Phase Transitions Involving Re-ordering of the Guest Molecules in a Solid Organic Inclusion Compound: Heptanoic Anhydride–Urea

Ian J. Shannon,[a] Kenneth D. M. Harris,[a] François Guillaume,[b] Eduardo H. Bocanegra,[c] Elizabeth J. MacLean[a]

[a] Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ

[b] Laboratoire de Spectroscopie Moléculaire et Cristalline, Université de Bordeaux I, CNRS URA 124, 33405 Talence Cedex, France

[c] Departamento de Física Aplicada II, Facultad de Ciencias, Universidad del País Vasco, 48080 Bilbao, Spain

Phase transitions below ambient temperature in the heptanoic anhydride–urea inclusion compound have been investigated using X-ray diffraction and differential scanning calorimetry; one of these phase transitions (at ca. 179 K on cooling) is associated with a change in the mode of three-dimensional ordering of the heptanoic anhydride guest molecules with no detectable change in the host (urea) structure, and represents the first reported example of this type of phase transition for urea inclusion compounds.

Crystalline urea inclusion compounds,[1,2] in which 'guest' molecules are constrained to occupy one-dimensional tunnels within the solid 'host' (urea) structure, have recently attracted considerable attention with regard to their structural and dynamic properties. Although the conventional urea inclusion compounds all possess the same host structure,[3,4] at least on a space-average and time-average, details of the structural and dynamic properties of the guest molecules can differ substantially between one family (i.e. homologous series) of guest molecules and another, and, in some cases, even between different guest molecules within a given family (vide infra). For the alkane–urea and α,ω-dibromoalkane–urea inclusion compounds, a low temperature phase transition involving a change in the host structure from hexagonal to orthorhombic is well established,[5–7] but is apparently not associated with any change in the mode of three-dimensional ordering of the guest molecules. Here we report that the urea inclusion compound containing heptanoic anhydride (HA) as the guest component exhibits new behaviour with regard to low temperature phase transitions, not observed hitherto for urea inclusion compounds.

In the conventional urea inclusion compounds,[3,4] the host structure comprises an extensively hydrogen-bonded arrangement of urea molecules, within which there are parallel, unidirectional tunnels (diameter[8] ca. 5.5–5.8 Å). The guest molecules are densely packed along the tunnels,[9] and generally there is sufficient ordering of the guest molecules to allow an average three-dimensional lattice to be defined,[10–13] despite substantial dynamic disorder of the guest molecules at ambient temperature. In the conventional urea inclusion compounds, there is usually an incommensurate relationship[14] between the host and guest substructures along the tunnel axis. A detailed discussion of the structural and diffraction properties of urea inclusion compounds is given in ref. 4. Three-dimensional ordering of guest molecules in urea inclusion compounds is conveniently considered in terms of two parameters[11] (Fig. 1): (i) the periodic repeat distance (c_g) of the guest molecules along the tunnel axis; and (ii) the offset (Δ_g), along the tunnel axis, between the centres of mass of guest molecules in adjacent
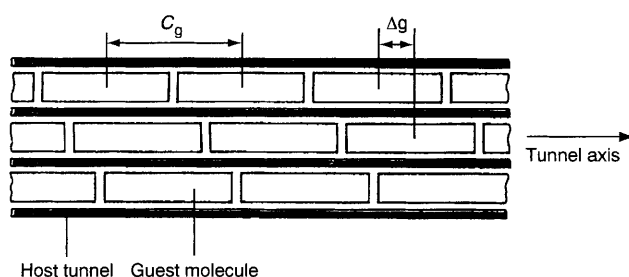

Fig. 1 Schematic two-dimensional representation of a urea inclusion compound, viewed perpendicular to the tunnel axis, indicating the definitions of c_g and Δ_g

tunnels. The method for determining Δ_g from de Jong–Bouman or precession X-ray diffraction photographs for urea inclusion compounds has been developed in ref. 11.

The structural properties at ambient temperature of urea inclusion compounds containing carboxylic acid anhydride guest molecules $Me(CH_2)_nCO_2CO(CH_2)_nMe$ (with $n = 3$–8 and 10) have been studied previously[13] by single crystal X-ray diffraction. All of these materials possess the conventional (hexagonal) urea tunnel structure, but exhibit different modes of ordering of the guest molecules, with $\Delta_g = 2.3$ Å for HA ($n = 5$) and $\Delta_g = 0$ for all the other carboxylic acid anhydrides studies. As reported in this paper, the HA–urea inclusion compound exhibits further novel behaviour concerning its structural properties below ambient temperature.

The HA–urea inclusion compound was crystallized by cooling a solution containing HA and urea in dry 1,1-dimethyl-propanol from 60 to 25 °C. The crystals were washed with 2,2,4-trimethylpentane to remove any molecules of HA adhering to their external surfaces. Powder X-ray diffraction and solid state ^{13}C NMR confirmed that these crystals were urea inclusion compounds of HA with the conventional urea host structure. Differential scanning calorigrams were recorded on a Perkin–Elmer DSC-7 instrument; the sample was subjected to a cycle of cooling and heating between 298 and 103 K at a cooling/heating rate of 10 K min^{-1}. Single crystal X-ray diffraction photographs were recorded using Ni-filtered Cu-Kα radiation on an Enraf–Nonius Weissenberg camera (for oscillation photographs) and on a Huber precession camera.

On cooling HA–urea, differential scanning calorimetry (Fig. 2) indicates exotherms (peak maximum temperatures; associated enthalpy changes in brackets) at 179 K (-0.09 J g^{-1}) and 122 K (-1.5 J g^{-1}). These results identify three temperature regimes, denoted phase I (above 179 K), phase II (179–122 K) and phase III (below 122 K). On warming HA–urea, endotherms are observed (Fig. 2) at 133 K (1.4 J g^{-1}) and 187 K (0.06 J g^{-1}). Clearly there is significant thermal hysteresis in these transitions. There is possibly an additional transition (at ca. 152 K on cooling and ca. 157 K on heating), although more detailed investigations are required to establish the existence and nature of this transition.

Single crystal X-ray diffraction experiments were carried out to investigate the structural properties of HA–urea in phases I, II and III. At ambient temperature (phase I), the host is the conventional urea tunnel structure[3,4] and the guest molecules exhibit three-dimensional ordering with $\Delta_g = 2.3$ Å, as discussed previously.[13] Six domains of this guest structure can be distinguished by diffraction, with each domain having an identical packing of guest molecules but a different (although equivalent) orientation with respect to the host structure; the different domains are related by $m\pi/3$ rotation ($m = 0, 1, ..., 5$) about the tunnel axis. At 160 K (phase II), a new mode of inter-tunnel ordering of the guest molecules, corresponding to $\Delta_g = 1.5$ Å, is observed (again with six domains related by $m\pi/3$ rotation about the tunnel axis); in addition, there is evidence

(from weak diffraction features) for some co-existence of regions corresponding to Δ_g = 2.3 Å. In phase II, the host is still the hexagonal ('high-temperature') structure of the conventional urea inclusion compounds. At 111 K (phase III), the inter-tunnel ordering of the guest molecules is described predominantly by Δ_g = 0, but with some co-existence of regions corresponding to Δ_g = 1.5 Å; at this temperature, the host is the orthorhombic ('low-temperature') structure characterized previously[5–7] for alkane–urea and α,ω-dibromoalkane–urea inclusion compounds. On warming the inclusion compound to 145 K (phase II), the Δ_g = 1.5 Å mode of ordering of the guest molecules is again generated and the host structure is again the hexagonal structure of the conventional urea inclusion compounds; in the guest substructure, there is some co-existence of regions corresponding to Δ_g = 0 and there is also evidence (although very weak diffraction features) for co-existence of additional regions with Δ_g = 2.3 Å.

In summary, the transition between phases I and II is associated with a change in the mode of three-dimensional ordering of the guest molecules with no (detectable) change in the host structure; this is the first example of such a phase transition for a urea inclusion compound. The transition between phases II and III is associated with the conventional hexagonal-to-orthorhombic change in the host structure concomitant with a change in the mode of three-dimensional ordering of the guest molecules.

Several aspects of these transitions in HA–urea remain to be understood, including identification of the interactions responsible for inducing the changes in the ordering of the guest molecules. In this regard, the fact that the host structure does not change at the transition between phases I and II suggests that the re-ordering of the guest molecules at this transition is not associated with a change in the incommensurate/commensurate nature of the inclusion compound.† Nevertheless, if the

inclusion compound is incommensurate, the transition between phases I and II will be associated with changes in the incommensurate modulations within the host substructure (which control the propagation of the ordering of guest molecules between adjacent tunnels.[15] The transition between phases II and III raises further important issues, including the contrasting behaviour between the HA–urea inclusion compound and the alkane–urea and α,ω-dibromoalkane–urea inclusion compounds; in the latter cases, the transition involving a change in the host structure from hexagonal to orthorhombic is not associated with a change in the mode of three-dimensional ordering of the guest molecules.

Our future investigations of the HA–urea inclusion compound will focus on a more detailed determination of the temperature-dependence of the structural properties, with particular interest in establishing how the co-existence of regions with different modes of ordering of the guest molecules changes as a function of temperature within phase II. In this regard, the possible existence of an additional transition at ca. 152 K merits a detailed study.

Footnote

† As discussed in ref. 13, one possible explanation for the fact that HA–urea exhibits a different mode of guest molecule ordering at ambient temperature than the other carboxylic acid anhydride-urea inclusion compounds is that it may actually be a commensurate inclusion compound. However, there is presently no direct evidence to support the definitive assignment of HA–urea as a commensurate inclusion compound at ambient temperature (phase I).

References

1 K. Takemoto and N. Sonoda, in Inclusion Compounds, eds. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, New York, 1984, vol. 2, p. 47.
2 K. D. M. Harris, J. Solid State Chem., 1993, 106, 83.
3 A. E. Smith, Acta Crystallogr., 1952, 5, 224.
4 K. D. M. Harris and J. M. Thomas, J. Chem. Soc., Faraday Trans., 1990, 86, 2985.
5 Y. Chatani, Y. Taki and H. Tadokoro, Acta Crystallogr., 1977, B33, 309.
6 Y. Chatani, H. Anraku and Y. Taki, Mol. Cryst. Liq. Cryst., 1978, 48, 219.
7 K. D. M. Harris, I. Gameson and J. M. Thomas, J. Chem. Soc., Faraday Trans., 1990, 86, 3135.
8 A. R. George and K. D. M. Harris, J. Mol. Graphics, 1995, 13, 138.
9 F. Laves, N. Nicolaides and K. C. Peng, Z. Kristallogr., 1965, 121, 258.
10 K. Fukao, H. Miyaji and K. Asai, J. Chem. Phys., 1986, 84, 6360.
11 K. D. M. Harris and M. D. Hollingsworth, Proc. Royal Soc. A, 1990, 431, 245.
12 K. D. M. Harris, S. P. Smart and M. D. Hollingsworth, J. Chem. Soc., Faraday Trans., 1991, 87, 3423.
13 I. J. Shannon, N. M. Stainton and K. D. M. Harris, J. Mater. Chem., 1993, 3, 1085.
14 A. J. O. Rennie and K. D. M. Harris, Proc. Royal Soc. A, 1990, 430, 615.
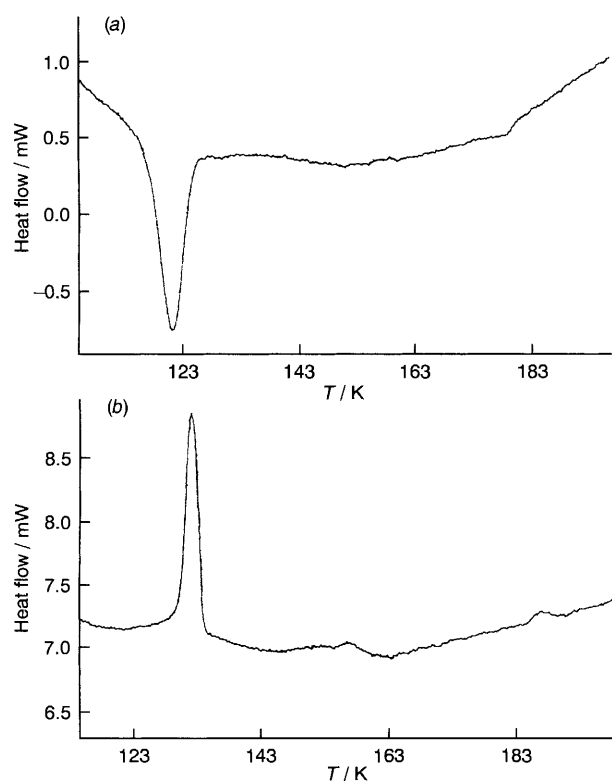15 S. van Smaalen and K. D. M. Harris, Proc. Royal Soc. A,, in the press.

Fig. 2 Differential scanning calorigrams for HA–urea on: (a) cooling from 298 to 103 K, and (b) warming from 103 to 298 K