(c) $B_5H_9 \cdot$ tmed   Molecule 1

B(2)-N(1)-C(3)-C(4)	-17.82
N(1)-C(3)-C(4)-N(2)	-39.28
C(3)-C(4)-N(2)-B(2)	+43.82
C(4)-N(2)-B(2)-N(1)	-29.42
N(2)-B(2)-N(1)-C(3)	+7.34

Molecule 2

B(2)-N(1)-C(3a)-C(4a)	-48.56	C(3a)-C(4a)-N(2)-B(2)	-17.50
B(2)-N(1)-C(3a)-C(4b)	-35.32	C(3a)-C(4b)-N(2)-B(2)	+9.28
B(2)-N(1)-C(3b)-C(4a)	.+8.12	C(3b)-C(4a)-N(2)-B(2)	+15.99
B(2)-N(1)-C(3b)-C(4b)	+28.42	C(3b)-C(4b)-N(2)-B(2)	+47.28
N(1)-C(3a)-C(4a)-N(2)	+42.46	C(4a)-N(2)-B(2)-N(1)	-10.11
N(1)-C(3a)-C(4b)-N(2)	+17.04	C(4b)-N(2)-B(2)-N(1)	-26.79
N(1)-C(3b)-C(4a)-N(2)	-14.98	N(2)-B(2)-N(1)-C(3a)	+34.97
N(1)-C(3b)-C(4b)-N(2)	-46.75	N(2)-B(2)-N(1)-C(3b)	+0.63

* Defined as in R. Bucourt, Topics Stereochem., 1974, 8, 159.

TABLE VII.8

Atomic co-ordinates (x 10^3), bond distances (Å) and bond angles (^{o}) for the disordered tetrahydrofuran solvent in compound (1)[†]. The estimated standard deviations in these measurements are shown beneath each section.

Atomic Co-ordinates

Atom	$\underline{X}$	$\underline{Y}$	$\underline{Z}$
C(261)	495	289	457
C(271)	398	229	425
C(281)	347	274	374
C(291)	450	347	379
C(301)	463	363	439
C(262)	494	233	439
C(272)	371	251	393
C(282)	356	334	378
C(292)	458	361	413
C(302)	523	326	448

Estimated standard deviation:	± 10	± 5	± 4

Bond distances and angles

(a) Distances (Å)

C(261)-C(271)	1.46	C(262)-C(272)	1.48
C(271)-C(281)	1.47	C(272)-C(282)	1.44
C(281)-C(291)	1.47	C(282)-C(292)	1.23
C(291)-C(301)	1.41	C(292)-C(302)	1.11
C(301)-C(261)	1.34	C(302)-C(262)	1.60
C(261)-C(262)	1.02	C(291)-C(282)	0.77
C(261)-C(302)	0.70	C(291)-C(292)	0.83
C(271)-C(262)	0.83	C(301)-C(292)	0.59
C(271)-C(272)	0.86	C(301)-C(302)	0.80
C(281)-C(272)	0.62		
C(281)-C(282)	1.01		

(b) <u>Angles</u> (^{o})

C(301)-C(261)-C(271)	112	C(302)-C(262)-C(272)	89
C(261)-C(271)-C(281)	102	C(262)-C(272)-C(282)	115
C(271)-C(281)-C(291)	102	C(272)-C(282)-C(292)	98
C(281)-C(291)-C(301)	106	C(282)-C(292)-C(302)	127
C(291)-C(301)-C(261)	98	C(292)-C(302)-C(262)	110
C(302)-C(261)-C(262)	136	C(261)-C(262)-C(271)	103
C(262)-C(271)-C(272)	123	C(271)-C(272)-C(281)	167
C(272)-C(281)-C(282)	121	C(281)-C(282)-C(291)	110
C(282)-C(291)-C(292)	101	C(291)-C(292)-C(301)	167
C(292)-C(301)-C(302)	105	C(301)-C(3os)-C(261)	126

† The estimated standard deviations in the bond distances and angles quoted
are $\approx \pm 0.10$ Å and $\pm 10^{o}$ respectively.

†† Numbering of the atoms in the disordered solvent is:-
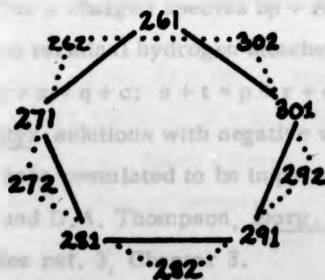
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11. For a charged species $BpHp^c + q + c$, the equations become $s + x = q + c$; $s + t = p + c$; $t + y = p - c - q/2$.

12. For a charged species $Bp + rHp^c + q + c$ in which r boron atoms have no terminal hydrogen attached, the equations become
$s + x = q + c$; $s + t = p + r + c$; $s + r = 2y + 3c + x$

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CHAPTER VIII

Crystallographic Methods

(VIII.1.)   X-Ray Diffraction

The basis of X-ray crystallography is the property of a crystal, whose internal dimensions are of the same order of magnitude as the wavelength of X-rays, to act as a three dimensional diffraction grating for X-rays. The data collected are the intensities of an X-ray beam which is diffracted only when the crystal is at particular orientations to the incident beam.   The pattern of these diffracted intensities depends on the distribution of electron density within the crystal and, of course, electron density is concentrated around the atomic nuclei and its maxima will indicate atomic positions.   It is, however, the square root of the intensity, the structure factor with which the crystallographer works. These structure factors can be expressed as a series of Fourier coefficients, and related to the pattern of electron density within the crystal as explained later.   There is one major problem in this procedure.   Whilst the experimental intensity of each reflection can be directly measured and reduced to a structure factor, there is at present no method available to directly measure the phase angle associated with each reflection.   It is this loss of phase information - the phase problem - which is central to all the different methods used in crystallographic studies.

Much has been written about the general background and mathematical principles involved in X-ray crystallography.[1]   In the following paragraphs a few of the most important principles and equations used throughout the present work are summarised.

(VIII.2.)   Structure Determination

The course of a single structure determination consists of the following main stages:

(a)   Collecting and processing of the raw X-ray data, the experimental intensity measurements, to give structure factors, F(hkl), which are proportional to the square root of the measured intensities.

(b)   Solving the phase problem, usually by statistical methods or interpretation of the Patterson function.   This latter is a Fourier summation performed with intensity rather than $\sqrt{\text{intensity}}$ as coefficients, and it reveals all the vectors between atoms in the structure, a peak being approximately of height $Z_1 * Z_2$, where Z_1 and Z_2 are the atomic numbers of the two atoms.   This means that vectors associated with a heavy atom normally dominate the map.

(c)   A Fourier inversion of the phased F(hkl) values (a complex number) to yield an electron density map of the structure in which atoms can be identified.

(d)   Least squares or further Fourier refinement to find the atomic positions which give best agreement between the observed and calculated data.

(e)   Calculation of derived parameters, that is bond lengths, bond angles and conformations, together with the assignment of their chemical importance and explanation of other physical and chemical properties of the substance.

During each determination there are, therefore, a large number of computations involved.   Most of these are of the number crunching variety, and efficient programs are essential.   The majority of the structures described in this thesis have been solved using the X-RAY suite of crystallographic programs[2] and the details relating to each of the steps enumerated above are discussed with particular reference to individual program links of that system.

(VIII.3.)   Data Collection

In the first step the amount of data collected for each crystal is large; typically 2000 to 5000 diffracted intensities for a structure of moderate size.   The actual quantity depends on the symmetry and volume of the unit cell.   Each diffracted intensity is a function of both the number of electrons involved and the distribution of atoms in the plane of the crystal which is in position to diffract according to Bragg's law.   Whilst the maximum amount of data (number of planes) is finite but exceedingly large, and the accuracy of derived parameters can be related to the size of the data set collected, practical considerations normally limit the amount of data collected.   All data

sets for the compounds discussed were collected using a Syntex $P2_1$ four circle diffractometer by the use of graphite monochromatised radiation.[3] The diffractometer is controlled on-line by a Data General Nova computer and all data is recorded on 7-track magnetic tape before processing to paper tape and/or disk files on the computer.

A distinct advantage with the Syntex $P2_1$ is the ability to work with a randomly orientated crystal. Once the crystal has been centred, so that it is rotating about an arbitrary axis, a φ rotation photograph is taken. From this photograph the co-ordinates of several (max.15) reflections are accurately centred. In the centring process the 2θ and χ angles are calculated for each reflection and, with ω assumed to be zero, the φ circle is rotated at low speed until a reflection with an intensity greater than a specified default is encountered. The program will then home in on the refined angular co-ordinates until consecutive refinements give angles within specified tolerances. In each refinement step the angles are refined in the order, first ω, then 2θ, ω again and then χ. If default parameters are used, each iteration will scan at $\sim 5^{\circ}/$min in ω over a maximum range of $\pm 1^{\circ}$, recording the position of the half-height peak intensity, then at $\sim 5^{\circ}/$min in $2\theta \pm 2^{\circ}$, again at $\sim 5^{\circ}/$min in $\omega \pm 1^{\circ}$ and finally at $30^{\circ}/$min in $\chi \pm 20^{\circ}$. Normally φ is held fixed (but would be scanned at $\sim 5^{\circ}/$min if refined). At the end of each iteration 2θ, ω, φ, χ and the peak intensity are printed. The procedure is the same for refining approximate angular values except the preliminary ω scan can sometimes be omitted, and for the weaker higher angle reflections it is necessary to slow the scan speeds in the refinement to a half or a quarter of their normal values.

Once all the reflections have been refined, their refined angular co-ordinates are used to generate sets of possible axial vectors which would give integer ± 0.1 values for all the hkl indices of the refined reflections. This program can be used a priori for determining the unit cell although it is better to have some form of photographic confirmation. The choice of the best axial vectors is based on axial lengths and the cosine of the inter-vector angles. In an a priori

situation where no preliminary precession or Weissenberg photographs
have been taken, it is essential to take axial photographs about the
chosen axial vectors from which the spacing of the layer lines will
give approximate axial lengths and the presence or absence of mirror
symmetry about the horizontal line in the photograph indicates the
presence or absence of a symmetry axis.[4] Any spots lying off layer
lines probably indicate twinning or the presence of satellite subcrystals.
Thus, if the auto-indexing shows three vectors with their inter-vector
cosines zero, then this solution would require mirror symmetry to be
found in all three axial photographs before the unit cell could be
accepted as being orthorhombic or of higher symmetry. The choice
of Laue and space group symmetries can similarly be found by
performing rapid data collections over specified reflections (see below).[4]

From the chosen set of axial vectors, the auto-indexing program
assigns indices to all reflections in the reflection array and calculates
a unit cell volume. If negative, the choice of axes has given a left
handed cell. Interchange of two axes or making one axis negative will
solve this problem. Similar interchanges are necessary in the tri-
clinic and monoclinic cases to give the correct cell with angles $> 90^{o}$.
For any triclinic cell it is necessary to reduce it to its most primitive
form, a process named after Delauney.

From the assigned indices and the refined values of $2\theta, \omega$, φ and χ
an orientation matrix relating the crystal unit cell to the diffractometer
reference axes can be determined by least squares methods. This
orientation matrix can then be used to reverse the process and
calculate the angles with (1) φ held constant and (2) ω constrained to
be $\frac{1}{2}(2\theta)$. Finally the indices of each reflection are calculated from
the orientation matrix and the observed angles. The least squares
refined unit cell parameters are also printed along with a measure of
the standard deviation in each value. Although in the calculation of
the unit cell parameters from the refined angular co-ordinates the
crystal system is always treated as if it was triclinic, it is found that,
providing the crystal is well centred, the calculated unit cell

parameters are normally within three standard deviation (typically 0.02^O) of the crystallographically correct values.[5] Such differences are considered insignificant and in subsequent programs mean axial lengths and/or angles of 90°, 120°, etc. where appropriate to the lattice symmetry are used.[4] In the data collection, the values calculated do allow for instrumental and other alignment errors.

The accuracy of the orientation matrix can be improved by centring (at slow speeds if necessary) on up to 15 higher angle (2θ) reflections determined either from previous photographs or else by collecting a shell of data at higher scan speeds. It is good practice to avoid axial reflections and ensure all regions of reciprocal space are investigated.

Once a satisfactory orientation matrix has been obtained, the data collection can proceed. The conditions associated with the collection of each data set are listed in the individual chapters. However, data sets were normally collected using the $2\theta : \theta$ method in which both the counter (2θ circle) and crystal (ω circle) are rotated at relative angular rates given by

$$\Delta 2\theta = 2 \Delta \omega$$

In the course of a data collection the data are collected out to a maximum practical 2θ (in shells if required), each peak being scanned over a specified range above and below the α_1 and α_2 peaks. The scan speed over the peak depends on the intensity of a preliminary count. The count rates for collection at the extreme speeds are pre-set by the user, and intermediate speeds are determined by the program. A coincidence correction is applied automatically to particularly intense reflections with a number of counts exceeding 12,000 cps. Backgrounds for each reflection are measured for a specified amount (normally, a quarter on each side) of the time taken to measure each peak.

Several standard reflections at various 2θ values are remeasured at regular intervals to check for variations in intensity due to decomposition or crystal movement (corrected by re-centring the crystal at intervals or after a specified drop in the intensity of the standards).

Generally, the intensities of the standard reflections will show only statistical fluctuations due to small variations in temperature and in the intensity of the incident beam. These fluctuations will be in opposite directions, preventing any valid corrections. This procedure is different from that used by some crystallographers who scale individual measurements of a single standard to a common value.

However, when there is a significant drop in the intensities of the standards due to decomposition, the effects of this decomposition can be reduced by scaling the intensities or more particularly the calculated structure factors, using a scaling equation of the form

$$F_{corr} = F_{calc} * (1 + \alpha * t)(1 + \beta * t * \sin \theta/\lambda) \qquad (1)$$

where F_{corr} = corrected structure factor.

F_{calc} = structure factor calculated from the observed intensity for that reflection collected at time t (hrs) and at a particular $\sin \theta/\lambda$.[6]

The co-efficients α and β in the above equation are determined by plotting the values of F_{calc} for each standard against the times of measurement. Assuming this graph shows a linear decay for the whole data on a particular standard, then a second graph of F_{t_1}/F_{t_2} ($t_1 < t_2$) against $\sin \theta/\lambda$ is plotted for all of the standards. The gradients of the second graph give two values of the F_{t_1}/F_{t_2} ratio at two values of $(\sin \theta)/\lambda = 0$ and $(\sin \theta)/\lambda = x$ from which α and β are calculated from

$$\alpha = \left[1 - (F_{t_1}/F_{t_2} \text{ at } (\sin \theta)/\lambda = 0)\right] \div \text{Exposure time} \qquad (2)$$

$$\beta = \left[1 - \frac{(F_{t_1}/F_{t_2} \text{ at } (\sin \theta)/\lambda = x)}{(F_{t_1}/F_{t_2} \text{ at } (\sin \theta)/\lambda = 0}\right] \div \frac{}{[\text{Exposure time}] * x} \qquad (3)$$

This correction is applied after the observed intensities have been reduced to structure factors F_{hkl} using the program SYNDAT.[7] The relationship between F_{hkl} and intensity I is given in equation (4).

$$F_{hkl} = \sqrt{\frac{KI_{hkl}}{Lp}} \qquad (4)$$

where p, the polarisation factor is a simple function of 2θ given by

$$p = \frac{1 + \cos^2 2\theta}{2} \qquad (5)$$

and the Lorentz factor L for the diffractometer is given by

$$L = \frac{1}{\sin 2\theta} \qquad (6)$$

In fact, for the present monochromater geometry the parallel vector of the incident radiation is affected more than the perpendicular vector so that the actual polarisation factor used is

$$p = \frac{1 + \cos^2 2\theta_m \cos^2 2\theta}{2(1 + \cos^2 2\theta_m)} \qquad (7)$$

where $\cos 2\theta_m = (1.0 - 0.44447\lambda^2)$ $\qquad (8)$

λ = wavelength of incident radiation.

The program SYNDAT applies these factors, corrects any affects of crystal decay, and finally prints out a list of h, k, l, F and $\sigma(F)$ values. Normally a reflection is considered observed if $I/\sigma(I) \geq 3.0$ $(F/\sigma(F) \geq 6.0)$.[8a] The program also flags any reflections with $B_l - B_r > 3\sqrt{B_l + B_r}$ (B_l and B_r are the left and right backgrounds of each reflection) as faulty but does not exclude them.[7, 8b]

Whilst the calculated structure factors F_{hkl} are associated with real atoms and hence are dependent on atomic scattering factors which fall off as a function of $\sin\theta$,[4] it is necessary in direct methods and in some Patterson methods to use structure factors which do not have any $\sin\theta$ dependence. These, the normalised structure factors E_{hkl}'s, are associated with ideal point atoms and can be calculated from equation (9)

$$|E_{hkl}|^2 = \frac{|F_{hkl}|^2_{abs}}{\epsilon \sum_{j=1}^{N} f_j^2} \qquad (9)$$

where ϵ is a weighting factor, f_j is the atomic scattering factor for atom j and thus includes the thermal vibration of the atom and the

$\left| F_{hkl} \right|_{abs}$ values are corrected for any scale or temperature effects. The form of this correction can be calculated by two methods - the Wilson plot (equation 10 and ref. 9) and by the K-curve method (ref. 10). Details of these two methods are given elsewhere. One important use of the final E-values is that their final statistical distribution is an important discriminatory test between possible centric and acentric space groups.[11]

$$\ln \left(\frac{I_{rel}}{\sum_{l=1}^{n} fo_l^2} \right) = \ln C - 2B \left(\frac{\sin^2\theta}{\lambda^2} \right) \tag{10}$$

where K is related to C by $K = \dfrac{1}{\sqrt{C}} = \left| \dfrac{F_{abs}}{F_{rel}} \right|$

(VIII. 4.) Structure Solution

The determination of the part of the structure - the phasing model - which is approximately correct and will reveal further information about the structure can be approached using two main methods:-

(VIII. 4. 1.) The Patterson method.[12]

As mentioned above, Patterson in 1935 defined a function $P(u, v, w)$ given by equation (11)

$$P(u, v, w) = v \int_0^1 \int_0^1 \int_0^1 \rho(x, y, z) \cdot \rho(x+u,\ y+v,\ z+w)\ dxdydz \tag{11}$$

$$\{ \rho(x, y, z) = \frac{1}{v} \sum_h \sum_k \sum_{l=-\infty}^{+\infty} \left| F(hkl) \exp[\ -2\pi i(hx + ky + lz)] \right| \} \tag{12}$$

On substituting expressions for $\rho(x, y, z)$ and $\rho(x+u,\ y+v,\ z+w)$ given by equation (12) and rearranging, the expression for $P(u, v, w)$ can eventually be written

$$P(u, v, w) = \frac{1}{v} \sum_h \sum_k \sum_{l=-\infty}^{+\infty} \left| F(hkl) \right|^2 \cos 2\pi^2 (hu + kv + lw) \tag{13}$$

from which it can be seen that $P(u, v, w)$ is real for all u, v and w, and is independent of any phase information for the individual reflections. Hence a Fourier synthesis using $\left| F \right|^2$ as coefficients describes vectors between the electron densities at the points (x, y, z) and

$(x + u, \ y + v, \ z + w)$ so that vectors will appear as peaks with weights given by $\rho(x, y, z) \cdot \rho (x + u, \ y + v, \ z + w)$, i.e. $Z_i \cdot Z_j$, where Z_i and Z_j are the atomic numbers of the atoms concerned for an interatomic vector. Clearly if one atom is heavier than the rest, then the vectors associated with that atom will dominate the Patterson map.

In interpreting any Patterson maps there are several general principles which are of importance and these have been discussed in detail elsewhere.[1] In particular, Harker planes or lines in the Patterson map can be of considerable use. The Harker lines and planes are concentrations of vector points on certain planes or lines produced by symmetry related atoms. Every atom, heavy or light, will produce a peak on these lines or planes with enhanced weights. The position(s) of these lines or planes can, therefore, provide valuable information on atomic positions, as well as providing a useful check on the space group symmetry.

In some space groups, the information gained from the Harker lines or planes may not be sufficient to assign all of the heavy atom(s) co-ordinates, in which case one or more of the co-ordinates may be assigned arbitrarily, but once assigned cannot be refined. This can then result in additional symmetry in the resulting Fourier phased by the heavy atom(s). To give an example, in the monoclinic space group $P2_1$, the equivalent positions are x, y, z and $\bar{x}, \ \frac{1}{2} + y, \ \bar{z}$. The heavy atom vectors between symmetry related atoms, therefore, are to be found on the Harker plane $u, \frac{1}{2}, w$ with $u = 2x$ and $w = 2z$. For a single heavy atom the dominant peak on this plane allows the x and z co-ordinates to be calculated and the y co-ordinate may be assigned arbitrarily to determine the origin point with respect to the polar b axis in the space group. However, the two heavy atoms in this space group will then be centrosymmetrically related ($x, \frac{1}{4}, z$ and $\bar{x}, \frac{1}{4}, \bar{z}$ if y is assigned the value $\frac{1}{4}$) although the space group is non-centrosymmetric. As a result, the phase angles calculated for all reflections will be 0 or π resulting in a Fourier containing both

the true structure and its mirror image. This additional symmetry is normally broken by including the position of a second atom or several atoms from a molecular fragment in the calculation of the phase angles and re-examining the Fourier to see which peaks have remained and hence belong to the 'true' structure. It is important in the early stages to ensure atoms all come from the same molecule and to avoid false peaks due to the overlap of mirror related images of a peak. In some cases, even when a molecular fragment such as a phenyl ring has been located and refined, the false symmetry may still be present and chemical intuition could be useful in sorting out the remaining atoms from their mirror images. A case in point is the structure of iodoxybenzene described in Chapter II.

(VIII. 4. 2.) Direct methods

For structures where no one atom is much heavier than the rest, statistical methods may be needed to find the correct phases for the data. These methods are all based on an original equation developed by Sayre.[13] In these cases one attempts to set up an initial subset of data with signs/phases which in all probability are correct. The Sayre equation and triple product relationships are used in a bootstrap operation until all the data have been assigned a phase and a probability that that phase is correct. This procedure involves setting up many thousands of relationships between the h, k, l indices associated with each datum, normally in the form of triplets as in equation (14) below, where $S(h_1, k_1, l_1)$ means the _sign of_ the datum identified by the indices h_1, k_1, l_1.

$$S(h_1, k_1, l_1) \cdot S(h_2, k_2, l_2) = S(h_1 + h_2, k_1 + k_2, l_1 + l_2) \qquad (14)$$

The procedures involved in applying direct methods to light atom structures have been the subject of several computer programs. In the X-RAY system, the program links NORMSF, SINGEN and PHASE (or APHASE) are available and are single solution methods. Alternatively MULTAN,[14] which is available as a link in XRAY76 (with NORMSF) or as

a separate program (along with a program NORMAL[15] to calculate normalised structure factors), is a multi-solution program which has been successfully applied in all the light atom structures in this thesis and will be described in some detail.

The program MULTAN[14] is based on the tangent formula of Karle and Hauptmann[16] and consists of three parts; SIGMA2, CONVERGE and FASTAN. SIGMA2 sets up all phase relationships of the form

$$\varphi_{\underline{h}} \approx \varphi_{\underline{h}'} + \varphi_{\underline{h}-\underline{h}'} \tag{15}$$

where φ_n is the phase of $F_{\underline{h}}$ after "standardising" the reflection indices so that they all lie in the same part of the reciprocal lattice, a process that may involve a phase shift on standardisation. Each relationship is assigned a weight $K_{hh'}$ defined as

$$\varkappa_{hh'} = 2\sigma_3\sigma_2^{-3/2} \left| E_h E_{h'} E_{h-h'} \right| \tag{16}$$

where $\sigma_n = \sum_{j=1}^{N} Z_j^n$ and E_n is the normalised structure factor associated with reflection $\underline{h}$ ($\equiv h, k, l$). Only a specified number of these relationships with the highest $K_{hh'}$ values are retained for use in the tangent formula.

The second part of the program, CONVERGE, uses the phase relationships from SIGMA2 to determine a starting set of reflections which are involved in the most important phase relationships and enable the origin and enantiomorph of the cell to be accurately defined. Included in the starting set are any reflections which the sigma 1 ($\sum_1$) formula has determined with a reasonably high probability of being correct as well as several starting reflections. In a centric space group there would be assigned values of ± 1; in an acentric space group values of $\pm \pi/2$ if they are special reflections or else all combinations of the values $\pm \pi/4$ or $\pm 3\pi/4$ if they are general reflections. Normally only two or three of these starting reflections are chosen, and their various combinations of values provide a multiple starting point for the tangent formula.

The actual application of the tangent formula occurs in the third part of the program, FASTAN, and results in several sets of phases for all the reflections being calculated from the convergence mapping of the phase relationships. Output with each set of phases are several figures of merit which are measures of the internal consistency of the set of phases.

The actual tangent formula used in FASTAN is given in equation (17) where the weight $\underline{w}_h$ associated with each phase φ_h is given by equation (18)

$$\tan \varphi_{\underline{h}} \approx \frac{\sum_{\underline{h}'} w_{\underline{h}'} w_{\underline{h}-\underline{h}'} \left| E_{\underline{h}'} E_{\underline{h}-\underline{h}'} \right| \sin (\varphi_{\underline{h}'} + \varphi_{\underline{h}-\underline{h}'})}{\sum_{\underline{h}'} w_{\underline{h}'} w_{\underline{h}-\underline{h}'} \left| E_{\underline{h}'} E_{\underline{h}-\underline{h}'} \right| \cos (\varphi_{\underline{h}'} + \varphi_{\underline{h}-\underline{h}'})} = \frac{T_{\underline{h}}}{B_{\underline{h}}} \quad (17)$$

and $w_{\underline{h}} = \tanh \{ N^{-\frac{1}{2}} \left| E_{\underline{h}} \right| (T_{\underline{h}}^2 + B_{\underline{h}}^2)^{\frac{1}{2}} \}$ (18)

The initial weights for the starting set of phases are taken as unity, except for the $\sum_1$ phases where, if the sign is determined with a probability P, the weight used is 2P-1, based on an expectation value for the sign. The specification of the four alternative values $\pm \pi/4$, $\pm 3\pi/4$ for a general acentric starting reflection gives a maximum error of 45° for any reflection and an expectation error of $22\frac{1}{2}^o$.

In MULTAN, three figures of merit are normally used. The absolute figure of merit ABSFORM is related to $\sum_{\underline{h}} \alpha_{\underline{h}}$, where α_h is defined by

$$\alpha_{\underline{h}} = 2N^{-\frac{1}{2}} \left| E_{\underline{h}} \right| (T_{\underline{h}}^2 + B_{\underline{h}}^2)^{\frac{1}{2}} \quad (19)$$

so that (18) can be rewritten

$$w_{\underline{h}} = \tanh (\tfrac{1}{2} \alpha_{\underline{h}})$$

The actual value for ABSFORM is

$$ABSFORM = \frac{\sum_{\underline{h}} \alpha_{\underline{h}} - \sum \alpha_r}{\sum \alpha_e - \sum \alpha_r} = M_{abs}$$

where $\sum \alpha_e$ is the sum of the expected values of α_h^2 as given by equations (20) and (21).

$$\sum \alpha_e = \sum_{\underline{h}}' < \alpha_{\underline{h}}^2 >_{exp}^{\frac{1}{2}} \tag{20}$$

where

$$< \alpha_{\underline{h}}^2 >_{exp} = \sum_{\underline{h}'} \varkappa_{\underline{h},\underline{h}'}^2 + 2 \sum_{\underline{h}'} \sum_{\underline{h}''} \varkappa_{\underline{h},\underline{h}'} \cdot \varkappa_{\underline{h},\underline{h}''} \cdot$$

$$\frac{I_1(\varkappa_{\underline{h},\underline{h}'})}{I_0(\varkappa_{\underline{h},\underline{h}'})} \cdot \frac{I_1(\varkappa_{\underline{h},\underline{h}''})}{I_0(\varkappa_{\underline{h},\underline{h}''})} \tag{21}$$

where the $I_0(\varkappa)$ and $I_1(\varkappa)$ are modified Bessel functions,[17] and $\sum \alpha_r$ is a random expectation value assuming no internal consistency in the contributions to α

$$\sum \alpha_r = \sum_{\underline{h}} < \alpha_{\underline{h}}^2 >_{rand}^{\frac{1}{2}} = \sum_{\underline{h}} \left(\sum_{\underline{h}'} \varkappa_{\underline{h},\underline{h}'} \right)^{\frac{1}{2}} \tag{22}$$

For a set of phases with almost no self-consistency, the value of M_{abs} will be zero, whilst for the correct set of phases $\sum \alpha_h \approx \sum \alpha_e$ and correct phase sets normally have values of ABSFORM $\approx 1.2 \pm 0.2$. Other figures of merit are related to ABSFORM except PSI ZERO which is also a valuable discriminator between phase sets. The PSI ZERO test uses selected weak reflections, below a specified E_{min}.[18]

(VIII.5.) Electron Density Maps

Whether the structure is solved by the Patterson method or by direct methods, each approach eventually requires the calculation of a density map. For the Patterson map, the peaks in the map will represent inter-atomic vectors and the expression relating the Patterson function $P(u, v, w)$ to the structure factors has already been given. However, once heavy atom positions are known further refinement proceeds using F_o Fouriers to locate further atoms in the structure. The Fourier expression for a F_o Fourier is given in equation (12) where the coefficients, the $F(h, k, l)$ values are not merely the moduli of the structure factors, which are readily available as $\left| F_o \right|$'s calculated from the observed intensities, but also require a knowledge of the phase associated with each reflection.

Equation (4) contains the various

$$F(hkl) = \left| F(hkl) \right| e^{i\alpha} = \left| F(hkl) \right| \cos\alpha + i \left| F(hkl) \right| \sin\alpha$$

$$= A(hkl) + i\, B(hkl) \tag{23}$$

computational expressions used. In the direct methods, equation (12) is modified to use normalised structure factors E(hkl)'s instead of F(hkl)'s and the phase angles associated with each E(hkl) are of course calculated by the tangent formula of MULTAN or the appropriate direct methods program. If the process is reasonably efficient, these phase angles will be reasonably accurate and the majority of the structure will be located in the resulting E-map. However, the majority of E-maps contain many spurious peaks,with the result that perhaps only a molecular fragment may be located.

In both Patterson and the direct methods, an electron density map calculated using the measured structure factors and the trial calculated phases as Fourier co-efficients (a F_o Fourier) usually reveals more of the structure and enables the shifts in the atoms of the partial structure to be calculated. Incorporating the new atoms and the new positions for the atoms of the phasing model enables the process to be repeated. Several such steps normally converge to the correct structure.

At later stages in the refinement (or earlier stages if a really heavy atom that dominates the scattering is present), it is necessary to continue refinement using difference Fouriers. These are essential in locating hydrogen atoms in the structure since they are too small relatively to show up in an F_o Fourier. Even in a difference Fourier, the relative scattering power of the hydrogen atom may be of the same order as the observational errors in $\left| F_{obs} \right|$ unless very accurate data is available.

For a difference Fourier, the heavy atom contributions are subtracted out by using equation (24)

$$\rho(x,y,z) = \sum_{h}\sum_{k}\sum_{l} \left| F(h,k,l) - F_{calc}(h,k,l) \right| e^{i\varphi_{calc}(hkl)} \tag{24}$$

Since a Fourier synthesis with co-efficients $\left| F_{calc}(hkl) \right| \cdot e^{i\varphi}{}_{calc}{}^{(hkl)}$
generates only the electron density due to the heavy atoms, the
equation (24) will generate the difference between the actual electron
density and that due to the phasing model. Therefore, if the phases
of the partial model are correct, then the synthesis provides a
measure of the difference between the partial model and the true
structure. If the phases are in some error, the difference Fourier
is still of considerable use. Apart from indicating missing atoms
(hydrogen or otherwise) as positive peaks, the difference in $\rho_0 - \rho_c$
at each heavy atom position can either be positive or negative due to
site occupancy errors caused by wrongly identified atoms or, if a
characteristic pattern of positive peaks and negative holes appears
round an atomic site, this can be taken to indicate an anisotropically
vibrating atom and its temperature factor components U_{ij}
appropriately refined. In the most accurate analyses, it may even
be possible to gain some information on the positions of the valence
electrons associated with each bonding or lone pair orbital.[19]

At the end of the refinement, the few residual peaks remaining
will probably be close to the heaviest atom in the structure. In a
good analysis these peaks, if present, will be small. The rest of
the final difference map should also be featureless.

(VIII.6.) Least Squares Refinement

Although improved atomic positions can be obtained by calculation
of the peak positions in electron density maps, the positional and
thermal parameters associated with each atom can also be subjected
to least squres refinement, which is unfortunately non-linear in the
X-ray program CRYLSQ. The function minimised is a formalised
difference between the observed structure factors and the structure
factors calculated from the trial or approximate atomic positions.
A full matrix refinement of a structure containing 20 atoms all of whose
positional and isotropic thermal parameters together with a scaling
factor can vary independently would require the setting up of 81 normal

equations to be solved for the 81 variables. This problem, although relatively small in crystallographic terms, obviously involves immense calculations.

Normally several cycles of least squares refinement are required at each step in the structure solution and it is this calculation that accounts for the bulk of the computer time expended on each structure. For reasons of economy, in the earlier stages of refinement it may be better to use a subset of the data. However, the estimates of the standard deviations which are obtained from least squares refinement are unreliable unless the process is carried to completion with the full data set.

At each stage of the refinement, a measure of the accuracy of the current structural model is given by a Reliability Index or Residual $\underline{R}$ given by

$$R = \frac{\sum w \cdot \left| |F_o| - |F_c| \right|}{\sum w \cdot |F_o|}$$

This R-factor decreases as the trial structure is refined towards the true structure. In the early stages it also is a good indicator of whether the starting phasing model is likely to result in the rest of the structure being found, as it has been calculated that a random distribution of atoms in an acentric space group will give a R-factor of 0.59 (0.83 in a centric space group).[1] In the early stages it is also advisable to give each reflection hkl a weight w of unity. However, towards the end of the refinement the weights are normally chosen to remove any intrinsic errors in the data set (see below).

For diffractometer collected data, a well refined structure will normally give a R factor < 0.05. It may be necessary during certain refinements to remove correlations between various group parameters by refining that group as a rigid body.[20] This procedure is best suited to tetrahedral groups and phenyl rings, although the use of a rigid   6/mmm model of a phenyl ring may introduce

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errors and in the final refinement cycles it may be better to remove the rigid body constraints on phenyl-rings (see Section VII.4) For further details see ref. 21.

(VIII.7.)   Systematic Errors[27]

Whilst a very good idea of most structures can be obtained using data simply corrected for Lorentz and polarisation effects, there are a number of systematic errors which are likely to affect the data set. These can be relatively easily identified, and a correction applied. However, at the end of any determination there will still remain a number of intrinsic errors in the data set and the calculated model which a good weighting scheme can minimise.   The following sections summarise two of these systematic errors, their effects and how they are corrected for.

(VIII.7.1.)   Absorption

As the beam of radiation passes through the crystal, it is attenuated by absorption effects to an extent given by the equation

$$I = I_o e^{-\mu T}$$, where I = measured intensity; I_o = incident intensity, τ = total distance travelled through the crystal and μ = a linear absorption co-efficient given by the equation

$$\mu = \rho \sum_n (P_n/100)(\frac{\mu}{\rho})_{En, \lambda} \tag{25}$$

where P_n = percentage of element n in compound and μ/ρ = mass absorption co-efficient for the element n at wavelength λ.[4]   Obviously μ/ρ can be roughly related to the atomic number of the elements and the wavelength (penetrating power) of the radiation, so that absorption effects are most serious for compounds with odd shaped crystals containing a high percentage of a heavy element.   Previously crystals with large absorption factors had to be ground into spheres or cylinders so that absorption factors could be calculated.   Nowadays exact absorption corrections are calculated, using programs such as ABSCOR, providing the crystal faces can be measured exactly.[22] A method for describing and measuring the crystal has been given.[23]   Once the crystal has been accurately described, the program ABSCOR works by dividing the crystal into Howell's polyhedra so that rays are entering or leaving via one face only.   Within these polyhedra the loci

of constant absorption are planes; these may lie in any direction, but
their position is determined from the absorption of rays diffracted at
the corners of the polyhedra. For each of the polyhedra, the
contribution to the total diffracted intensity (A_T) is found. -The
transmission is then given by A_T/V (V = crystal volume).[22]

VIII.7.2.) Extinction

There are two forms of extinction called primary and secondary.
The mathematical treatment of extinction was originally given in
the work of Darwin.[24] Both primary and secondary extinction lower
the intensity of the diffracted beam because of interactions between
the incident and diffracted rays inside the sample. Primary
extinction relates to an interference process whereby an incident ray
is multiply reflected by a particular series of planes. As on each
reflection a phase change of $\pi/2$ occurs, a ray multiply reflected
n times within a crystal will interact with a reflection which has been
multiply reflected (n-2) times since there will be a phase difference
of π between them. Hence the net result is that the diffracted ray
is proportional to $|F|$ not $|F|^2$ assuming the crystal is ideally
perfect. However, Darwin's treatment of extinction recognised
that a crystal is not ideally perfect but consists of small mosaic
blocks which are slightly misaligned to each other so that the perfect
planes required for primary extinction do not extend over appreciable
regions in the crystal. The effect of primary extinction in a real
crystal with some mosaic spread causes the diffracted intensity to be
proportional to $|F|^n$ where $1 \ll n < 2$. The value of n for most
crystals is near 2, so that primary extinction effects can normally
be neglected.

However, secondary extinction is more important and several
mathematical models relating to extinction effects have resulted in
approximate equations which can be readily implemented. The
effect is important when the mosaic blocks are fairly well aligned

since, for reflections of appreciable intensity, the effect occurs
when an appreciable amount of the incident radiation is reflected by
the initial planes encountered so that deeper planes receive less
incident intensity and therefore reflect less. The effects of
secondary extinction are more pronounced at lower $(\sin \theta)/\lambda$ values
because the general level of intensities is higher in this region. The
effect is clearly observed in intense reflections which are
systematically less than their calculated values. Unlike absorption
which can be corrected for exactly (as far as theory permits) the
effects of extinction are determined by least squares refinement
of the appropriate parameters in the relevant expressions relating
observed data to the calculated intensities including extinction
effects. In the X-RAY system, the form of the extinction correction is
a modified equation from Zachariasen's[25] mathematical treatment of
Darwin's early work due to Larson.[26] This equation (26) is again
based on a mosaic model for the crystal with the term r^* related
to both the size (r) and spread (g) of the individual domains in the
crystal by equation (28).

$$\left| F_c^* \right| = K \cdot \left| F_c \right| \cdot [(1 + 2r^* \left| F_c \right|^2 \delta)]^{-\frac{1}{4}} \qquad (26)$$

where $\delta = \dfrac{e^2}{mc^2} \cdot \dfrac{1}{v^2} \cdot \dfrac{\lambda^3}{\sin 2\theta} \cdot (\dfrac{P_2}{P_1}) \cdot \overline{T}$ $\qquad (27)$

$P_n = (1 + \cos^{2n} 2\theta)/2$ are polarisation factors and $\overline{T}$ transmission
factors (set as 0.03 cm if no values given)

$$r^* = \beta(1 + (\beta/g)^2)^{-\frac{1}{2}} \qquad (28)$$

and $\beta = r/\lambda$ r is radius of a single domain. The magnitude
of r^* is useful because it enables the crystal to be classified as
Type I or II.[25]

(VIII.7.3.) Other factors;[27] weighting schemes

The above absorption and extinction are the principal sources of
error in the measured data. There are other sources of systematic

errors in the data, but their effects are increasingly smaller and are normally calculated _a posteriori_ only in the most accurate work. The most important use of these calculations is in experiments designed to show the valence electron density distribution around atoms. However, the majority of the calculations involve numerous approximations. The effects covered include contributions from the anisotropy of the extinction effect, thermal diffuse scattering, multiple wave interference effects, etc.[27]

Whether these effects are allowed for or not, there still remains small errors in the molecular model even after introducing atomic scattering factors for charged atoms and the allowing for anomalous dispersion effects.[4] These are normally the result of small but systematic biases introduced by the least squares refinements using unit weights for all reflections. A careful statistical analysis of the data in ranges of F and $\sin\theta$ at this stage is likely to have a distribution similar to that in Fig. 1. By careful selection of an appropriate weighting scheme, it is possible to produce an even distribution of w*deltafsq values and refinement with these calculated weights will reduce any bias in the data (the extinction factor should be fixed at the value at the end of the refinement with unit weights). Although the use of $(1/\sigma(F))^2$ as weights is common, the X-RAY system offers a choice of weighting schemes. It has, however, been found that a modified scheme that downweights reflections at the extreme F and $\sin\theta$ ranges has been useful in the majority of the later structures. The scheme gives a reflection a weight of $\approx$ zero if $A*F_{obs}$ is greater than $\left| F_c \right|$, otherwise the weights for the reflection are given by $w = X*Y*Z$ where $Z = 1.0$ or $Z = (1/\sigma(F))^2$. The values of X and Y are given as follows.

If $\sin\theta < B$ then $X = \sin\theta/B$ or if $\sin\theta > D$ then $X = D/\sin\theta$, otherwise $X = 1.0$. Similarly, if $F_{obs} < E$ then $Y = F_{obs}/E$ or if $F_{obs} > C$ then $Y = C/F_{obs}$, otherwise $Y = 1.0$. It has been found that this scheme is extremely flexible and weights can be calculated

using just a few parameters which effectively divide Fig. 1 up into 3 sections with straight lines approximating the curves. A good weighting scheme should eventually result in w*deltasq values being as equivalent as possible and in particular not greater than twice the minimum w*deltasq.

Although no such correction has been applied to any of the tables of bond distances and angles in this thesis, it should be mentioned that a correction can be made to final tables of atomic parameters calculated from the positional co-ordinates to include correlations between the thermal motions of individual atoms of each bond which has a foreshortening effect on bond lengths. Such effects can be removed if a rigid-body model is assumed in which all inter-atomic separations remain fixed. For further details the reader is referred to ref. 28.
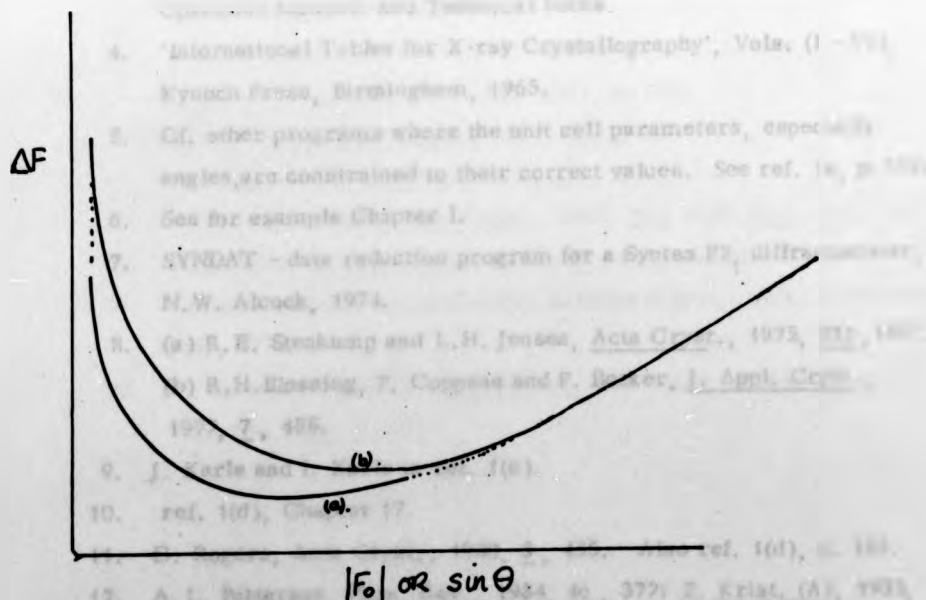
Fig. VIII.1 Typical $|\Delta F|$ vs. F (sin θ) curves for diffractometer data before the application of any weighting scheme.
(a) Large crystal. (b) Small crystal.

(VIII.8.) References

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Appendix A

Final Structure Factor Tables

Final structure factor tables for the diethyl tin dihalides are
available as Supplementary Publication No. SUP 21983 (14 pp.,
1 microfiche); those for (Z, Z)-2, 4-Dibromo-1, 5-diphenyl-
penta-1, 4-dien-3-one as Supplementary Publication No. SUP
31357 (16 pp., 1 microfiche).   Due to the size of the tables
for the other compounds and since they will eventually be deposited
when details of the individual structures are finally published, the
other structure factor tables have been omitted from this thesis
but are available on request.

(Z, Z)-2,4-Dibromo-1,5-diphenylpenta-1,4-dien-3-one

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Abstract ...

Introduction. ...

APPENDIX B

Published Papers
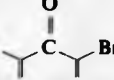
Acta Cryst. (1976). B32, 285

(Z, Z)-2,4-Dibromo-1,5-diphenylpenta-1,4-dien-3-one

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Abstract. $C_{17}H_{12}OBr_2$, monoclinic, $P2_1/c$, $a=41\cdot080$ (11), $b=6\cdot527$ (2), $c=11\cdot118$ (3) Å, $\beta=97\cdot77$ (2)°, $V=2953$ (1) Å^3 at 18 °C, $Z=8$, $D_x=1\cdot76$ g cm^{-3}. There are two essentially identical molecules in the asymmetric unit both having approximately planar conformations with Br and O adjacent. Intramolecular repulsions result in substantial deviations from planarity.

Introduction. The title compound (m.p. 97–98 °C), recrystallized from ethanol, was prepared and supplied by Professor Shoppee. The crystals appear as chunky needles (needle axis *c*). Systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$, indicate space group $P2_1/c$ with two independent molecules in the asymmetric unit. The crystals also display pseudo-absences $hk0$, $h \neq 2n$.

Data were collected on a Syntex $P2_1$ diffractometer with graphite-monochromatized Mo $K\alpha$ radiation to $2\theta_{max}$ of 50° in two shells with $\omega/2\theta$ scans over the range $(K_{\alpha 1}-0\cdot9)-(K_{\alpha 2}+0\cdot8)$°. In the first shell (0° <

Table 1. *Atomic coordinates* ($\times 10^4$) *and anisotropic temperature factors* ($\times 10^4$)
with standard deviations in parentheses

$$T=\exp\{-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\}.$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(11)	1573 (1)	−1534 (4)	3388 (3)	88 (2)	30 (2)	78 (2)	19 (2)	27 (2)	4 (2)
Br(12)	917 (1)	4886 (5)	5324 (2)	124 (3)	75 (2)	39 (1)	56 (2)	32 (2)	10 (2)
O(1)	1190 (4)	776 (24)	4988 (14)	74 (12)	29 (9)	42 (9)	1 (9)	18 (9)	10 (8)
C(11)	1581 (5)	2553 (34)	2564 (20)	18 (14)	26 (10)	39 (13)	6 (11)	−5 (11)	−15 (11)
C(12)	1449 (6)	1279 (39)	3262 (20)	20 (14)	50 (13)	42 (13)	12 (12)	−12 (11)	10 (13)
C(13)	1223 (6)	1899 (35)	4102 (20)	42 (15)	34 (13)	49 (14)	4 (12)	23 (12)	−32 (13)
C(14)	1024 (5)	3721 (30)	3849 (18)	23 (13)	20 (12)	28 (11)	16 (10)	8 (10)	−10 (10)
C(15)	894 (5)	4363 (32)	2773 (16)	40 (16)	31 (14)	11 (10)	0 (11)	14 (10)	14 (9)
C(111)	1825 (5)	2373 (39)	1725 (21)	4 (13)	53 (15)	51 (14)	12 (12)	1 (11)	−5 (14)
C(112)	2025 (7)	4138 (39)	1561 (21)	40 (18)	64 (16)	37 (14)	−8 (14)	−7 (13)	6 (12)
C(113)	2264 (9)	4079 (59)	701 (30)	65 (28)	113 (29)	60 (20)	4 (21)	14 (20)	−19 (20)
C(114)	2292 (7)	2315 (52)	94 (22)	55 (19)	76 (23)	41 (15)	−7 (17)	−1 (13)	−5 (16)
C(115)	2124 (7)	610 (39)	276 (23)	43 (19)	60 (16)	47 (15)	27 (14)	16 (15)	−6 (13)
C(116)	1894 (6)	575 (43)	1063 (22)	46 (18)	70 (20)	35 (14)	4 (14)	−4 (13)	−10 (14)
C(121)	660 (5)	6054 (33)	2421 (20)	7 (12)	42 (13)	38 (13)	6 (10)	−8 (10)	21 (11)
C(122)	445 (6)	5732 (40)	1282 (23)	43 (16)	56 (17)	53 (16)	10 (14)	18 (13)	25 (14)
C(123)	201 (8)	7149 (44)	922 (28)	45 (22)	53 (19)	67 (21)	5 (15)	23 (17)	15 (16)
C(124)	169 (6)	8876 (46)	1625 (29)	24 (16)	71 (20)	90 (22)	14 (13)	24 (16)	37 (18)
C(125)	395 (7)	9236 (42)	2716 (27)	57 (20)	61 (18)	66 (20)	13 (16)	28 (17)	23 (15)
C(126)	643 (7)	7840 (41)	3096 (21)	84 (24)	37 (17)	49 (14)	4 (15)	22 (14)	−10 (13)
Br(21)	4084 (1)	9898 (5)	4436 (2)	119 (3)	70 (2)	28 (1)	−46 (2)	1 (1)	−6 (2)
Br(22)	3445 (1)	3329 (4)	1931 (3)	96 (3)	35 (2)	69 (2)	−16 (2)	−9 (2)	7 (2)
O(2)	3804 (5)	5763 (24)	3900 (13)	107 (15)	34 (10)	31 (8)	−15 (9)	15 (9)	6 (7)
C(21)	4112 (6)	9277 (44)	1912 (23)	19 (19)	56 (20)	61 (16)	16 (14)	6 (14)	−24 (14)
C(22)	3970 (5)	8677 (34)	2892 (20)	10 (12)	48 (14)	37 (13)	13 (11)	1 (10)	−6 (12)
C(23)	3776 (6)	6793 (36)	2928 (21)	32 (14)	24 (12)	59 (15)	−4 (11)	13 (12)	−15 (13)
C(24)	3542 (6)	6133 (30)	1830 (22)	49 (18)	6 (10)	59 (15)	−9 (10)	26 (14)	−2 (11)
C(25)	3401 (6)	7260 (35)	1013 (20)	60 (20)	35 (12)	24 (12)	11 (12)	−4 (12)	−25 (12)
C(211)	4344 (6)	10955 (31)	1752 (20)	40 (16)	16 (11)	38 (12)	−22 (11)	−9 (12)	−6 (10)
C(212)	4549 (6)	10647 (38)	824 (19)	17 (14)	65 (16)	43 (12)	23 (13)	11 (11)	3 (12)
C(213)	4791 (7)	12076 (42)	697 (22)	39 (19)	68 (19)	46 (16)	−4 (15)	32 (14)	17 (15)
C(214)	4823 (8)	13850 (38)	1428 (23)	89 (25)	42 (16)	37 (16)	9 (14)	−14 (16)	24 (14)
C(215)	4593 (7)	14167 (39)	2339 (24)	53 (19)	35 (16)	75 (18)	−3 (14)	32 (15)	12 (13)
C(216)	4379 (5)	12745 (31)	2455 (18)	2 (12)	29 (13)	37 (12)	−5 (9)	−6 (10)	0 (10)
C(221)	3166 (6)	7070 (39)	−71 (19)	21 (14)	52 (19)	35 (13)	7 (12)	5 (11)	16 (13)
C(222)	2987 (7)	8737 (42)	−531 (27)	31 (19)	61 (19)	90 (22)	13 (14)	10 (17)	21 (16)
C(223)	2753 (7)	8807 (40)	−1569 (27)	50 (18)	56 (18)	80 (20)	10 (14)	−38 (17)	−9 (16)
C(224)	2701 (7)	6778 (62)	−2137 (23)	45 (20)	110 (29)	32 (15)	−16 (22)	−4 (14)	−17 (20)
C(225)	2896 (8)	5114 (44)	−1717 (25)	73 (21)	51 (17)	62 (17)	−44 (17)	−4 (16)	14 (17)
C(226)	3115 (8)	5260 (38)	−663 (28)	49 (22)	36 (15)	60 (22)	−15 (14)	−17 (18)	−2 (16)

$2\theta \le 35°$) all reflexions were collected; in the second ($35° < 2\theta \le 50°$) a reflexion was only collected if the intensity of an 8s preliminary count was greater than 40 c.p.s. A variable scan rate, 1·0–29·3° min⁻¹ depending on the intensity of the preliminary count was used. Cell constants and errors were obtained by least-squares refinement of the positions of 15 reflexions (Mo $K\alpha$, $\lambda = 0·71069$ Å).

The positions of the four Br atoms were located with *NORMAL* and *MULTAN* (Germain & Woolfson, 1968) applied to the 274 reflexions with $E > 1·50$ in the first shell of data. Fourier and least-squares refinement with the 1865 observed [$I/\sigma(I) > 3·0$] reflexions in both shells located the remaining non-hydrogen atoms. The final refinement was with Br, C and O with anisotropic temperature factors to an R of 0·081. Scattering factors were from Cromer & Mann (1968). The weighting scheme was $\sqrt{w} = 1·0/(186 - 335 \sin \theta)$. H atoms were not included and no correction for absorption was performed. Computing was carried out with the X-RAY system (1972) on a CDC 7600 computer.

Fig. 1 shows the atomic numbering, bond lengths and angles; Fig. 2 gives views of the two molecules. Atomic coordinates and temperature factors are given in Table 1, and molecular planes in Table 2.*

Discussion. The primary aim of the investigation was to determine the conformation of the compound [regarded to have the Z,Z configuration (Shoppee & Cooke, 1973)]. There was also the possibility of intermolecular Br···O secondary bonds (Alcock, 1972), important in many brominated steroids (Peck, Duax, Eger &

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31357 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Norton, 1970). The independent molecules are virtually identical. Both approximate to a planar

Fig. 1. Atomic numbering, bond lengths and angles (in square brackets for the second molecule) with standard deviations in parentheses. For the second molecule, the initial digit in each atom's number is (2) instead of (1).
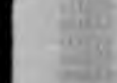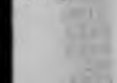
Table 2. *Least-squares planes*

(a) Equations of the least-squares mean planes $PI + QJ + RK = S$* in orthogonal space. Deviations of atoms forming these planes are insignificant and are not shown.

Plane	Defining atoms	P	Q	R	S
1	Br(11), C(11), C(12), C(13)	0·6583	0·2039	0·7246	6·4071
2	Br(12), C(13), C(14), C(15)	0·8072	0·5902	0·0119	4·3591
3	Br(21), C(21), C(22), C(23)	0·7768	−0·5879	0·2257	13·6357
4	Br(22), C(23), C(24), C(25)	0·8316	−0·1868	−0·5230	11·2415
5	C(12), C(13), C(14), O(1)	0·6604	0·5265	−0·5354	5·9584
6	C(22), C(23), C(24), O(2)	0·7835	−0·5312	−0·3223	11·8726
7	C(111)–C(116)	0·6055	−0·2893	0·7414	5·3629
8	C(121)–C(126)	0·7137	−0·4736	−0·5161	2·1855
9	C(211)–C(216)	0·5654	−0·4721	0·6764	10·9384
10	C(221)–C(226)	0·7973	0·2218	−0·5614	10·0034

(b) Angles (°) between planes or lines

(1)–(2)	48·7	(3)–(4)	50·4
(1)–(5)	21·6	(3)–(6)	32·0
(1)–(7)	28·7	(3)–(9)	29·6
(2)–(5)	31·8	(4)–(6)	23·2
(2)–(8)	31·8	(4)–(10)	23·8

* With the orthogonal unit vector I parallel to A, K perpendicular to A in the AC plane and J perpendicular to the AC plane.
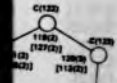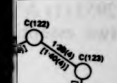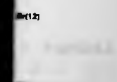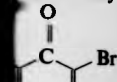
Fig. 2. Views of the two molecules showing the deviations from planarity.
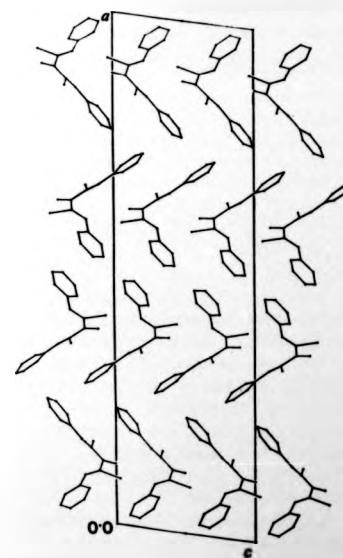

Fig. 3. Packing diagram, viewed down **b**. The rows contain respectively (from the bottom) molecules 1,2,1,2, those in each row being related by the glide plane.

conformation with Br and O adjacent. This probably arises because rotation by 180° about either C–C bond would lead to Br–H or Br–Br repulsion. Maximum π-conjugation requires the molecule to be completely planar,* but intramolecular repulsions lead to large deviations from this. Each C=O is twisted out of the

plane on either side of it by angles of between 22 and 32°, with the Br atoms on opposite sides of the

plane. This still leaves comparatively short O–Br contacts of 2·93–2·95 Å. Further, the phenyl rings are twisted out of plane by between 24 and 32° to increase the Br–H(*ortho*) contact distances resulting in values between 2·61 and 2·78 Å (H in calculated positions). The (Ph)C–C angles are also substantially larger than expected, presumably for the same reason. Other bond lengths and angles have normal values.

The molecular packing (Fig. 3) proved not to be controlled by Br···O secondary bonds. Instead, the phenyl rings take up the typical herring-bone arrangement.

* This is found in 1,5-diphenylpenta-1,4-dien-3-one itself [investigated as its uranyl complex (Alcock, Herron, Kemp & Shoppee, 1975)].

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Secondary Bonding. Part 2.[1] Crystal and Molecular Structures of Diethyltin Dichloride, Dibromide, and Di-iodide

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The crystal and molecular structures of the diethyltin dihalides, R_2SnX_2 [(1) X = Cl, (2) X = Br, (3) X = I], have been determined from diffractometer data. Crystal parameters are : (1), monoclinic, space group $P2_1/c$, a = 9.677(3), b = 9.835(2), c = 9.243(3) Å, β = 102.73(2)°, Z = 4, 811 observed reflections, R 0.047 ; (2), ortho-rhombic, space group $C222_1$, a = 9.786(2), b = 10.006(3), c = 9.494(2) Å, Z = 4, 289 observed reflections, R 0.058 ; (3), orthorhombic, space group $Pbcn$, a = 13.469(4), b = 5.385(2), c = 13.733(4) Å, Z = 4, 342 observed reflections, R 0.049. In (2) and (3), the individual molecules have crystallographic symmetry 2. All three compounds which are not associated by secondary bonds to the O, S, and N ligands appear to be much stronger than those to chlorine. It also appears bonds such that the geometry may be described as intermediate between tetrahedral and octahedral. The lengths of the secondary bonds in (1) and (2) are 3.461(4) and 3.777(4) Å, 0.39 and 0.17 Å less than the sum of the respective van der Waals radii, with C–Sn–C angles opened to 134.0(6) and 135.9(10)°. For (3) the secondary bond distance is 4.284(5) Å, longer than the sum of the van der Waals radii, although the C–Sn–C angle [130.2(11)°] shows that the interaction is still stereochemically important. The packing in (3) also differs from that in (1) and (2).

The lengths of these secondary bonds are compared with other known examples in organotin(IV) chemistry, and factors influencing the strength of the interactions are discussed.

THERE have been a wealth of physical measurements made on organotin(IV) compounds since Sn is readily adaptable to many physical techniques. In particular, their crystal chemistry has been extensively investigated,[2] and there has been much discussion of molecular association.

This discussion concerns the significance of certain inter- and intra-molecular contact distances in the crystal, which are less than the sum of the relevant van der Waals radii. Furthermore, these interactions appear to be stereochemically important in affecting the primary geometry at the tin atom and the packing in the crystal. The name ' secondary bonds '[3] has been suggested by us for these interactions, although other terms have been used.

These long bonds have been discussed in terms of electrostatic interactions between the atoms, but a more satisfactory description is in terms of three-centre four-electron (3c–4e) molecular orbitals.[3] In a system of the type Y–A · · · X, the secondary bond A · · · X is formed by donation from a lone pair on X into the σ* orbital of the Y–A primary bond. Alternatively (and equivalently), the interaction of the three σ-symmetry atomic orbitals (on Y, A, and X) gives a filled bonding molecular orbital concentrated between A and Y, a filled non-bonding or weakly bonding orbital concentrated between A and X, and an empty antibonding orbital. The overall scheme is identical to the MO description of the hydrogen bond.

This paper forms part of a systematic investigation of secondary bonding. Here the effect of the halogen and

organo-groups on the degree of association in the di-organotin dihalides are studied.

Previous Results.—Of the four diorganotin(IV) di-halides whose crystal structures are known, Me_2SnF_2 has the Sn atoms octahedrally co-ordinated by forming two *trans*-bonds to methyl groups and four equal Sn–F bonds (2.14 Å), giving a regular two-dimensional layer lattice.[4] In both Me_2SnCl_2 (ref. 5) and $(CH_2Cl)_2SnCl_2$ (ref. 6) the tin atoms can be regarded as being four-co-ordinate, but it is also possible to distinguish infinite chains in the crystal held together by weak inter-molecular interactions. The tin atoms are strongly dis-torted from the expected tetrahedrally co-ordinated arrangement by further secondary bonds to chlorine atoms of other molecules. In the crystal structure of Ph_2SnCl_2, the original authors described the structure in terms of isolated molecules without any intermolecular tin–chlorine bridging.[7] This has been criticised by Bokii *et al.*[6] who point out that the Sn–Cl bond lengths are different, and that the chlorine atoms involved in the longer of the Sn–Cl bonds are also involved in short intermolecular interactions of 3.77—3.78 Å with the tin atoms of neighbouring molecules. These interactions produce linear groups of four molecules, the two terminal tin atoms remaining four-co-ordinate while the central tin atoms can be viewed as six-co-ordinate.

As well as the diorganotin(IV) dihalides, the crystal structures are known of several nominally four-co-ordinate dialkyltin(IV) compounds containing pseudo-halides[8] and many trialkyl- and triaryl-tin(IV) halides

[1] Part I, N. W. Alcock and R. M. C. Countryman, *J.C.S. Dalton*, 1977, 217.

[2] For reviews see R. Okawara and M. Wada, *Adv. Organo-metallic Chem.*, 1967, 5, 137; N. G. Bokii and Yu. T. Struchkov, *J. Struct. Chem.*, 1968, 9, 643; B. Y. K. Ho and J. J. Zuckerman, *J. Organometallic Chem.*, 1973, 49, 1; P. J. Smith, 'A Bibliography of Organotin X-ray Crystal Structures,' No. 438, London, TRI, 1975.

[3] N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, 15, 1.

[4] E. O. Schlemper and D. Britton, *Inorg. Chem.*, 1966, 5, 995.

[5] (a) J. D. Graybeal and D. A. Berta, U.S. Nat. Bur. Stand., Spec. Publ. No. 301, 1967, p. 393 (This structural analysis was based upon an incorrect space group); A. G. Davies, H. J. Milledge, D. C. Puxley, and P. J. Smith, *J. Chem. Soc. (A)*, 1970, 2862.

[6] N. G. Bokii, Yu. T. Struchkov, and A. K. Prokofiev, *J. Struct. Chem.*, 1972, 13, 619.

[7] P. T. Greene and R. F. Bryan, *J. Chem. Soc. (A)*, 1971, 2549.

[8] Y. M. Chow, *Inorg. Chem.*, 1970, 9, 794; 1971, 10, 673; R. A. Forder and G. M. Sheldrick, *J. Organometallic Chem.*, 1970, 22, 611; J. Konnert, D. Britton, and Y. M. Chow, *Acta Cryst.*, 1972, B28, 180.

and pseudohalides.[9] Three review articles[10] have dis-cussed the intermolecular bonding in the organometallic pseudohalides of several heavy atoms including tin in terms of donor–acceptor bonding. Most of these com-pounds are also associated in the crystal, and the secondary bonds to the O, S, and N ligands appear to be much stronger than those to chlorine. It also appears that some compounds which are not associated by secondary bonding at room temperature may be associ-ated at lower temperatures. This is seen in triphenyl-tin(IV) chloride whose room-temperature crystal struc-ture shows discrete molecules with the valence angles about the tin being very close to normal tetrahedral values.[11] The authors suggested that the significant difference in the ^{35}Cl n.q.r. spectra at 303 and 77 K (ref. 12) was due to the appearance of a polymeric structure with trigonal-bipyramidal tin and a weak secondary bond Sn · · · Cl (as has been suggested[13] for Me_3SnCl) at the lower temperature. However, a recent series of Mössbauer measurements over a range of temperatures has failed to discover any gross structural changes in Ph_3SnCl, whilst the association in Me_3SnCl_2 becomes stronger at lower temperatures.[14]

EXPERIMENTAL

The title compounds were recrystallised from dry iso-pentane, and to prevent air-moisture hydrolysis were sealed under nitrogen in Lindemann capillary tubes which had been baked *in vacuo* for several hours.

Crystal Data.—Unit-cell and space-group data are listed in Table 1. Unit-cell constants and their standard devi-ations were obtained from least-squares refinement of the

diffracting positions of 15 reflections on a Syntex $P2_1$ diffractometer, by use of Mo-K_α radiation ($\lambda = 0.710 69$ Å). D_m measurements were not made because of the moisture sensitivity of the crystals and their solubility in most organic solvents, although D_c values are in reasonable agreement with the values quoted for Me_2SnCl_2 and Ph_2SnCl_2. All reflection data were collected on a Syntex $P2_1$ diffractometer under the following conditions, by use of graphite-monochromated Mo radiation.

(a) Et_2SnCl_2, *Compound* (1). Data were collected from a needle-shaped crystal of dimensions 0.052 $\times$ 0.052

$\times$ 0.48 mm bounded by the faces {001}, {010}, {100}. Systematic absences $h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$, indicate space group $P2_1/c$. Reflections were measured using a θ—2θ scan and scan range (K_{α_1} — 0.95) to (K_{α_2} + 0.95), to $2\theta_{max}$ of 50°. A variable scan-rate of 1.3—29.5° min^{-1} was used, depending on the intensity of a preliminary 2-s count. Background counts were recorded at each end of the scan. The intensities of 3 standard reflections moni-tored every 80 reflections showed a steady loss of intensity and the collected data were rescaled according to the equation $F = F_o(1 + 0.000 65k)(1 + 0.002 54\sin \theta/\lambda \cdot t)$. The maximum rescale factor was 1.1458. 1 709 Data were collected, of which 811 were considered observed having $I/\sigma(I) \geqslant 3.0$.

(b) Et_2SnBr_2, *Compound* (2). Data were collected from a crystal of dimensions 0.211 $\times$ 0.260 $\times$ 0.343 mm bound by the faces {110} and {001}. Systematic absences hkl, $h + k \neq 2n$; 00l, $l \neq 2n$, indicate space group $C222_1$, with the Sn on special positions, symmetry 2. Reflections were measured as in (a), scan range (K_{α_1} — 0.9) to (K_{α_2} + 0.9), and variable scan rate of 1.5—29.3° min^{-1} to $2\theta_{max}$ of 55°. The intensities of 4 standard reflections recorded after every 50 reflections again showed a steady loss in inten-sity, and collected data were rescaled according to the equa-tion $F = F_o(1 + 0.000 420 4t)(1 + 0.001 272 4 \sin \theta/\lambda \cdot t)$; maximum rescale factor 1.0524. Of 1 263 data measured, including systematic absences due to the centering con-dition, 289 were considered observed.

(c) Et_2SnI_2, *Compound* (3). Data were collected from a needle-shaped crystal, needle axis a (dimensions un-known). Systematic absences $0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$; $hk0$, $h + k \neq 2n$, indicate space group $Pbcn$ with the Sn on special positions, symmetry 2. Reflections were measured as before, scan range (K_{α_1} —0.9) to (K_{α_2} +0.9), variable scan rate of 3—29.3° min^{-1} to $2\theta_{max}$ of 52°. The intensities

TABLE 1

Unit-cell data for the diethyltin(IV) dihalides

Compound	System	Space group	a/Å	b/Å	c/Å	β/°	U/Å^3	Z	D_c	μ(Mo-K_α)/cm^{-1}
Et_2SnCl_2	Monoclinic	$P2_1/c$	9.677 (3)	9.835 (2)	9.243 (3)	102.73(2)	858.1(4)	4	1.92	35.35
Et_2SnBr_2	Orthorhombic	$C222_1$	9.786 (2)	10.006 (3)	9.494 (2)		929.7(4)	4	2.40	117.70
Et_2SnI_2	Orthorhombic	$Pbcn$	13.469 (4)	5.385 (2)	13.733 (4)		996.0(6)	4	2.87	87.61

of 3 standard reflections recorded after every 60 reflections showed a steady drop in intensity, and collected data were rescaled in two sections according to the equations: $F = F_o(1 + 0.007 655t)(1 — 0.004 628 \sin\theta/\lambda \cdot t)$ for $t \leqslant 15.18$, and $F = F_o(1 + 0.002 832 3t)(1 — 0.000 960 8 \sin\theta/\lambda \cdot t)$ for $t > 15.18$; maximum rescale factor 1.0682. Of 1 187 data measured, 342 were considered observed.

For compounds (1) and (2) Lorentz, polarisation, and absorption corrections were applied, the last with the program ABSCOR.[15] For (3) Lorentz and polarisation corrections were made, but crystal decomposition prevented

[9] R. A. Forder and G. M. Sheldrick, *J.C.S. Dalton*, 1900, 1125; *J. Organometallic Chem.*, 1970, 21, 115; R. Hulme, *J. Chem. Soc.*, 1963, 1524; N. Kasai, K. Yasuda, and R. Okawara, *J. Organo-metallic Chem.*, 1965, 3, 172; E. O. Schlemper and D. Britton, *Inorg. Chem.*, 1966, 5, 507; Y. M. Chow and D. Britton, *Acta Cryst.*, 1971, B27, 856; H. C. Clark, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, 1964, 2332; J. B. Hall and D. Britton, *Acta Cryst.*, 1972, B28, 2133; A. M. Domingos and G. M. Sheldrick, *J. Organometallic Chem.*, 1974, 67, 257.

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[11] N. G. Bokii, G. N. Zahkarova, and Yu. T. Struchkov, *Zhur. strukt. Khim.*, 1970, 11, 895.

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[13] H. A. Stöckler, personal communication, quoted in *J. Amer. Chem. Soc.*, 1966, 88, 3224; A. G. Davies, H. J. Milledge, and D. C. Puxley, unpublished work, quoted in M.T.P. Internat. Rev. Sci., 1972, 6, 250.

[14] G. M. Bancroft, K. D. Butler, and T. K. Sham, *J. Chem. Soc.*, (A), 1975, 1483.

[15] N. W. Alcock, ' The Analytical Method for Absorption Correction,' in ' Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970.

any measurement of the dimensions of the crystal for absorption correction.

In all three cases, structure solution was attempted successfully, using three-dimensional Patterson maps to
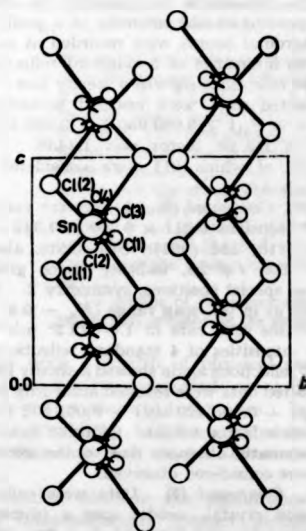

FIGURE 1 Et$_3$SnCl$_3$ projected down a; primary bonds are shown closed; secondary bonds open

locate the heavy atoms and Fourier maps to locate the other non-hydrogen atoms. Block-diagonal least-squares refinement with anisotropic temperature factors for all atoms, with correction for the effects of anomalous dispersion, produced final R factors of 0.047 (1), 0.058 (2), and
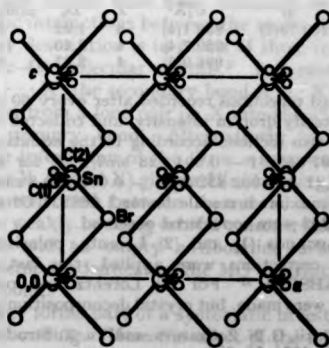
FIGURE 2 Et$_3$SnBr$_3$ projected down b

0.049 (3). The weights used were based on counting statistics. Scattering factors for neutral non-hydrogen atoms were taken from ref. 16. Computing was on an ICL 4130 computer with the programs of Dr. D. Russell. Final co-ordinates are listed in Table 2, significant bond

* See Notice to Authors No. 7, in J.C.S. Dalton, 1976, Index issue.

lengths and angles in Table 3. Structure factors and anisotropic thermal parameters for the three compounds are listed in Supplementary Publication No. SUP 21983

TABLE 2

Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	X	Y	Z
(1) Et$_3$SnCl$_3$			
Sn	2 788(1)	2 312(1)	7 006(1)
Cl(1)	2 774(5)	705(4)	5 071(4)
Cl(2)	2 738(4)	672(4)	8 898(4)
C(1)	751(14)	3 238(15)	6 542(16)
C(2)	−413(20)	2 217(25)	6 152(34)
C(3)	4 912(16)	3 100(15)	7 494(16)
C(4)	6 028(16)	2 021(18)	7 800(20)
(2) Et$_3$SnBr$_3$			
Sn	431(3)	0(0)	5 000(0)
Br	2 100(3)	48(21)	3 002(3)
C(1)	−420(26)	1 956(25)	4 745(31)
C(2)	393(28)	3 001(31)	5 366(61)
(3) Et$_3$SnI$_3$			
I	1 245(1)	965(5)	1 531(1)
Sn	0(0)	4 080(6)	2 500(0)
C(1)	904(19)	5 829(54)	3 644(15)
C(2)	1 501(21)	3 739(77)	4 220(17)

(14 pp., 1 microfiche).* Views of the compounds are in Figures 1—3.

DISCUSSION

In all three compounds, the individual molecules interact to form chains. Probably as a result, there are significant angular distortions from tetrahedral values in the individual molecules. The values of the angles C–Sn–C and X–Sn–X are respectively 134.0(6) and
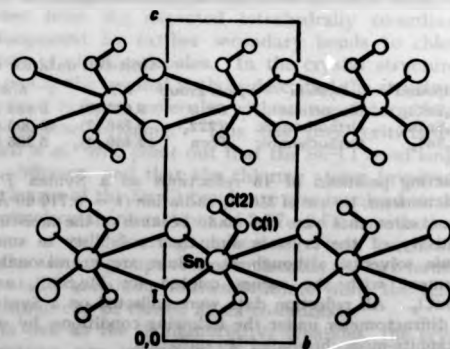

FIGURE 3 Et$_3$SnI$_3$ projected down a

96.0(1) for (1), 135.9(10) and 98.5(1) for (2), and 130.2(11) and 104.0(2)° for (3).

Although there are few other Sn–C(Et) bond distances available for comparison, there should be little difference between Sn–C(Me) and Sn–C(Et). The Sn–C(Et) bond in dichloro(ethyl)hydroxotin[17] is 2.20(3) Å and a large number of Sn–C(Me) distances in the solid state for a

[16] 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[17] P. C. Lecomte, J. Protas, and M. Devaud, Acta Cryst., 1976, B32, 923.

variety of distorted geometries at tin give Sn–C from 2.07 to 2.22 Å.[18] The Sn–C distance in SnMe$_4$ has been determined most recently by gas-phase electron diffraction as 2.144(3) Å.[19] The present values are quite close to those quoted, but they do seem to show a slight systematic increase from (1) to (3). For Sn–Cl bonds, electron diffraction has shown a regular contraction in the bond length with increasing halogen

The present mean Sn–Cl bond length 2.384 Å does not differ significantly from those for the other two dialkyltin dichlorides listed in Table 3 although it is ca. 0.04 Å longer than that in Ph$_2$SnCl$_2$. It is clearly considerably longer than that in Me$_2$SnCl$_2$ in the gas phase.[20]

Examples of Sn–Br and Sn–I bond distances are less numerous. The observed values [Sn–Br 2.505(4) and Sn–I 2.719(4) Å] are again longer than the gas-phase

TABLE 3

Bond distances (Å) and bond angles (°) with standard deviations in parentheses

(a) Distances

Compound	Sn–X	Sn–C	C–C	Sn···X	Δ[a]	Sn···X[b]	X···X
Me$_2$SnCl$_2$[c]	2.40(4)	2.21(8)		3.54(5)	1.14	3.85	
(CH$_2$Cl)$_3$SnCl$_3$[d]	2.37(2)	2.18(7)		3.71 (3.21)[e]	1.34(0.84)		
Et$_2$SnCl$_2$[f]	2.385(3)	2.132(13)	1.452(25)	3.483(4)			3.544(6)
	2.384(4)	2.167(15)	1.471(22)	3.440(4)	1.08		
Et$_2$SnBr$_2$[f]	2.505(4)	2.162(26)	1.456(46)	3.777(4)	1.27	3.95	3.795(4)
Et$_2$SnI$_2$[f]	2.719(4)	2.178(27)	1.573(49)	4.284(5)	1.565	4.08	
Ph$_2$SnCl$_2$ (1)[e]	2.353(2)	2.119(5)		3.78	1.44		4.284(3)
	2.336(2)	2.105(5)				3.85	
(2)	2.357(2)	2.118(5)		3.77	1.44		
	2.336(2)	2.112(5)					

(b) Angles

Compound	X–Sn–X	C–Sn–C	C–Sn–X		Sn–C–C	X···Sn–X	Sn···X–Sn
Me$_2$SnCl$_2$	93.0(20)	123.5(45)	109.0(45)				
(CH$_2$Cl)$_3$SnCl$_3$	97.0(20)	135.0(60)	105.0(20)				
Et$_2$SnCl$_2$	96.0(1)	134.0(6)	106.3(4)		112.1(12)	173.0(1)	104.0(1)
			105.4(4)		113.6(10)	172.0(1)	102.8(1)
Et$_2$SnBr$_2$	98.5(1)	135.9(10)	97.5(9)		114.0(20)	179.5(5)	98.2(1)
Et$_2$SnI$_2$	104.0(2)	130.2(11)	105.6(8)		110.0(21)	188.0(1)	98.0(1)
Ph$_2$SnCl$_2$ (1)	101.7(1)	123.9(2)	106.0(2)	108.8(2)			
			106.5(2)	107.8(2)			
(2)	97.8(1)	127.0(2)	110.1(2)	105.0(2)			
			107.1(2)	105.9(2)			

[a] Δ = (Sn···X) minus (Sn–X). [b] van der Waals distance, from A. Bondi, J. Phys. Chem., 1964, 68, 441. [c] Ref. 5. [d] Ref. 6. [e] Value in parenthesis is Sn–Cl intramolecular distance. [f] This work. [g] Ref. 7.

substitution in the series Me$_{4-n}$SnCl$_n$ ($n = 1$—4). The Sn–Cl distances are 2.351(7) (Me$_3$SnCl), 2.327(3) (Me$_2$SnCl$_2$), 2.304(3) (MeSnCl$_3$), and 2.281(4) Å (SnCl$_4$). The Sn–C distances are essentially constant (2.104—2.108 Å).[20] The Sn–Cl distance in (chloromethyl)trichlorostannane is 2.340 Å, intermediate between those for Me$_3$SnCl and Me$_2$SnCl$_2$, presumably owing to the inductive effect of the chloromethyl group.[21]

Crystallographic determinations of the Sn–Cl bond length have generally fallen in the range from 2.318 to 2.584 Å,[22] with the length of the Sn–Cl bond increasing as the co-ordination of the tin changes from tetrahedral to octahedral. The longest recorded Sn–Cl distance is 2.696(3) Å in [Me$_2$SnCl$_3$],[23] although bridging Sn···Cl distances of 2.805, 2.96, and 2.78 Å occur in the transition-metal complexes [(bipy)Mo(CO)$_3$(SnMeCl$_2$)Cl], [(dth)W(CO)$_3$(SnMeCl$_2$)Cl], and [(dth)Mo(CO)$_3$(SnCl$_3$)-Cl][24] (bipy = $\alpha\alpha'$-bipyridyl, dth = 2,5-dithiahexane) and

bond lengths in SnBr$_4$ and SnI$_4$ [2.44(2) and 2.64(4) Å],[25a] while in crystalline SnBr$_4$ and SnI$_4$ the respective values are 2.41 and 2.69(2) Å.[25b] Electron-diffraction measurements on Me$_2$SnX$_{4-n}$ (X = Br and I) are probably not very accurate as the molecules were assumed to be tetrahedral and no allowance was made for scattering phase shift; in Me$_2$SnX$_2$ Sn–Br was 2.45(2) and Sn–I 2.69(3) Å, and for this series a contraction was reported with increasing halogen substitution,[26] although the values quoted above for SnX$_4$ seem not to bear this out.

Considering solid-state values, the observed Sn–Br value is in good agreement with that [2.504(5) Å] in (4-bromo-1,2,3,4-tetraphenyl-cis,cis-buta-1,3-dienyl)dimethyltin bromide which is also distorted from tetrahedral geometry by secondary-bond interactions.[27] In the two isomers of bis[1,2-bis(ethoxycarbonyl)ethyl]tin dibromide, Sn–Br distances of 2.516(6), 2.588(6), and

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2.504(5) Å were found in distorted octahedral structures.[28] The only other examples of solid-state Sn–Br distances are for organotin–transition-metal compounds, where more complex bonding and packing effects occur, e.g. $[(Br_3Sn)Fe(CO)_2(\eta-C_5H_5)]$ mean 2.501(2), $[(Br_3Sn)\{Mn(CO)_5\}_2]$ 2.548(2), and $[(BrSn)\{Co(CO)_4\}_3]$ 2.520(5) Å.[29] The mean value for $[(Br_3Sn)Mo(\eta-C_5H_5)Br]$ is 2.506(8) Å, but this compound also possesses a long bridging Sn–Br distance of 3.411 Å (cf. ref. 24) which results in trigonal-bipyramidal geometry at the tin atom.[29d]

The observed Sn–I for (3) also agrees with that [2.729(3) Å] in 1,4-bis(iododiphenyl)-1,4-distannabutane which contains a tetrahedral tin atom.[30]

Intermolecular Interactions.—The strength of the intermolecular interactions can be deduced from the length of the secondary bonds and the angles around tin (especially C–Sn–C). In Et_2SnCl_2 and Et_2SnBr_2 the lengths of the secondary bonds (see Table 3) are 0.39 and 0.17 Å less than the sum of their appropriate van der Waals radii. The weakest interaction occurs in Et_2SnI_2, where the Sn $\cdots$ I secondary-bond distance [4.284(5) Å] is greater than the sum of the tin and iodine van der Waals radii. However, it can be argued that the interaction is still present since the value of the C–Sn–C angle of 130.2(11)° is much larger than the tetrahedral value. Taking into account only the difference between the secondary-bond distance and the sum of the van der Waals radii, it would appear that the strength of the secondary bonding is in the order Cl > Br > I. However, if the apparent difference in the C–Sn–C angle is genuine, then the order may be Cl ≈ Br > I. It has also been suggested, from n.q.r. measurements, that bromine bridging is stronger than chlorine bridging.[31] Zahrobsky,[32] by use of a simple stereochemical model which optimises the van der Waals forces between the bonded and neighbouring atoms (regarded as spheres), has predicted intermolecular distances of 3.81 and 4.11 Å for Me_2SnBr_2 and Me_2SnI_2. The distances quoted are reasonable although the steric requirements of the larger ethyl group might affect these results. However, this model only calculates the C–Sn–C angles as being 125 and 124° respectively.

The mode of bridging in the Et_2SnCl_2 and Et_2SnBr_2 chains is also different from that in Et_2SnI_2 where both bridging secondary bonds Sn $\cdots$ I involve the halogen atoms on the same neighbouring molecule (Figure 3). In Et_2SnCl_2 and Et_2SnBr_2 the distorted octahedral arrangement around each tin is completed by two secondary bonds involving the halogen atoms of two neighbouring molecules (Figures 1 and 2). Both

$(CH_2Cl)_2SnCl_2$ and Ph_2SnCl_2 associate in the same chelating manner as does Et_2SnI_2; Me_2SnCl_2, however, has the second bridging-type of association. It is not readily apparent which type of bridging arrangement a system containing secondary bonds will adopt, but the chelating bridges seems to be favoured with the longer weaker bonds. Brown and Shannon [33] have attempted to classify the bridging environments in certain inorganic structures using the bond valences of the bridging atoms, and this method may be applicable to secondary-bonded systems.

The lengths of the Sn $\cdots$ Cl secondary bonds (Table 3) can be compared to that [3.486(7) Å] for quinolinium trichlorodimethylstannate(IV) where this bond links two $Me_2SnCl_3^-$ ions into dimeric units.[34] The cation here is very important since in $[Me_2Sn(terpyridyl)]$-$[Me_2SnCl_3]$ the anion shows no Sn $\cdots$ Cl contacts <3.7 Å;[35] nor does the ion $[Me_2SnCl_3]^-$ in $[Mo_2(\eta^5-C_5H_5)_2S_4][Me_2SnCl_3]$, although it does contain a very long Sn–Cl distance (2.696 Å).[33]

The Sn $\cdots$ Br secondary bond in Et_2SnBr_2 has the same length [3.774(5) Å] as the intramolecular interaction of bromine with tin in (4-bromo-1,2,3,4-tetraphenyl-cis,cis-buta-1,3-dienyl)dimethyltin bromide (resulting in an axially substituted trigonal bipyramid with equatorial organic groups).[37] In that compound also, the C(butadienyl)–Sn–Me angle has opened to 129.0° and Me–Sn–Me to 112.7°. A series of analogous 4-chloro- and 4-bromo-compounds has been investigated in which Sn–Ph replaces Sn–Br. In these compounds, the interaction is drastically weakened so that the Sn $\cdots$ Cl (4.28) and Sn $\cdots$ Br distances (4.35 Å) are both greater than the sum of the two corresponding van der Waals radii. The difference in the two Sn $\cdots$ Br distances is 0.57 Å. Similarly the C(butadienyl)–Sn–Me angles are reduced to 116.5 (4-chloro) and 117.1° (4-bromo).[36]

Factors affecting Intermolecular Interactions.—A CNDO calculation of the valence-electron distribution in a series of Sn^{IV} compounds has shown that for isolated halogeno(dimethyl)stannanes the $5s$ and $5p$ orbital occupancies are strongly dependent on the electronegativity of the halogen.[37] Although the methyl groups donate electrons to the tin, they are unable to replace all the electron density removed by the halogen atoms, leaving a slightly electron-deficient tin atom which can then form secondary bonds. The decreasing electronegativity of the halogens and decreasing overlap with the more diffuse orbitals on bromine and iodine would then qualitatively explain the observed strengths of the secondary interactions. There is also a clear

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connection between secondary-bond strength and the nature of the organic group.

In Me_2SnCl_2, Et_2SnCl_2, and Et_2SnBr_2 the secondary bonding is considerably stronger than in Ph_2SnCl_2. The effect of replacing methyl by ethyl in R_2SnCl_2 is to strengthen the intermolecular bonding by shortening the secondary bond from 3.54(5) to 3.461(4) (mean) Å with the corresponding C–Sn–C angle opening out from 123(4) to 134.0(6)°. These angles are still considerably less than in the more-associated dimethyltin pseudo-halide compounds $Me_2Sn(CN)_2$ [148.7(3.5)°] and $Me_2Sn-(NCS)_2$ [145.9(1.4)°]. The phenyl group produces a significant weakening of the secondary interaction as can be seen from Table 3 and from the dimethyl(tetraphenyl-butadienyl)tin compounds already mentioned. This is presumably due to the ability of the phenyl group to involve available orbitals on the tin atom in inductive and mesomeric interactions so that they cannot overlap effectively with further orbitals. Similarly, the chloro-methyl-group, with a reasonably strong inductive effect, also weakens the secondary bonding. However, the C–Sn–C angle of 135(6)° in $(CH_2Cl)_2SnCl_2$ compared with 123.9(2) and 127.0(2)° in the two crystallographically independent Ph_2SnCl_2 molecules suggests a stronger interaction in the former. If the viewpoint of Bokii et al.[6] is accepted, the difference of 4° between the C–Sn–C angles in the two Ph_2SnCl_2 molecules is directly attributable to secondary-bonding effects.

Hybridisation Models and Other Physical Measurements. —The C–Sn–C angle is important when describing any tin hybridisation model and in interpreting other physical measurements made on tin. Sham and Bancroft,[18] using a simple theoretical model, have correlated the ^{119}Sn Mössbauer quadruple splittings with the C–Sn–C angle in a number of distorted Me_2Sn^{IV} compounds. They find that Me_2SnCl_2 and $Me_2Sn(NO_3)_2$ lie in intermediate positions between the two predicted curves for Me_2SnL_2 and Me_2SnL_4. Recent Mössbauer results have also shown that the amount of tin $5s$ character in the bonds from tin to transition metals and organic groups in the series of compounds X_nR_{3-n}SnM [X = Cl, Br, or C_6F_5; R = Me or Ph; M =

$Mn(CO)_5$ or $Fe(CO)_2(\eta-C_5H_5)]$ decreases in the order: $Sn–Fe(CO)_2(\eta-C_5H_5) > Sn–Mn(CO)_5 > Sn–Me > Sn–Ph > Sn–C_6H_5 > Sn–Cl \approx Sn–Br$. By use of this series they have rationalised the known distortions from tetrahedral geometry in several tin compounds.[28]

The values of the coupling constants $J(^{119}Sn–CH_3)$ also indicate that the s character in the Sn–Me bonds decreases substantially as the C–Sn–C angle decreases.[39] There should be a corresponding increase in the Sn–C distance, which is not always readily seen owing to the difficulty of determining this distance accurately. The idea of a linear relationship between the $J(^{119}Sn–CH_3)$ values and the percentage s character in the Sn–C bonds was advanced by Holmes and Kaesz[40] but has been criticised by McFarlane.[41] van den Berghe and van der Kelen[42] have since suggested that the coupling constants are proportional to the percentage s character of sp^n hybrid orbitals only, since any d orbital involvement in bonding would increase orbital overlap and hence bond strength, whilst not increasing the amount of s character of the hybrid orbital.

In *trans*-octahedral complexes, the bonding may, therefore, be described in terms of sp_z hybridisation of the tin with p_x and p_y orbitals used in the equatorial bonds.[43] The resulting equatorial bonds should then be longer than those observed for tetrahedral compounds as is generally found (*cf.* Ph_2SnCl_2 and Et_2SnCl_2). In the present compounds (1)—(3), which are clearly intermediate between tetrahedral and *trans*-octahedral, the tin hybridisation must be intermediate between sp^3 and sp and involvement of the $3d$ orbitals is possible. The Mössbauer parameters and other physical measurements have been made on the present compounds as well as on a series of related mixed-halogen species.[44]

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# Preparation and X-Ray Structure of a Novel Pseudo-polyhalide Anion [Me₂N(ICl)₂]⁻

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Summary The reaction of dimethylchloramine with an excess of iodomethane at room temperature gives a yellow crystalline material which has been shown by low temperature X-ray analysis to contain the [Me₄N]⁺ cation and the novel anion [Me₂N(ICl)₂]⁻ which can be regarded as having the structure (A), analogous to [I₄]²⁻, with [NMe₂]⁻ as a pseudo-halide ion.

During the study of the halogen-substituted ammonium cations, the reactions of dimethylchloramine with a series of potential alkylating agents were investigated and it was found that powerful alkylating agents such as methyl fluorosulphate gave salts of the colourless trimethylchloroammonium ion [equation (1)].

$$Me_2NCl + MeO.SO_2F \longrightarrow [Me_3NCl]^+[SO_3F]^- \quad (1)$$
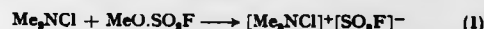
In contrast to this, when dimethylchloramine was dissolved in an excess of iodomethane at room temperature, a fine yellow solid slowly precipitated. The elemental analysis showed the compound to have the empirical formula C₃H₉ClIN. The product was formed quantitatively on the dimethylchloramine taken, with respect to equation (2).

$$2Me_2NCl + 2MeI \longrightarrow [Me_4N]^+[Me_2N(ICl)_2]^- \quad (2)$$

The compound represented an isomer of the known adduct of trimethylamine with iodine monochloride,[1] but the i.r. spectrum clearly showed that the compound was of a different structure. Crystals of the compound were obtained by its slow preparation in tetrahydrofuran at 243 K over a number of months.

Crystal data: C₆H₁₈Cl₂I₂N₂, M 442·92, monoclinic, a = 11·233(3), b = 5·773(1), c = 11·087(2) Å, β = 98·24(2)°, U = 711·6(3) Å³, D_c = 2·067 for Z = 4, D_m = 2·08 g cm⁻³, Mo-K_α radiation, λ = 0·71·69 Å, space group P2/c.

(A)
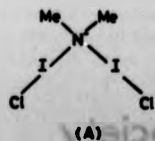
The crystals decompose in a few hours at 20 °C, so all X-ray work was performed at −60 °C using a Syntex P2₁ diffractometer with an LT-1 low temperature device. Three-dimensional data were collected to a maximum 2θ of 60° and reduced to 1855 observed reflections [I/σ(I) ≥ 3·0]. The structure was solved by Patterson methods. The crystals are invariably twinned (a' = c) but the effects

of this were removed by excluding all data with sin θ/λ < 0·5 from the final refinement. Least-squares refinement using the remaining 1045 reflections resulted in an R factor of 0·066 (I and Cl with anisotropic temperature factors).†
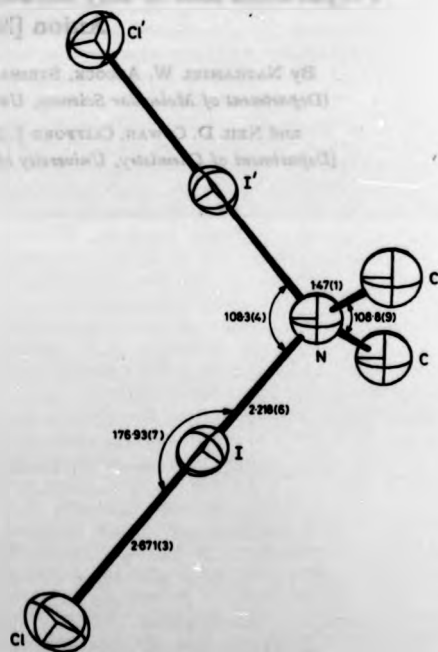
Figure. Structure of the [Me₂N(ICl)₂] ion. Primed atoms are related to unprimed ones by the crystallographic 2-fold axis. Bond distances are in Å.

The crystal has been found to consist of [NMe₄]⁺ and [Me₂N(ICl)₂]⁻ ions, each with crystallographic two-fold symmetry (Figure). The only possible analogues to the novel anion are the polyhalide anions, in particular [I₄]²⁻ which exists as a nearly planar V-shaped ion.[2] In parallel with this, the present anion can be regarded as having the structure (A) with [Me₂N]⁻ considered as a new pseudo-halide. The N–I and I–Cl distances in the anion are 2·219(6) and 2·671(3) Å, respectively, and the N–I–Cl system is very nearly linear [∠N–I–Cl = 176·9(1)°].

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Other angles around nitrogen have values close to those for a tetrahedron. The I–Cl bond length is considerably longer than in gaseous ICl (2·321 Å)[3] or in the adducts of iodine monochloride with pyridine (2·510 Å),[4] 2-chloroquinoline (2·446 Å),[5] and trimethylamine (2·52 Å).[1] The observed N–I distance is shorter than the N–I bond lengths in the same adducts (2·29, 2·43, and 2·30 Å, respectively). However, the N–I distance is longer than the single N–I bond lengths of 2·09 and 2·14 Å observed in the adducts NI₃·C₅H₅N and NI₃·I₂C₅H₁₁N₄,[6] though the former also has a longer N–I bond of 2·36 Å to a further iodine linking NI₃ tetrahedra together.

If the bonding in the present anion is described in terms of charge transfer interactions between lone pairs of electrons on the nitrogen atom and two iodine monochloride molecules, the short N–I and long I–Cl distances

indicate that these interactions are the strongest so far observed for iodine monochloride adducts.

The study of this and similar compounds is continuing. When dimethylbromamine is treated with methyl iodide, the corresponding bromo-compound is produced, formulated as [Me₄N]⁺[Me₂N(IBr)₂]⁻, but the interaction of dimethylchloramine with methyl bromide gives the compound Me₃NBrCl. When methyl chloride is used as the alkylating agent, only decomposition products of the chloramine are obtained.

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Isomeric *Hypho* Borane Structures B₈H₉.L [L = (Ph₂P)₂CH₂, (Ph₂PCH₂)₂, or (Me₂NCH₃)₂]; *X*-Ray Crystal and Molecular Structures

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Summary The X-ray crystal structures of the 1:1 complexes, containing *hypho* boron polyhedra, derived from pentaborane(9) and the ligands bis(diphenylphosphino)-methane (dppm), bis(diphenylphosphino)ethane (dppe), and tetramethylethylenediamine (tmed) are reported; the dppm and dppe structures both show the phosphorus atoms bridging the apical and basal atoms of a flattened pyramidal B₅ framework (with rearrangement of the hydrogen atoms), the tmed complex differing markedly, with the ligand chelating one of the originally basal boron atoms, which becomes singly bonded to the apical boron atom and is separated from the remaining basal atoms by typical non-bonded contact distances.

The boranes and carbaboranes form *closo-*, *nido-*, *arachno-*, and *hypho-*derivatives,[1] and a knowledge of all these classes is required before their co-operative role in rearrangement reactions of polyhedral frameworks, or as reaction intermediates can be fully rationalised.[2] Unfortunately, very few examples of the *hypho-*class are known. Such systems should possess (*n* + 4) skeletal electron pairs with the framework atoms occupying *n* vertices of an (*n* + 3) vertex polyhedron, and some support for this proposal has come from the crystal structures of the adducts B₅H₉·2L and B₆H₁₀·2L (L = PMe₃).[3,4] We now report the properties and crystal structures of three further derivatives which are isoelectronic with the hypothetical *hypho-*B₅H₁₄³⁻ ion, *viz.* B₅H₉·L [L = dppm, (I); dppe, (II); and tmed, (III)]†] and which show significant differences, illustrating the diversity possible within such a related series.

The colourless adducts (I) (m.p. 185—187 °C), and (II) (m.p. 158—160 °C) were prepared by stirring equimolar quantities of B₅H₉ and the ligand in tetrahydrofuran
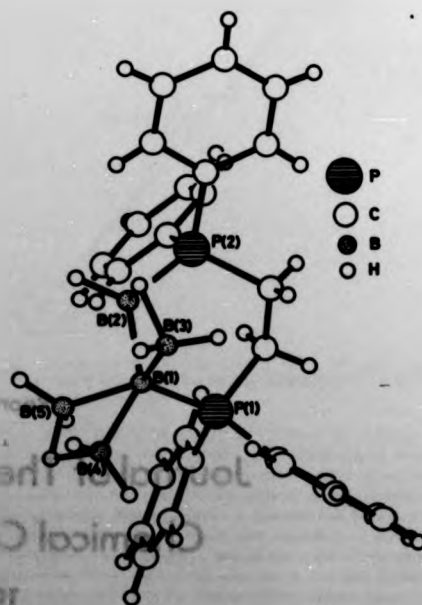

Figure 1. General view of molecule of (II). Distances P(1)–B(1) and P(2)–B(2) are 1·962(4) and 1·929(4) Å, respectively.

† dppm = bis(diphenylphosphino)methane, dppe = bis(diphenylphosphino)ethane, tmed = tetramethylethylenediamine.

(THF) at 25 °C for 72 h; variations in the conditions led to high-melting polymeric products. Both adducts are stable in air, and only slowly hydrolysed by hot water or acid, which is remarkable for B₅H₉ derivatives. However, the anions, B₅H₉·L⁻ (L = dppm or dppe), are similar to B₅H₈⁻ itself, and are readily hydrolysed. The adduct (III), obtained by condensing an excess of B₅H₉ on the ligand, was air-sensitive and could only be stored or recrystallised without decomposition if an excess of ligand was present.

Crystal data: (I), C₂₅H₃₁B₅P₂·½C₄H₈O, *M* 481·5, orthorhombic, *a* = 7·931(4), *b* = 16·816(5), *c* = 23·271(8) Å, *U* = 3105(2) Å³, *D*ₒ = 1·03 g cm⁻³, *Z* = 4, space group *P*2₁2₁2₁, (II), C₂₆H₃₃B₅P₂, *M* 461·6, orthorhombic, *a* = 14·297(4), *b* = 16·492(6), *c* = 22·280(9) Å, *U* = 5243(3) Å³, *D*ₒ = 1·17 g cm⁻³, *Z* = 8, space group *Pbca*. (III), C₆H₂₀B₅N₂, *M* 179·3, orthorhombic, *a* = 12·940(2), *b* = 12·911(3), *c* = 15·046(2) Å, *U* = 2513·9(8) Å³, *D*ₒ = 0·95 g cm⁻³, *Z* = 8 (2 independent molecules), space group *P*2₁2₁2₁.

Three-dimensional X-ray data for all three compounds were collected on a Syntex P2₁ diffractometer using Mo-*K*α radiation (λ = 0·71069 Å). 1850, 2643, and 1200 independent reflections with *I*/σ(*I*) > 3·0 were collected for compounds (I), (II), and (III), respectively. All three structures were solved using the direct methods programs NORMAL and MULTAN. Block diagonal least-squares refinement has produced *R* factors of 0·070 (I), 0·047 (II), and 0·062 (III), using anisotropic temperature factors for all non-hydrogen atoms except for the disordered THF solvent in (I) and for one of the tmed ligands in (III) which exists in two different conformations.‡
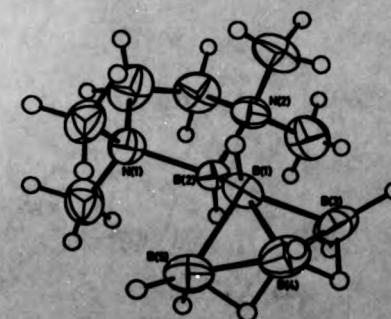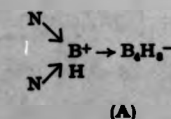

Figure 2. ORTEP view of the ordered molecule of (III). Some distances are: N(1)–B(3), 1·694(9); N(2)–B(3), 1·663(9); B(1)–B(3), 1·718(10); B(1)–B(2), 1·823(12); B(1)–B(4), 1·806(12); and B(1)–B(5), 1·906(12) Å. The non-bonded distances B(3) ··· B(3) and B(3) ··· B(5) are 2·735(12) and 2·713(11) Å, respectively.

In both B₅H₉·dppm (I) and B₅H₉·dppe (II) (Figure 1), the B₅H₉ species has become a shallow pyramid with major rearrangements of the hydrogen atoms; the hydrogen at the apex has moved to the base where three BH₂ groups and two symmetrical B–H–B bridges are found. The phosphorus atoms bridge the apical and basal positions, and the angle between opposite triangular B₃ faces is 130·4° (I) and 126·5° (II) compared with 90—91° in B₅H₉. With 9 electron pairs to accommodate in the *hypho-*B₅ skeleton, the boron atoms should occupy all but three vertices of an 8-vertex polyhedron, the most common example of which is the dodecahedron. However, the present B₅ geometry more closely resembles a hexagonal bipyramid with a centre to apex height of 0·64 Å and with edge lengths of 1·81 (equatorial) and 1·77 Å (apex to base) in (I). The corresponding values in (II) are 0·645, 1·82, and 1·78 Å. Although full structural parameters have not been published, the *hypho-*B₅ group in B₅H₉·2PMe₃ is apparently similar to those in (I) and (II). The average non-bonded distances of B(2) ··· B(5) and B(3) ··· B(4) in (I) and (II) are 2·76 and 2·74 respectively, close to the corresponding distance of 2·97 Å in B₅H₁₁.[5]

In B₅H₉·tmed (III) (Figure 2), both independent molecules contain a B₅ framework which is markedly different from those in (I) and (II). Both nitrogen atoms donate to the same 'basal' boron atom. This atom has become singly bonded to the apical boron atom of the remaining B₄H₈ and is separated from the remaining basal atoms by non-bonded contact distances. Such an arrangement of atoms at the 'basal' boron appears to be unique amongst the boranes and their ions. The overall atomic arrangement is still an example of the *hypho* class, however, although the structure can be interpreted in terms of a zwitterionic canonical form (A), since it shows strong

$$N \searrow \atop N \nearrow \ B^+ \rightarrow B_4H_8^-$$

(A)

similarities to adducts of the type L·B₄H₈, where the B₄ fragment would be an *arachno* species.[6] The parent polyhedron for (III) can again be seen as a hexagonal bipyramid [∠B(3)–B(4)–B(5) 106·2 and 107·0°] especially as the B(1),B(3),B(4)–B(1),B(4),B(5) dihedral angles (129·4 and 127·4°) are higher than the value of 118·1° in B₅H₁₀.[7] A structure involving the ligand chelating at a single boron position was previously favoured on the basis of i.r. and n.m.r. evidence, although the arrangement of boron and hydrogen atoms was uncertain.[6] A gross movement of one of the basal boron atoms also occurs when B₆H₁₀ is converted into B₆H₁₀·2PMe₃, although in this case the resulting *hypho-*B₆ fragment forms an open framework resembling the equatorial belt of an icosahedron rather than occupying all but three vertices of a 9-vertex polyhedron such as a tricapped trigonal prism.[4]

The differences between the structures of (I) and (II) compared with (III) are surprising. In B₅H₉ there is residual negative charge at the apical boron atom, and the ability of the phosphine ligands to withdraw electron density through π-type interactions might account for their preferential co-ordination at the apical position,[2,3] while the co-ordination of tmed at the basal positions could be predicted since no π-effects are possible. The different

framework arrangements in (I) and (II) and (III) could also reflect the need to delocalise the greater electron density placed on the B_4 skeleton by the tmed ligand, and the retention of an integral B_4 unit in (III) is significant in contrast to the two distinct B_2 fragments in (I) and (II). Finally, the presence of a chelate effect is apparent in all the adducts, the monodentate ligand species being much less stable, so that, for example, $B_5H_9 \cdot 2PPh_3$ is completely dissociated at 25 °C.[10] We are investigating the influence of related ligands on the skeletal atom arrangement.

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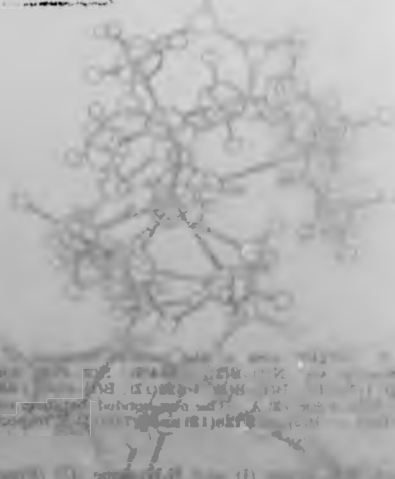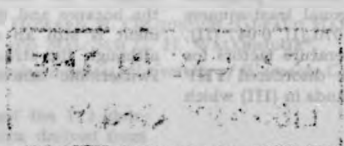[5] L. R. Lavine and W. N. Lipscomb, J. Chem. Phys., 1954, 22, 614.
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