***Ab-Initio* Random Structure Searching of Organic Molecular Solids: Assessment and Validation Against Experimental Data**

Miri Zilka,#, a Dmytro V. Dudenko,#, a, b Colan E. Hughes,b P. Andrew Williams,b Simone Sturniolo,c W. Trent Franks,a Chris J. Pickard,d Jonathan R. Yates,\*, e Kenneth D. M. Harris\*, b and Steven P. Brown\*, a

*a Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom*

*b School of Chemistry, Cardiff University, Park Place, Cardiff CF10 3AT, United Kingdom*

*c Scientific Computing Department, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom*

*d Department of Materials Science & Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, United Kingdom*

*e Department of Materials, University of Oxford, Oxford OX1 3PH, United Kingdom*

**Experimental data as reported in PCCP 2017**

**Figure 2** Le Bail fit (red + marks, experimental data; green line, calculated data; magenta line, difference plot; black tick marks, predicted peak positions) of an experimental powder XRD pattern (recorded at 70 K) of form III of *m*‑ABA starting from the structure obtained following *precise geometry optimization* of the reported crystal structure of form III (see Table 2).

|  |  |
| --- | --- |
| samples | pXRD data |
| mABA III | mABAIII\_70K\_1.raw  mABAIII\_70K\_2.raw  mABAIII\_70K\_3.raw  mABAIIIsum.cpi |

**Figure 3** Results from Le Bail fitting of experimental powder XRD data recorded at 70 K: (a) initial unit cell from structure **1** and experimental data for form III, (b) initial unit cell from structure **2** and experimental data for form III, and (c) initial unit cell from structure **7R** and experimental data for form IV.

|  |  |
| --- | --- |
| samples | pXRD data |
| (a) (b) mABA III | mABAIII\_70K\_1.raw  mABAIII\_70K\_2.raw  mABAIII\_70K\_3.raw  mABAIIIsum.cpi |
| (c) mABA IV | mABAIV\_70K\_1.raw  mABAIV\_70K\_2.raw  mABAIV\_70K\_3.raw  mABAIVsum.cpi |

**Figure 5** 1H-13C (600 MHz) heteronuclear correlation spectra recorded for (a) form III and (b) form IV of *m*‑ABA (MAS frequency, 60 kHz; CP contact time, 100 s). Experimental conditions for (a): 50 *t*1 FIDs with *t*1 increment 83.3 s (using the States-TPPI method to achieve sign discrimination); 128 transients co-added for recycle delay 1.5 s; experimental time 2.7 hrs. The same experimental conditions were used for (b), except: 32 *t*1 FIDs; 512 transients; experimental time 6.8 hrs. In (a), GIPAW calculated chemical shifts are indicated for structure **1** (blue crosses) and the reported crystal structure of form III (red crosses). In (b), GIPAW calculated chemical shifts are indicated for structure **7R** (blue crosses), structure **7** (green crosses) and the reported crystal structure of form IV (red crosses).

|  |  |
| --- | --- |
| samples | NMR data |
| (a) mABA III | Recorded 09/05/2016  Dataset: 2016May09\_mABAtypeIII\_1.3mm |
| (b) mABA IV | Recorded 09/05/2016  Dataset: 2016May09\_mABAtypeIII\_1.3mm |
|  | GIPAW data |
| (a) airss 1 | airss-1.magres |
| (a) mABA III | form-III.magres |
| (b) airss 7 | airss-7.magres |
| (b) airss 7R | airss-7-rot.magres |
| (b) mABA IV | form-IV.magres |

**Computational Files**

AIRSS output

\*.res output of the AIRSS run. Crystal structure in Shelx format

maba.cell / maba.param AIRSS input files

AIRSS\_precise\_bc

\*.cif crystal structures after precise DFT optimisation

MAGRES files

\*.magres magres files containing calculated NMR parameters