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Structure determination and phase transition behaviour of mesitylene

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Abstract. The crystal structures of three low-temperature phases of perdeuteromesitylene, 1,3,5-trimethylbenzene $(CD_3)_3C_6D_3$, have been determined using high-resolution neutron powder diffraction. The equilibrium phase I structure is cubic, in the space group $P2_13$, with the molecule situated on a 3-fold symmetry axis. Phase II, obtained by freezing over-cooled liquid, is monoclinic, in the space group $P2_1/c$, and comprises one molecule in the asymmetric unit with disordered methyl groups. The phase III structure is triclinic and is reached through a displacive transition at ca. 100 K from the phase II structure. Complementary X-ray single crystal studies confirm the phase II crystal structure and also confirm a fourth and previously unreported phase.

Introduction

1,3,5-trimethylbenzene, more commonly known as mesitylene, is a simple aromatic hydrocarbon with a melting point of 227 K. The high hydrogen density of the compound and the assumption of weakly-hindered rotation of the methyl groups in the solid make mesitylene a candidate neutron moderator material [1-3] and this has stimulated interest in the structure and dynamics in the solid phase. DSC and Raman spectroscopy [4] indicate a rich polymorphism in solid mesitylene. Most recently, neutron spectroscopy [5,6] has been applied to characterise the material and has revealed the presence of both stable and metastable phases. Relatively slow cooling (< 2 K/min) results in the over-cooled liquid passing through phase I and freezing in a metastable phase II. The phase II structure transforms to phase III at around 90 K and this transition is reversible as long as the phase II structure is kept below some 180

K. The phase II structure can be stabilised down to 4.2 K following a set annealing time-temperature profile [5]. The phase II to phase I transition onset is seen at around 190 K and annealing at 220 K produces a phase pure sample which is then stable down to 4.2 K. These three phases of mesitylene can thus be stabilised at 4.2 K making it a model system for the study of the excitation energies of the different methyl group environments whilst the inter-molecular interaction potentials are assumed to remain constant. However until now, interpretation of these spectroscopic data [6] has been restricted due to a lack of crystal structure information.

Experimental

Neutron powder diffraction measurements

A 5 g sample of perdeuteromesitylene, $(CD_3)_3C_6D_3$ (99+%D), obtained from Sigma-Aldrich, was used for all the neutron diffraction measurements. To prepare phase I, the sample was frozen using liquid nitrogen and ground in a stainless steel mortar before loading in to an 11 mm diameter vanadium sample can. The sample was loaded in a vanadium-tailed 'orange' cryostat and annealed at 215 K before cooling to 2 K. Time-of-flight high-resolution neutron powder data were recorded using HRPD at the ISIS pulsed neutron source at 2 K (120µAh, ca. 3.1 h) and then data were recorded every 5 mins while warming the sample to 200 K. To prepare phases II and III, glass wool was added to the sample can to promote the growth of fine crystallites on freezing and the sample loaded in the cryostat at 250 K and then cooled at ca. 2 K/min down to 2 K. Data were recorded at 2 K (75 µAh, ca. 2.1 h) and 140 K (150 µAh, ca. 4.3 h). Data were recorded at backscattering, $<2\theta>=168°$, over a time-of-flight range of between 30 ms to 230 ms, corresponding to a d-spacing range of between 0.6 Å and 4.6 Å. Under these experimental settings the instrumental resolution, $\Delta d/d$, is approximately constant and equal to 8×10^{-4}.

Neutron powder diffraction data were also collected on the OSIRIS spectrometer on a slow-cooled sample in order to characterise the low-temperature phase behaviour. Data were recorded at 2 K at backscattering, $<2\theta>=160°$, over a time-of-flight range of between 11.7 ms to 193.2 ms, corresponding to a d-spacing range of between 0.5 Å and 11 Å with a resolution $\Delta d/d \sim 2 \times 10^{-3}$. The sample was heated in 20 K steps up to 160 K and then in 10 K steps up to 220 K and data collected at each temperature for some 6 h.

A section of the thermogram recorded on OSIRIS on warming is shown in figure 1 and clearly shows the phase III to II transition around 100 K and growth of the phase I structure at ca. 200 K. Intriguingly a fourth phase is visible in a single data set at 180 K which has not been reported previously. The diffraction patterns recorded on HRPD at 2 K (for phase III and I) and at 140 K (phase II) were indexed based on the positions of the first 20 peaks using TOPAS-Academic [7]. Unit cell constants for the three phases are given in table 1 and were in good agreement with the corresponding values determined from the OSIRIS data. At this stage, no reliable unit cell constants could be determined for the phase IV data recorded at 180 K.

Both structures were solved by simulated annealing implemented by TOPAS-Academic using a molecular template based on calculated coordinates of an isolated molecule [5] determined by the Hartree-Fock method. The phase I structure was solved in the space group $P2_13$ with the molecule constrained to lie on a three-fold axis. The structure was then refined without constraints and using anisotropic displacement parameters for the methyl deuterium atoms. CCDC 617877 contains the supplementary crystallographic data for the phase I structure[1] and the final profile fit is shown in figure 2. The phase II structure was solved in the space group $P2_1/c$; however, attempts to refine the structure were unsatisfactory. All powder data sets in this phase showed a strong texture, despite the presence of glass wool in the sample can, which could not be modelled adequately. This restricted the scope of refinement to a model in which only a phenyl-ring C-C bond length, a ring-methyl group C-C bond length, a C-D bond length and three torsion angles in order to define the methyl group orientation were refined. Four isotropic displacement parameters were also refined discriminating between phenyl-ring and methyl-group carbon atoms and ring and methyl-group deuterium atoms. Based on the resulting anomalously large displacement parameters for the methyl-group deuterium atoms it was concluded that the methyl groups were disordered and were modelled subsequently with D-atom occupancies of 0.5. The phase behaviour and sample preparation route for phase II is always likely to produce a poor quality sample as the sample cannot easily be ground. Thus single-crystal methods were chosen in order to determine more reliable structural information.

Table 1. Unit cell constants for mesitylene-d12 determined on HRPD.

Phase	T /K	a /Å	b /Å	c /Å	α /°	β /°	γ /°	V_c /Å^3
I	2	9.0563(1)			90.00			742.78(1)
II	140	8.3200(1)	13.4307(2)	7.5938(3)	90.00	115.034(1)	90.00	768.85(3)
III	2	8.5309(2)	12.7717(2)	7.6990(2)	88.147(3)	116.771(2)	98.888(1)	739.27(3)

X-ray single crystal measurements

Single crystal X-ray diffraction data were collected with Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART Apex CCD diffractometer equipped with an Oxford Cryosystems variable-temperature device and an OHCD laser-assisted crystal growth device. The crystal was grown over the course of 30 min from a sample of the liquid (Sigma-Aldrich, $(CH_3)_3C_6H_3$), in a capillary held at 210 K using the Boese laser-assisted zone-refinement method [8]. Data sets were collected at 200 K, 150 K and 110 K. We report in full the results from the 110 K data collection. Following the 110 K data collection, the crystal was warmed to 200 and then 220 K but remained in the monoclinic phase II but showing signs of melting at the highest temperature. Phase I could not be obtained in single crystal form; however, a fourth phase was obtained direct from the liquid corresponding to a monoclinic structure, V_c=2377Å^3 at 200 K, and with three independent molecules in the asymmetric unit.

The phase II structure was solved by direct methods in $P2_1$ (SHELX-97, [9]; attempted solution in $P2_1/c$ failed), and refined by full-matrix least-squares against $|F|^2$ (SHELX97). It was evident from difference maps that the methyl groups were disordered and so H-atoms were initially placed in ideal positions on these groups in both possible orientations with respect to the phenyl ring. H-atom occupancies were initially fixed at 0.5, but later refined. The two

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[1] These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax +44 1223 336033.)

components were then refined as freely-rotating, variable-metric rigid bodies. The C(sp^2)-H atoms were also initially placed in ideal positions, but these were also treated as variable metric rigid groups. C(sp^3)-H and C(sp^2)-H distances were respectively restrained to be equal. Anisotropic displacement parameters were refined for all C-atoms. Isotropic displacement parameters were refined freely for all H-atoms. CCDC 618820 contains the supplementary crystallographic data for the phase II structure[1].

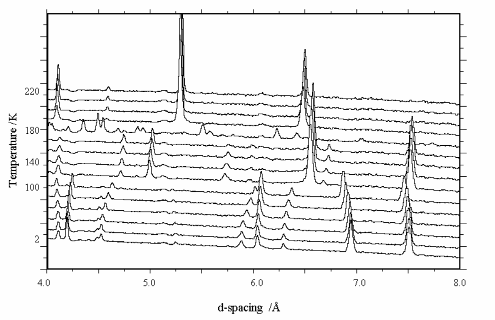

Figure 1. Section of the OSIRIS data thermogram recorded on warming.

Results and discussion

Phase I crystal structure

The asymmetric unit of the phase I structure comprises one third of a molecule and thus six independent atoms. In the structure (figure 3) the molecules are arranged around a three-fold axis via a close contact (at 2 K) of 2.447(2) Å between C(sp^2)-D2 atoms. The corresponding C2...D2 contact is 2.816(2) Å. The D2 atom makes a further 2.584(2) Å contact with methyl-group atom D11 which itself has a further 2.459(3) Å contact with D13. The intramolecular bond lengths and angles are unremarkable with C-C bond lengths of 1.382(2) and 1.387(2) Å around the phenyl ring and 1.523(2) Å to the methyl group C11 carbon atom. The C2-D2 bond length is 1.085(2) Å and the average C11-D bond length within the methyl group is 1.082(2) Å with an average D-C-D angle of 106.6(2) °. The methyl group is rotated slightly compared to the ideal orientation with one deuterium atom perpendicular to the phenyl ring with a C2-C1-C11-D11 torsion angle of 78.9(2) °.

The observation of one independent methyl group on a three-fold symmetry axis is fully consistent with the findings from rotational tunnelling spectroscopy for this phase [6].The phase I structure is the equilibrium phase for mesitylene but the variation of the unit cell parameter shown in figure 2 shows anomalous behaviour above 150 K. This requires further study but most likely is an indication of the onset of free rotation of the methyl group and would also be in line with the reported weak rotational potentials for the methyl groups and librational modes below 15 meV [6].

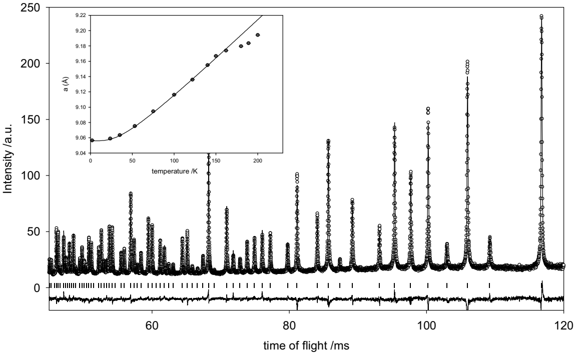

Figure 2. Section of the observed (points), calculated (line) and difference profiles (lower line) for phase I mesitylene at 2 K measured on HRPD. Inset: variation of the cubic lattice parameter with temperature, the line is a fit to the data up to 150 K using a Debye model.

Phase II crystal structure

There is one molecule on a general position in asymmetric unit of phase II and thus three independent although disordered methyl groups in the structure. The molecules are packed in sheets (figure 3) parallel to the crystallographic ab-plane with molecules linked within this plane by H...H contacts of 2.36(2) and 2.32(2) Å as determined by the single crystal refinement at 110 K. The molecular sheets are stacked along the c axis with H...H contacts of 2.36(2) and 2.30(2) Å. This layered nature of the structure most likely explains the severe preferred orientation effects that hampered refinement of the powder data in this phase. At 110 K the intramolecular bond lengths are 1.392(2) Å for the average C-C bond around the phenyl ring and 1.507(2), 1.511(2) and 1.508(2) for the methyl-group carbon bonds. This compares with 1.392(5) Å and 1.520(5) Å respectively determined from the powder refinement at 140 K. Both refinements found two methyl groups of the molecule oriented with an H/D atom essentially parallel to the phenyl ring with the third group oriented with an H/D atom essentially perpendicular to the ring.

The three independent methyl groups observed in the phase II structure is at variance with conclusions drawn from the rotational tunnelling spectroscopy [6] which suggests two inequivalent molecules in the unit cell with the methyl groups sitting on mirror planes to match the degeneracy of the tunnelling modes. It seems likely that the methyl group disorder observed in the present crystal structure determinations could explain the more complex features observed in the tunnelling data of phase II compared with both phases I and III.

Phase III crystal structure

Comparison of the powder diffraction data for phase III recorded using HRPD and OSIRIS show large discrepancies in peak intensities due to preferred orientation effects, as was observed previously for phase II. A full structure refinement for phase III has not been possible using the present data however examination of the lattice parameters for phases II and III (table 1) shows a clear relationship between the two enabling a basic location of the molecules in the phase III structure to be established. Assuming the space group $P\bar{1}$, there are two independent molecules in the asymmetric unit and thus six independent methyl groups in line with the observations from tunnelling and libration spectroscopy [6]. No conclusions can be made regarding disorder of the methyl groups or indeed can the space group *P*1 be ruled out for this structure.

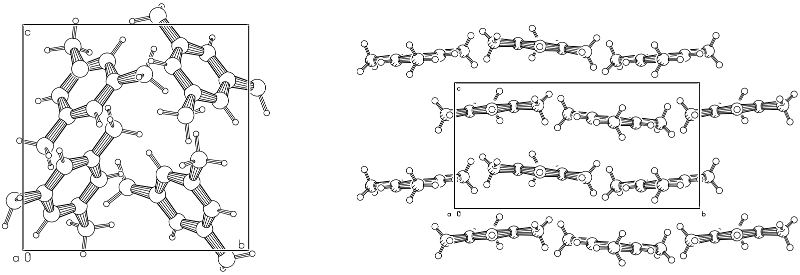

Figure 3. Perspective view of the molecular packing in phase I (left) and phase II (right) of mesitylene. For clarity the disordered hydrogen atoms have been omitted from phase II.

Concluding remarks

High-resolution neutron powder diffraction, in combination with X-ray single crystal diffraction, has been used to determine structural details for phases I, II and III of mesitylene. In addition, both techniques reveal a fourth phase, IIa, to be reported elsewhere and highlighting further the rich and unusual phase diagram of this simple organic compound.

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