Low-temperature form of urea adducts with *n*-paraffins.

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Orientational order–disorder transitions of the adducts of urea with *n*-paraffins (C_{10}, C_{16}, C_{20} and C_{36}) were evidenced by X-ray diffraction to be fairly strongly co-operative. The hexagonal crystals (high-temperature form) transform commonly into orthorhombic crystals (low-temperature form). In the low-temperature forms the hydrocarbon molecules are disposed in definite orientation with respect to the urea-channel axis; deformation of the pure-hexagonal channels of urea molecules is also involved.

Urea forms a series of adducts with *n*-paraffins. These adducts are commonly hexagonal, $P6_122$ (*e.g.* $a = 8.230$, $c = 11.005$ Å for *n*-hexadecane) at room temperature, in which urea (host) molecules form honeycomb-like channels with cavities about 5 Å in diameter (Smith, 1952). Although the hydrocarbon (guest) molecules included in the channels are essentially in planar zigzag conformation, they are rotating or randomly disposed over a finite number (probably three) of possible orientations about their chain axis, since the channel axis coincides with the sixfold screw axis in the unit cell. The motions of guest molecules have been investigated both from the viewpoint of NMR spectroscopy (Gilson & McDowell, 1961; Bell & Richards, 1969) and of the thermodynamical properties (Pemberton & Parsonage, 1965; Parsonage & Pemberton, 1967). In particular, the heat capacity measurements by Pemberton & Parsonage detected abnormal heat absorptions in narrow temperature regions (10–15°), the maxima of which were 110.9 for *n*-decane, 151.8 for *n*-hexadecane and 189.3 K for *n*-eicosane. They explained these heat absorptions in terms of order–disorder transitions with respect to the molecular orientation of guest molecules. In this communication, the phase transitions of urea adducts with several *n*-paraffins are revealed by X-ray diffraction.

Single crystals of urea adducts with *n*-decane $C_{10}H_{22}$, *n*-hexadecane $C_{16}H_{34}$, *n*-eicosane $C_{20}H_{42}$ and *n*-hexatriacontane $C_{36}H_{74}$ were grown from isopropyl alcohol; in particular, *p*-xylene was added for n-$C_{20}H_{42}$ and n-$C_{36}H_{74}$ in order to dissolve the hydrocarbons. A series of X-ray diffraction photographs of these adducts taken at several low temperatures revealed that the hexagonal crystals (high-temperature form) transformed reversibly into crystals of another form (low-temperature form) at their transition temperatures; although no transition temperature had been reported for the n-$C_{36}H_{74}$ adduct, the crystal was still hexagonal at 222 ± 5 K but was in another form at 190 ± 5 K. Our DTA measurement showed an endothermic peak at 218 K.
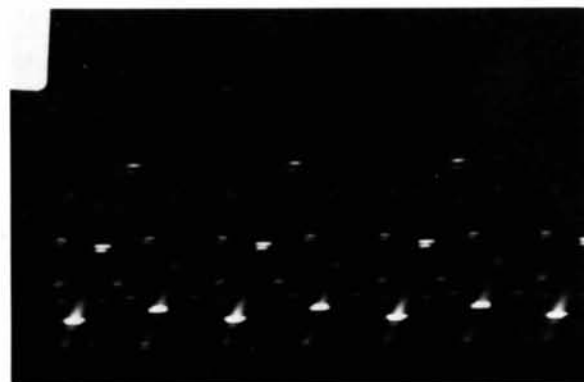
Fig. 1(*a*) and (*b*) shows zero-layer *c*-axis Weissenberg photographs of the high and low-temperature forms, respectively, of the n-$C_{16}H_{34}$ adduct.* The diffraction pattern of the low-temperature form was interpreted as due to a twinned crystal composed of three constituent orthorhombic crystals appearing every 120° about the channel axis (*c*

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31997 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

axis); crystal data for the n-$C_{16}H_{34}$ adduct at 98 ± 3 K are: orthorhombic, $P2_12_12_1$, $a = 8.263$ (8), $b = 13.871$ (10), $c = 10.988$ (12) Å [*cf.* at 165 ± 5 K, hexagonal, $P6_122$, $a = 8.169$ (9), $c = 11.010$ (13) Å]. Therefore, since the b/a ratio is 1.671 ($\simeq \sqrt{3}$), the orthorhombic cell is approximately obtained from the hexagonal cell by the following transformation:

$$\begin{pmatrix} \mathbf{a}_o \\ \mathbf{b}_o \\ \mathbf{c}_o \end{pmatrix} \simeq \begin{pmatrix} 1 & 0 & 0 \\ 1 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_h \\ \mathbf{b}_h \\ \mathbf{c}_h \end{pmatrix},$$
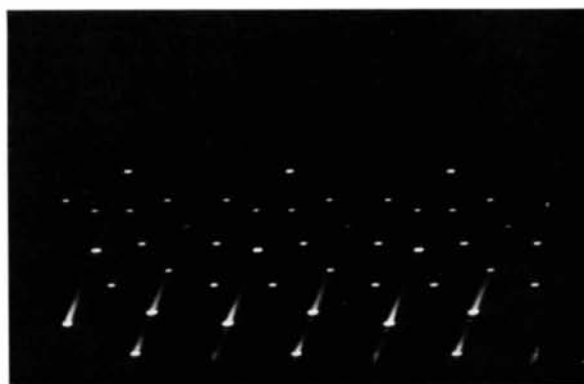
(*a*)

(*b*)

Fig. 1. Zero-layer *c*-axis Weissenberg photographs of urea + *n*-$C_{16}H_{34}$ adduct. (*a*) High-temperature form (at room temperature). (*b*) Low-temperature form (at 98 K).

and the mutual orientations of three constituent crystals are related in reciprocal space (**X**) by

$$\mathbf{X}_{o,1} = \mathbf{R}\mathbf{X}_{o,2} = \mathbf{R}^2\,\mathbf{X}_{o,3}$$

where

$$\mathbf{X}_{o,i} = \begin{pmatrix} h_{o,i}\,a^* \\ k_{o,i}\,b^* \\ l_{o,i}\,c^* \end{pmatrix} \quad \text{and} \quad \mathbf{R} = \begin{pmatrix} \cos 2\pi/3 & -\sin 2\pi/3 & 0 \\ \sin 2\pi/3 & \cos 2\pi/3 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

The reciprocal lattice points of the twinned crystal thus obtained (Fig. 2b) explained the diffraction patterns well. The other three adducts showed features quite similar to those exhibited by the n-$C_{16}H_{34}$ adduct. During observation of the X-ray patterns the crystals of the n-$C_{20}H_{42}$ and n-$C_{36}H_{74}$ adducts in particular, tended to break in the course of transition

(a)

(b)

Fig. 2. Weighted $hk0$ reciprocal lattice points of (a) high-temperature form and (b) low-temperature form of urea + n-$C_{16}H_{34}$ adduct.

from the high-temperature forms to the low-temperature forms. However, the twinned crystals or even somewhat broken crystals of the low-temperature forms of all the adducts recovered the nature of single crystals of the high-temperature forms when they were warmed beyond the transition temperatures.

The orthorhombic cell contains 12 urea molecules, $i.e.$ two urea channels pass through the unit cell. Therefore, there are three non-equivalent urea molecules. The channel length occupied by one guest molecule in each adduct was essentially the same as that in the hexagonal crystal, $e.g.$ the n-$C_{16}H_{34}$ molecule occupies twice the c dimension. Despite the difference between the two crystal symmetries, the orthorhombic crystal can retain the N—H$\cdots$O hydrogen-bonding scheme of urea channels in the hexagonal crystal. This feature has already been proved by structure analysis of the urea adduct with 1,3-butadiene which also forms orthorhombic crystals with space group $P2_12_12_1$ (Chatani & Kuwata, 1975). Fig. 3 shows the structure of the low-temperature form of the n-$C_{16}H_{34}$ adduct viewed along the channel axis. Fig. 4 shows the dimensions of the urea channel. It is clearly seen that the urea channel is distorted from pure hexagonal in the high-temperature form, and the orientation of the guest molecules enables them to occupy the channel. The R value

Fig. 3. Crystal structure of low-temperature form of urea + n-$C_{16}H_{34}$ adduct viewed along the c axis (at 98 K).

Fig. 4. Schematic representation of deformed urea channels of low-temperature form of urea + n-$C_{16}H_{34}$ adduct (at 98 K). Dimensions in Å.

for 104 out of the 146 $hk0$ reflexions observable with Cu $K\alpha$ radiation was 0·100 when the guest molecule was assumed to be zigzag planar [observed and calculated values of $\sqrt{(\Sigma F^2)}$ were compared for the overlapping reflexions]. The n-$C_{16}H_{34}$ molecule is actually shortened by 0·66 Å within the channel [from 22·64 Å for the extended conformation (Laves, Nicolaides & Peng, 1965) to 21·98 Å]. The deformed channel, however, is able to accommodate the slightly contracted molecular chain. Although more detailed analysis of these adducts is in progress, it is deducible from the present result that the order–disorder transitions are fairly strongly co-operative.

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Structural relationships between the polymorphs of silver nitrate.

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The unique structure of $AgNO_3$ II is shown to be a substantial distortion of the $TlNO_3$ III structure. It also has topological links with the aragonite structure of KNO_3 II. When there is sufficient thermal libration of the NO_3^- ion, the structure of II can be converted homogeneously to the high-$NaNO_3$ structure of phase I. The relationship between the structures of I and II helps to explain features of the previously published kinetics of propagation in the thermal transformation $AgNO_3$ I $\rightleftharpoons$ II. Filamentary crystals of phase II have been grown. Their transformation was followed by X-ray diffraction and microscopy. The observations are consistent with operation of structural relationships. Crystals tend to return to their original orientation after a thermal cycle II $\rightarrow$ I $\rightarrow$ II.

The structure of the room-temperature phase II of $AgNO_3$, being unique, has not appeared to fit into the series of $M(XO_3)$ structures. Accordingly, and since no orientation relations were recognizable, the structural transformation $AgNO_3$ II $\xrightarrow{159°C}$ I has been accepted as reconstructive (Asadov, 1968; Asadov, Nasirov & Jabrailova, 1972). This transformation has provided exceptionally extensive data on the kinetics of advance of a phase interface in single-crystal platelets (Kennedy & Schultz, 1963). Although the rates were highly temperature-dependent, as expected for a reconstructive mechanism (reaching a maximum at 110°C and being effectively zero at −30°C), the data led Kennedy & Schultz (1963) to the view that instead of transfer of individually thermally activated ions, micro-regions of many unit cells transformed cooperatively. Such a mechanism would be possible if there existed a direct path for the structural rearrangement. The path is relevant also to recent theories which consider the possibility of a diffuse interface (*e.g.* Temkin, 1973). Elucidation both of crystal packing and of mechanisms therefore requires examination of structural relationships. In the experimental study of transformations filamentary crystals (whiskers) offer the advantages of a

relatively low number of dislocations and relatively little accumulation of transformation stresses, which can cause plastic deformation. In the present work whiskers of $AgNO_3$ have been grown and their transformation observed; and by consideration of the structures the general arrangement of ions in phase II has been shown to be topologically related to the arrangement in phase I and other nitrate structures.

$AgNO_3$ I has the high-$NaNO_3$ structure, space group $R\bar{3}m$, $Z = 1$, $\alpha = 78\cdot0°$ (Fischmeister, 1956). This is calcite-like but has orientational disorder of the anions around their threefold axis (Strømme, 1969). The structure of phase II, symmetry $Pbca$, $Z = 8$, is predominantly ionic but distorted by the tendency of Ag to bond to O (Lindley & Woodward, 1966).

Experimental

Laue, oscillation and precession X-ray patterns were recorded before and after a thermal cycle II $\rightarrow$ I $\rightarrow$ II. The crystals were cemented to a glass fibre on the goniometer head and surrounded by a cylindrical heater. The transformation of whiskers was observed at a magnification of 250 on a polarizing microscope carrying a cine camera and fitted with a transparent glass heating stage. For both X-ray and optical work the temperature was automatically controlled to within 0·1°C. Specimens were heated at 7°C min^{-1} to 157°C, and thereafter very gradually until trans-

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