**MAS NMR Investigation of Molecular Order in an Ionic Liquid Crystal**

**Sarah K. Mann,a Mohit K. Devgan,b W. Trent Franks,a,c Steven Huband,a Chi Long Chan,b Jeraime Griffith,b David Pugh,b Nicholas J. Brooks,b Tom Welton,b Tran N. Pham,d Lisa L. McQueen,e Józef R. Lewandowski,\*c and Steven P. Brown\*a**

*aDepartment of Physics, University of Warwick, Coventry CV4 7AL, U.K, E-mail: S.P.Brown@warwick.ac.uk*

*bDepartment of Chemistry, Imperial College London, London, SW7 2AZ, U.K*

*cDepartment of Chemistry, University of Warwick, Coventry CV4 7AL, U.K, E-mail: J.R.Lewandowski@warwick.ac.uk*

*dGSK R&D, Stevenage, Hertfordshire SG1 2NY, U.K*

*eGSK R&D, Collegeville, PA 19426, U.S.A*

Correspondence email: S.P.Brown@warwick.ac.uk

In the following, the names of all raw data files from the measurements are presented.

1. **Raw files from SAXS experiments.** Measurements were performed by Steven Huband.

**Figures 2a and S6:** Variable temperature SAXS (recorded on 31/07/18). List of temperatures: **Temps.xls** , parameters: **Parameters.xls**, and raw data file for each temperature, formatted as three columns: *q* (Å-1), intensity (cm-1) and uncertainty (cm-1): **T\_####C.xye**

1. **Raw files from polarising optical microscopy.** Images taken by Chi Long Chanand Mohit K. Devgan.

**Figure 3:** Polarising optical micrograph (×) of CAGE oct: **4X\_heating\_4x\_2degmin15\_t2.tif** (recorded on 15/09/19).

**Figure S7:** Polarising optical micrographs (×20) of CAGE oct upon heating the sample (recorded on 15/09/19). Images taken from videos: **20x\_slow\_heating\_part1\_(from\_18C).avi** and **20x\_slow\_heating part2\_(from\_21C\_to 25).avi**

1. **Raw files from MAS NMR experiments.** Measurements were performed by Sarah K. Mann.

**Figure 4a:** 1H (500 MHz) one-pulse MAS (5 kHz) NMR spectrum (T = 273 K): **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/8**

**Figure 4b:** 1H (500 MHz) one-pulse MAS (5 kHz) variable temperature NMR spectra:

T = 268 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/7**

T = 273 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/8**

T = 278 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/9**

T = 283 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/10**

T = 288 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/11**

T = 293 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/12**

T = 298 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/12**

T = 303 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/14**

T = 308 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/15**

T = 313 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/16**

T = 318 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/17**

T = 323 K: **190130\_3.2mm\_HXY\_CAGE-oct\_1H1DVT/18**

**Figures 5 and S8:** 1H13C (500 MHz) HETCOR MAS (5 kHz) NMR spectrum, recorded with a CP contact time of 2.5 ms at 273 K: **180926\_3.2mm\_HX\_CAGE-oct\_CPbu\_HETCOR/8**

**Figure 6:** 1H13C (500 MHz) CP MAS (5 kHz) NMR build-up curves, recorded at 273 K: **180926\_3.2mm\_HX\_CAGE-oct\_CPbu\_HETCOR/5**

**Figures 8 and S11:** 1HDQ 1H SQ (500 MHz) MAS (5 kHz) NMR spectrum, recorded with POST-C7 recoupling for DQ = 1.2 ms at 273 K: **181019\_3.2m\_HX\_CAGE-oct\_DQC7/100**

**Figures 9 and S12:** 1HDQ MAS NMR (500 MHz, 5 kHz) build-up curves, recorded with POST-C7 recoupling at 273 K: **181019\_3.2m\_HX\_CAGE-oct\_DQC7/8**

**Figure S10:** *T*2-recDIPSHIFT profiles (500 MHz, 5 kHz), recorded with 8 rotor periods of recoupling at 273 K:

1H13C CP: **190323\_3.2mm\_HXY\_CAGE-oct\_CPDIPSHIFT/10**

DP: **181129\_3.2mm\_HXY\_CAGE-oct\_DPDIPSHIFT/10**

**Figure S13:** 1HDQ MAS NMR (500 MHz, 5 kHz) build-up curves, recorded with DQ pre-selection at 273 K: **181019\_3.2m\_HX\_CAGE-oct\_DQC7/3**

**Figure S14:** *T*2-recDIPSHIFT profiles (500 MHz, 5 kHz), recorded with 8 rotor periods of recoupling at variable temperatures:

243 K: **190920\_3.2mm\_HXY\_CAGE-oct\_DIPSHIFT\_-30/10**

253 K: **190815\_3.2mm\_HXY\_CAGE-oct\_DIPSHIFT\_-20/10**

257 K: **190323\_3.2mm\_HXY\_CAGE-oct\_CPDIPSHIFT/10**

1. **Raw files from solution NMR experiments.** Measurements were performed by David Pugh.

**Figure S1:**

Solution phase 1H NMR spectrum in (CD3)2SO (recorded on 11/09/17): **HNMR**

Solution phase 13C NMR spectrum in (CD3)2SO (recorded on 11/09/17): **CNMR**

1. **Raw files from IR (ATR).** Measurements were performed by David Pugh.

**Figure S2:** IR spectrum (recorded on 17/10/19): **IR**

1. **Raw files from MS.** Measurements were performed by Lisa Haigh.

**Figure S3:** Negative ion mass spectrum (recorded on 4/10/19): **MS-negative**

**Figure S4:** positive ion mass spectrum (recorded on 4/10/19): **MS-positive**

1. **Calculations.** Calculations were performed by Sarah K. Mann:

Initial CIF file: **CIQBEJ.cif**

CIF file after geometry optimisation of an isolated molecule: **CIQBEJ\_SM-out.cif**