Locked-in methyl groups in 1,5-dimethylnaphthalene close to the melting point

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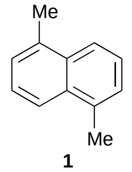
Single crystal neutron diffraction shows that the methyl group conformations in 1,5-dimethylnaphthalene are unchanged, with a hydrogen atom in the molecular plane, even as the crystal approaches the melting point.

Our recent work on variable temperature single crystal neutron diffraction using rapid data collection methods is aimed at changing the overall energy content of the system and monitoring structural changes. These can involve either the internal vibrations of the molecule as indicated by anisotropic thermal parameters, or the order-disorder characteristics of parts of the molecule. These neutron studies have focused on hydrogen atom motions[1] and ordering,[2,3] and the present work represents our first attempt at examining a steric effect using this technique.

We have chosen to study 1,5-dimethylnaphthalene **1**, in which a steric interaction between the methyl groups and the neighbouring hydrogen atoms is likely to occur, reducing the propensity of the methyl groups to freely rotate in the crystal structure. The aim of the present work was to extend previous neutron diffraction measurements of the structure of **1** to higher temperatures and to use the hydrogen thermal parameters to examine the methyl group rotation as the temperature approaches the melting point. The original X-ray study[4] found that the methyl groups in the title compound are sterically ‘frozen’ into a single orientation, a conclusion supported by room temperature neutron diffraction measurements.[5] There was, however, the expectation that these methyl groups would start to rotate from this orientation before the crystal melts (T_m = 353 K) with the rotation predicted to set in above 290 K, but this has not been examined until now.



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To this end, we have collected single crystal neutron diffraction data from the title compound at a series of temperatures, on the SXD at ISIS.[6]† Large single crystals were grown by repeated recrystallisation from an acetone solution of **1** purchased from the Aldrich Chemical Company. Since the samples are volatile, a crystal of dimension 3 × 2 × 2 mm was sealed in a glass capillary and mounted in standard fashion on a Displex helium refrigerator. Initial data frames confirmed the unit cell and space group to be in agreement with previous work. A limited data set was collected at 100 K, followed by full data sets at 290 and 320 K. To allow the final data set to be collected as close to the melting point as practicable, a second crystal was mounted identically to the first and placed into the same cooling device on the instrument. A series of data frames were then collected as the sample was heated from room temperature through the melting point. The intensities of a group of strong reflections in this frame were monitored and significant reduction in intensity found to set in at around 340 K, approximately 10 K below the melting point. It was therefore decided to collect the data at 340 K and the original sample was remounted in identical fashion, heated to this temperature and diffraction data collected.

At all temperatures data were collected and reduced to structure factors in the standard fashion.[6] The structural model from which refinement began was that of ref. 5, but in addition the methyl hydrogens were located in all cases using Fourier calculations, which were computed using the GSAS program.[7] Refinement of the crystal structure at each temperature was carried out by least-squares methods in GSAS, using anisotropic thermal parameters on all atoms (Fig. 1). The data/

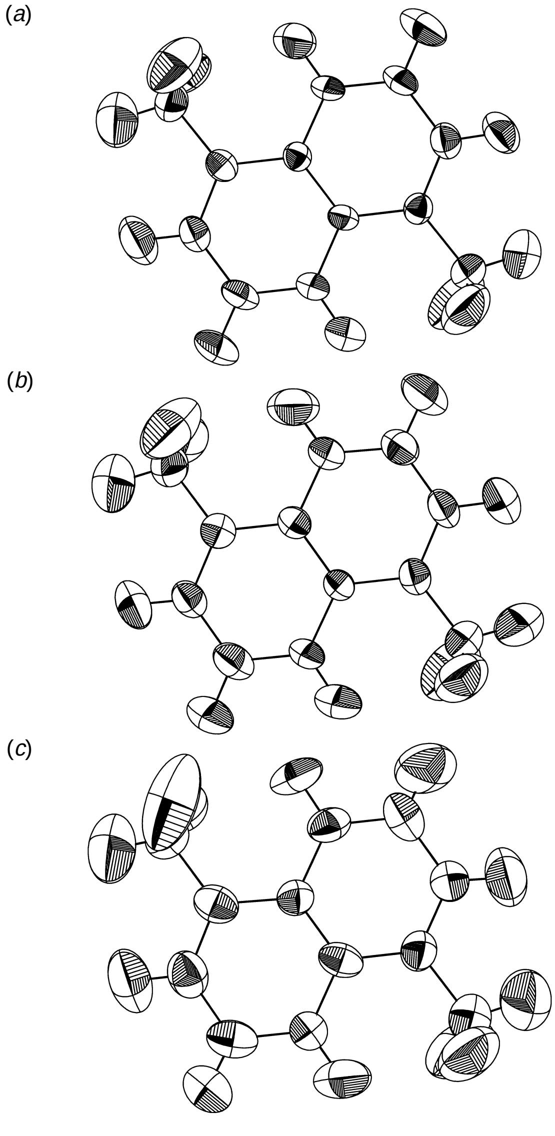

Fig. 1 ORTEP (ref. 10) views of the refined structure of 1,5-dimethylnaphthalene at (*a*) 290, (*b*) 320 and (*c*) 340 K. The ellipsoids are plotted at 50% probability. The plot shows the equilibrium orientation of the methyl groups to be unchanged with increasing temperature.

parameter ratio for the 340 K data set is rather low, due to the fact that the crystal was progressively decreasing in volume as the data collection proceeded; in fact the inter-frame scale factors show that approximately 50% of the crystal was lost during the two days of data collection at 340 K.

The refined anisotropic thermal displacement parameters were subjected to rigid body analysis using the TLS method,[8,9] in which the two methyl groups were treated as undergoing torsional motions about the C–C bonds connecting them to the naphthalene ring. Although the precision of the TLS analysis is rather low, particularly at 340 K because of the low data/parameter ratio, it permits the general trend with temperature to be observed (Fig. 2).

Two major points emerge from the refinements. First, the equilibrium orientation of the methyl groups is essentially the same at all temperatures, and the in-plane hydrogen atom found at room temperature[5] remains in-plane even at 340 K. This observation was confirmed both from the refinements using the room temperature structural model as starting point, and also was clearly indicated by the Fourier calculations, in which the six methyl hydrogens were unambiguously located at all temperatures with no indication of significant atomic density in any other chemically plausible position around these groups. Secondly, the torsional motions of both methyl groups broadly increase with temperature as expected. However, there is an indication of the effect of steric clashes in the relatively low magnitude of these librations even close to melting (compare $\langle \phi^2 \rangle_{340\,\mathrm{K}} = 300^{\circ 2}$ for **1** with $\langle \phi^2 \rangle_{330\,\mathrm{K}} = 940^{\circ 2}$ for a molecule with a methyl group undergoing unhindered rotation, *e.g.* paracetamol[1]).

In conclusion, we clearly have in 1,5-dimethylnaphthalene a sterically hindered molecule in which the propensity of the methyl groups to undergo large torsional oscillations at high temperature is frustrated by steric effects. The methyl groups appear to be restrained in a single equilibrium orientation even close to the melting point, undergoing progressively larger but still hindered vibrations.

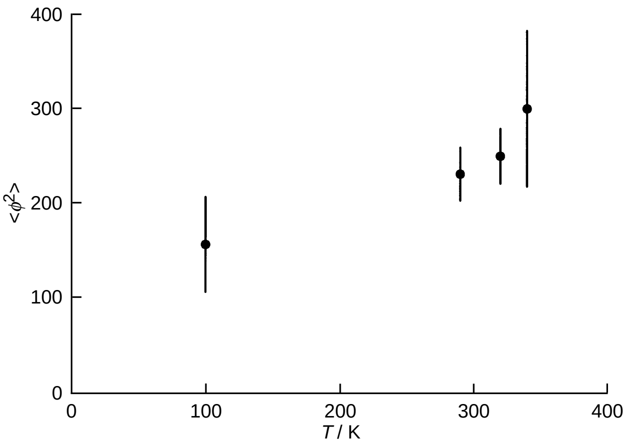

Fig. 2 The average mean square torsional amplitude $\langle \phi^2 \rangle$ for the two methyl groups in 1,5-dimethylnaphthalene as a function of temperature

Footnotes

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[†] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/481.

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Received in Cambridge, UK, 11th April 1997; Com. 7/02479G