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Low Temperature Phase Changes in the Urea–Trioxane Inclusion Compound

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Three reversible phase transitions have been detected in the urea trioxane inclusion compound between room temperature and −160°C. They involve a doubling of the hexagonal unit cell near −33°C and small distortions of the host lattice at lower temperature. Nitrogen pure quadrupole resonance experiments show that the nitrogen atoms are distributed between two different crystallographic sites. The nature of the phase changes is discussed.

Introduction

Urea is known to form inclusion compounds with a wide variety of organic molecules, such as normal long chain paraffins and their halogenated derivatives, fatty acids, etc. The symmetry of the urea host lattice in these clathrates belongs to the hexagonal space group $P6_122$ (*1*). Similar compounds are obtained with thiourea, but the host lattice then belongs to the space group $R\bar{3}2/C$ (*2*). Two excellent reviews of such compounds have been recently published by Fetterly (*3*) and Bhatnagar (*4*). Some years ago, Lenne (*5*, *6*) pointed out that urea, as well as thiourea, could yield inclusion compounds with a rhombohedral host lattice (space group $R\bar{3}2/C$). This occurs, in particular, with trioxane as the guest molecule.

It appeared that it would be interesting to compare the nitrogen quadrupole resonance spectrum of the thiourea–cyclohexane inclusion compound (*7*) with that of the urea–trioxane inclusion compound because of their similar crystallographic structure at room temperature. Furthermore, it was of interest to see whether the phase transitions as exhibited by the thiourea–cyclohexane inclusion compound (*7*) constituted a special or a general feature of this type of compound.

Experimental and Results

Preparation and Verification of Samples

The preparation of the urea–trioxane inclusion compound (UTIC) is not described in (*5*) or (*6*). The clathrate was obtained by dissolving 3 g of trioxane in 20 cm^3 of a saturated urea–methanol solution and then slowly cooling the solution to −10°C. Needlelike crystals which can reach 1 cm in length precipitate slowly. Thermogravimetric analysis yields a ratio of about 3 for the number of urea molecules to the number of trioxane molecules. Since the crystals decompose very quickly when exposed to the atmosphere, the analysis lacks precision and experimental values for this ratio were spread throughout the range 3.0–3.3. An X-ray diffraction pattern obtained with a rotating crystal could be indexed in accordance with the rhombohedral structure given by Lenne (*5*) for UTIC.

Differential Thermal Analysis (DTA)

A semimicro method (*8*) was used with samples in the range of 4–5 mg and a "Copper/Gold–Cobalt/Copper" probe. The sample was heated from −170°C to room temperature in a hydrogen atmosphere. Upon heating the sample, thermograms show three endothermic signals at −89°, −77° and −33°C. The corresponding transitions are reversible upon cooling (Fig. 1). Neither pure urea nor pure trioxane exhibit thermal effects in this range. A rough estimate of the enthalpy variations is given in Table I.

Nitrogen Pure Quadrupole Resonance

The study was carried out using a slightly modified Robinson (*9*, *10*) spectrometer. Various temperatures were obtained using a liquid bath

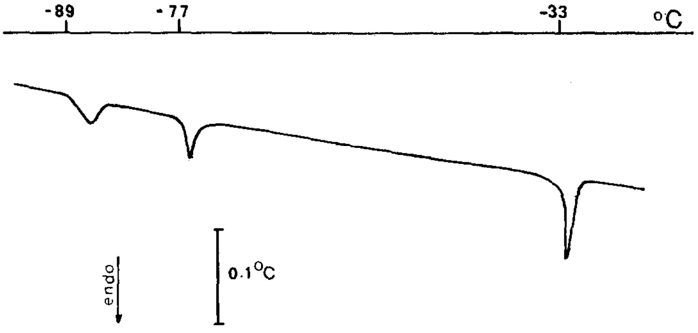

FIG. 1. Differential thermal analysis of UTIC.

of petrol ether contained in a Dewar vessel cooled with liquid nitrogen, and measured with a pentane thermometer, with an accuracy of ±1°C. This device could not be used below −140°C, because the bath solidified.

No resonance signals were found at liquid nitrogen temperature. Above −140°C, UTIC exhibits two ν_1 lines of approximately equal intensity. The signal to noise ratio was poor: 2/1 or 3/1. Only one ν_2 line was found, with a S/N ratio of about 2/1. The study of temperature dependence of the frequencies (Fig. 2) was made between −140° and +10°C. Above +10°C, the lines broaden and then disappear. Interestingly enough the curves $\nu(T)$ as well as their first derivatives do not exhibit any discontinuity at the temperatures corresponding to the DTA signals. Small departures ($\lesssim 1$ kHz) from a regular curve are of little significance because of errors in the temperature and frequency determinations. (The latter errors arise because of weakness of the signals.) The continuity of the $\nu(T)$ curves is in marked contrast with the discontinuities observed in the case of the thiourea–cyclohexane compound (7). Table 2 shows the frequencies measured at dry-ice temperature together with approximate values for the mean quadrupole coupling constant and asymmetry parameter. These values have been calculated using the mean frequency of the ν_1 lines and the single observed frequency of the ν_2 line. Values are very close to those obtained for pure urea.

TABLE I

THE DIFFERENT PHASES OF UTIC WITH ESTIMATES OF ENTHALPY VARIATIONS ASSOCIATED WITH THE DIFFERENT TRANSITIONS (PRECISION ON ΔH IS NOT BETTER THAN 30%

Phase	IV ↔ III	III ↔ II	II ↔ I
Temperature (±2°C)	−89°	−77°	−33°
ΔH per mole of trioxane (cal)	150	150	380

X-Ray Diffraction

The radiocrystallographic study was performed with a modified Debye–Scherrer camera described in a previous paper (7). A monocrystalline needle was put into a Linndeman glass, which was sealed immediately to avoid decomposition. The sample was then rotated about the longitudinal axis of the needle, i.e., the **c** axis of the rhombohedral crystal. X-ray patterns show the equatorial and the first layer lines. Reflections of the equatorial layer line were measured very precisely

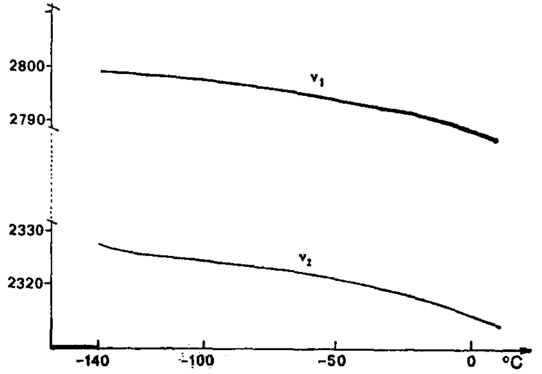

FIG. 2. Temperature dependence of the nitrogen pure quadrupole resonance lines ν_1 and ν_2 in UTIC (above −140°C).

TABLE II

THE ASYMMETRY PARAMETER AND QUADRUPOLE COUPLING CONSTANTS OF UTIC AND PURE UREA

$T = -77°C$	ν_1 (MHz)	ν_2 (MHz)	e^2Qq (MHz)	η
Urea–trioxane	2.892_8 2.798_2	2.324_7	3.450	0.30
Pure urea[a]			3.470	0.32

[a] M. Minematsu (13) and A. Peneau (private communication).

and indexed. Reflections on the first layer line were then indexed using Bernal's chart (*11*).

General considerations. X-ray diffraction patterns were obtained at –20°, –50° and –120°C, i.e., temperatures within ranges defined by the DTA signals. The range –89—77°C was too narrow to be studied with our apparatus. These three diagrams differ markedly from each other as there are many more reflections at low temperature. However, reflections still appear in layer lines at low temperature, showing that the crystal **c** axis has not been disoriented by the phase transformations. Furthermore, the distance between the equatorial and the first layer lines is the same on the three patterns. Hence the magnitude of the c parameter of the host lattice remains constant (about 11.0 Å).

Structure above –33°C. The rhombohedral cell found was identical to the one described in (*5*). When referred to hexagonal axes ($\mathbf{a}_1$, $\mathbf{a}_2$, Fig. 3), only reflections with $h_{\text{hex}} - k_{\text{hex}} + l_{\text{hex}} = 3\ n$ appear, and parameter a equals 14.26 Å at –20°C and 14.32 Å at +10°C.

Structure at –50°C. All reflections can be indexed in the orthorhombic unit cell with parameters:

$$a = 14.21 \pm 0.01\ \text{Å}$$
$$b = 24.64 \pm 0.01\ \text{Å}$$
$$c = 11.0 \quad \pm 0.05\ \text{Å}$$

(**a**, **b**, Fig. 3).

This cell is the smallest which can explain the reflections. There is a change of periodicity in the plane normal to **c**, but virtually no distortion of the host lattice ($a = 14.26$, $b = 24.70$ Å at –20°C). Precision of the indexing is 3×10^{-3} Å for all equatorial reflections with $d < 3$ Å.

The question arises of the periodicity of the sublattice formed by the guest molecules in the **c** direction. Above –33°C, the sublattice spacing is half that of the host lattice. Hence, guest molecules produce reflections every two layer lines (*5*). Below –33°C, on the first layer line, several reflections appear which cannot be indexed in the cell ($\mathbf{a}_1$, $\mathbf{a}_2$, **c**) which describes the empty host lattice. These reflections must belong to the guest sublattice which then has the same periodicity as the urea host lattice in the **c** direction.

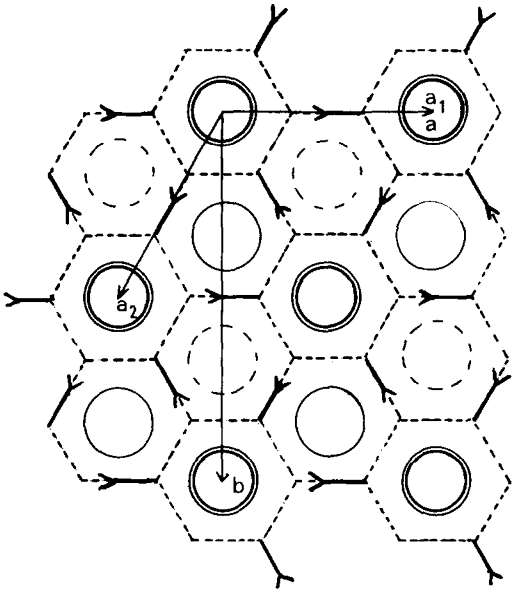

FIG. 3. Hexagonal cell ($\mathbf{a}_1$, $\mathbf{a}_2$) of UTIC above –33°C; ν axis is normal to the plane of figure; arrows indicate the O=C direction of urea molecules. Double, single and dotted circles represent trioxan molecules at respective levels O, $+(c/6)$, $-(c/6)$; vectors **a** and **b** define the orthorhombic unit cell of UTIC below –33°C.

Structure at –120°C. Reflections can be indexed with the orthorhombic unit cell, but contraction of the **a** axis appears along with expansion of the **b** axis.

$$a = 13.81\ \text{Å}$$
$$b = 24.92\ \text{Å}$$
$$c = 11.0\ \ \text{Å}$$

A tentative structure of the urea host lattice can thus be proposed (Fig. 4). For the unit cell of an empty host lattice a parallelepiped with axes **c**, **OP**, **OO′** can be chosen with its volume half that of the unit cell **c**, **OP**, **OQ** of the clathrate. Again the periodicity of the guest sublattice in the **c** direction is the same as that of the host lattice.

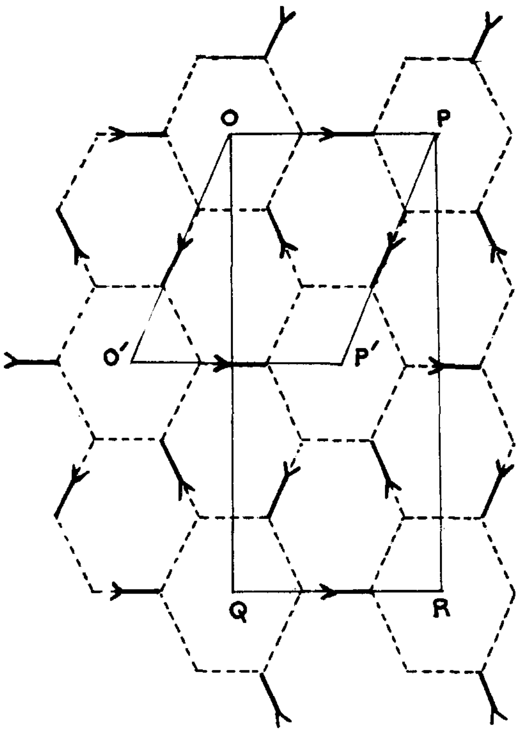

FIG. 4. Urea host lattice at −120°C (distortion exaggerated). *v* axic is normal to the plane of figure.

Since there are three equivalent ways to distort a regular hexagon, the crystal below −89°C probably fractures into three differently oriented crystals with a common *c* axis; as **c** is the rotation axis, these three crystals are not separated on the diffraction patterns.

A Comparison With the Low Temperature Phase of the Thiourea–Cyclohexane Inclusion Compound (TCIC)

TCIC exhibits two reversible phase transitions at −142°C and −125°C (*7*). At room temperature, the TCIC crystal structure is similar to that of UTIC. X-ray diffraction at −160°C of TCIC has been performed. Diagrams show many reflections which can be indexed in a unit cell similar to the orthorhombic cell described for UTIC. Parameters are:

$$a = 14.95 \text{ Å}$$
$$b = 27.75 \text{ Å}$$
$$c = 12.5 \text{ Å}$$

showing a contraction of 6% for *a* and an expansion of about 1% for *b* with respect to the room temperature phase. No change in *c* was observed for the thiourea host lattice. Cyclohexane sublattice seems to double its spacing in the **c** direction below −142°C.

Discussion

Results from DTA and X-ray diffraction experiments show four different phases with reversible transitions for UTIC.

Phase I is the room temperature phase described in (*5*).

Phase II has nearly the same interatomic distances as phase I, without any distortion of the host lattice. The sudden change of the unit cell accompanying the I → II transition probably arises from a change in the relative situation of the trioxane molecules. The superstructure at low temperature is obviously related to an ordering of trioxane molecules; this ordering may involve: (i) distribution of guest molecules inside a channel between the two possible sites 32 and $\bar{3}$; (ii) relative orientation of successive guest molecules inside a channel; (iii) relative orientation of nearest neighbour guest molecules outside the channel, i.e., in the general direction normal to **c**.

Phase III has not been studied here as mentioned in the section "X-Ray Diffraction."

Phase IV exhibits an appreciable distortion of the host lattice—with respect to phase II. It appears that the lower the temperature, the better the guest molecules organize themselves, and as a result induce a distortion of the host lattice. An exact description of the situation of the guest molecules in the low temperature phase is not yet possible.

Comparison of these results with those from NQR raises two problems. First, the fact that there are two resonance lines implies that the nitrogen atoms are distributed between two different crystallographic sites, even in Phase I. The space group of the urea host lattice being $R\bar{3}2/C$, sites 32 or $\bar{3}$ can be chosen for the positions of the centers of the trioxane molecules, and in fact, these molecules of symmetry $3m$ might simulate the symmetry $\bar{3}2/m$, because of their rotation and rattling in the channels (*5*). Either choice of these sites retains the space group $R\bar{3}2/C$ for the entire crystal. Therefore all the nitrogen atoms should be equivalent (a situation observed for TCIC above −125°C). Accepting the above suggestion for the simulated symmetry of trioxane the only explanation for two resonance lines in UTIC is that guest molecules occupy the $\bar{3}$ sites in some parts of the crystal, and the 32 sites in other parts. Although nitrogen atoms in a given part are equivalent, nitrogen atoms in two different parts do not see the same electric field gradient.

Second, there are no discontinuities in the $\nu(T)$ curves at transition temperatures. Complete knowledge of the structure at low temperature is necessary to understand this fact. It might be that small differences in organization of the guest lattice produce no appreciable effect on the quadrupole coupling constant of the nitrogen atoms. The disappearance of the resonance lines at about +10°C can be attributed to the hindered rotation of the NH_2 groups of the urea molecules around the C=O bond direction, as discussed elsewhere (*7*).

The behavior of UTIC is rather different from that of TCIC. In both cases, however, transitions (associated with similar enthalpy variations) occur, and both clathrates have the same type of distorted unit cell at low temperature. Some ordering in the guest molecule sublattice is certainly related to the transition in UTIC at −33°C and to the transition in TCIC at −125°C. An Ising treatment analogous to that proposed (*12*) in the case of *n*-paraffin–urea inclusion compounds could possibly justify their occurrence.

Note. Sharp DTA signals have been found in the case of inclusion compounds of thiourea with cyclooctane, cyclopentane and tetrahydropyran at −85°, −154° and −96°C, respectively, but a search for pure quadrupole resonance in the cyclooctane and tetrahydropyran inclusion compounds did not reveal any resonance lines.

Note added in proof: The orthorhombic (**a**, **b**, **c**) unit cell described for UTIC below −33°C is probably not primitive. A monoclinic cell, built on axes (**a**, **b**/3 + **c**/3, **c**), has a volume one third of the orthorhombic cell, and is consistent with the X-ray patterns.

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