

Structural Properties of the Low-Temperature Phase of the Hexadecane/Urea Inclusion Compound, Investigated by Synchrotron X-ray Powder Diffraction[†]

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The structural properties of the hexadecane/urea inclusion compound have been determined, using Rietveld refinement, from synchrotron X-ray powder diffraction data recorded at temperatures above and below the phase transition temperature (ca. 150 K) for this inclusion compound. Structural characterization of the low-temperature phase by single-crystal diffraction techniques is limited by the fact that single crystals of the inclusion compound become multiply twinned on cooling below the phase transition temperature. The structural properties determined for the high-temperature phase at ambient temperature are in agreement with those reported previously from single-crystal X-ray diffraction data; the urea molecules form a hexagonal host tunnel structure, with an incommensurate relationship between the periodicities of the host and guest substructures along the tunnel axis. The host structures in the low-temperature and high-temperature phases are sufficiently similar that the high-temperature host structure can be used as the initial structural model for Rietveld refinement of the low-temperature phase. The urea tunnel structure in the low-temperature phase (studied at 120 K) is orthorhombic ($P2_12_12_1$; $a = 10.98$ Å, $b = 13.89$ Å, $c = 8.25$ Å) and represents a distorted form of the hexagonal structure of the high-temperature phase. This represents the first accurate and reliable report of the low-temperature structure of an alkane/urea inclusion compound. The observed distortion of the urea tunnel is consistent with the fact that the reorientational motion of the guest molecules about the tunnel axis diminishes substantially upon entering the low-temperature phase. The strategy developed in this paper for structure determination of the low-temperature phase of the hexadecane/urea inclusion compound will have wider application to other incommensurate solid inclusion compounds that exhibit phase transitions at low temperatures. This approach is particularly important for cases in which single crystals of the inclusion compound become multiply twinned upon entering the low-temperature phase.

1. Introduction

There is currently considerable interest in urea inclusion compounds, in recognition of the fact that these solids exhibit a diverse range of interesting and important physicochemical properties.^{1,2} In crystals of the conventional urea inclusion compounds, the urea molecules form an extensively hydrogen-bonded host structure that contains linear, parallel, nonintersecting tunnels.^{3,4} The guest molecules are densely packed within these tunnels.

For most conventional urea inclusion compounds, the basic host structure (see section 2) is hexagonal at sufficiently high temperatures and the guest molecules are dynamic, undergoing reorientation about the tunnel axis and restricted translation along the tunnel. As the symmetry (hexagonal) of the average basic host structure is higher than the symmetry of an individual guest molecule, it is clear that the observed symmetry of the basic host structure represents a time average over the motion of the guest molecules. Most conventional urea inclusion compounds undergo a phase transition^{5–7} (or in some cases more than one phase transition) at sufficiently low temperature (for example, ca. 150 K for hexadecane/urea⁸ and ca. 143 K for 1,10-dibromodecane/urea⁹). In general, these transitions are associated with a lowering of the symmetry of the average host structure^{8–11} and a restriction (although not necessarily a cessation) of the motional freedom of the guest molecules.^{9,12–16} In many respects, the alkane/urea inclusion compounds represent

the prototypical family of the “conventional” urea inclusion compounds and have been the most extensively studied family to date, particularly with regard to the low-temperature phase transition.

Although the dynamic properties of the guest molecules have been probed as a function of temperature across the phase transition for several alkane/urea inclusion compounds, substantially less attention has been devoted to changes in the structural properties of the host. In part, this is because multiple crystal twinning usually accompanies the transition from the high-temperature phase to the low-temperature phase, limiting the prospects for using single-crystal X-ray diffraction to investigate structural properties of the low-temperature phase (single crystals grown under ambient conditions represent the high-temperature phase). In reflection of this fact, there has been only one reported determination of the host structure in the low-temperature phase^{10,11} from poor-quality single-crystal X-ray diffraction data (for hexadecane/urea) that were affected significantly by the problem of crystal twinning. Although this work led to a qualitative understanding of the host structure in the low-temperature phase, including the fact that it is orthorhombic with space group $P2_12_12_1$, no atomic coordinates were actually reported or deposited. Due to the inherent uncertainties and inaccuracies associated with the determination of this structure, and in view of the importance of understanding in detail fundamental aspects of the phase transitions in urea inclusion compounds, a more definitive determination of the low-temperature host structure is clearly of prime importance.

In view of the crystal twinning discussed above, it has been recognized⁸ that powder diffraction is, in principle, more appropriate than single-crystal diffraction for structure deter-

[†] Dedicated to Professor Sir John Meurig Thomas on the occasion of his 65th birthday.

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mination of the low-temperature phase. Our aim in the present work was to develop and apply a strategy for determination of the host structure in the low-temperature phase of a conventional urea inclusion compound by Rietveld profile refinement¹⁷ of powder diffraction data, using knowledge of the basic host structure in the high-temperature phase (from previous single-crystal X-ray diffraction studies) as the initial structural model. This approach for structure determination of the low-temperature phase is advantageous over single-crystal diffraction, as the powder diffractogram should not be affected by the occurrence of twinning (provided each individual twin is still sufficiently large that particle size effects do not give rise to serious line broadening). Indeed, structural properties of the low-temperature phase of the chlorocyclohexane/thiourea inclusion compound (a commensurate inclusion compound) have been determined successfully,¹⁸ using a similar strategy, from synchrotron X-ray powder diffraction data. Clearly the hexadecane/urea inclusion compound represents a significantly more challenging problem, as the incommensurate relationship between the host and guest substructures in this solid (see section 2) leads to additional complications⁴ in the interpretation of its X-ray diffraction pattern.

2. Structural Rationalization of Conventional Urea Inclusion Compounds

For the conventional urea inclusion compounds, there is an incommensurate relationship between the periodic repeat distances (denoted c_h and c_g , respectively) of the host and guest substructures along the tunnel axis (classically, for an incommensurate system, it is not possible to find sufficiently small integers p and q for which $pc_h \approx qc_g$). Although the host and guest substructures have different structural periodicities, they are not independent, as each substructure exerts an incommensurate modulation upon the other. The host substructure is best considered in terms of a basic structure which is subjected to an incommensurate modulation mediated by the guest substructure; the basic structure can be described using conventional crystallographic principles (e.g., three-dimensional space group symmetry). In a similar manner, the guest substructure can be considered in terms of an incommensurately modulated basic structure. The incommensurate modulations describe perturbations to the basic structures which arise as a consequence of host–guest interaction. A full discussion of these structural issues for urea inclusion compounds is given in refs 4 and 19. Clearly four basis lattice vectors are required to define the periodicity of the composite inclusion compound and may be denoted as \mathbf{a}_h , \mathbf{b}_h , \mathbf{c}_h , and \mathbf{c}_g (as defined above); in principle, the value of $|\mathbf{c}_h|/|\mathbf{c}_g|$ is irrational, or in practice, it may be approximated by a rational number with high denominator. Correspondingly, the symmetry of the composite inclusion compound is described by a four-dimensional superspace group, as discussed in detail elsewhere.^{19,20}

On transforming this structural description to reciprocal space, it is clear that the diffraction pattern is described by four basis reciprocal lattice vectors (\mathbf{a}_h^* , \mathbf{b}_h^* , \mathbf{c}_h^* and \mathbf{c}_g^*) and four integer Miller indices (h , k , l , and m). Thus, a reciprocal lattice vector \mathbf{S} is defined by the linear combination

$$\mathbf{S} = h\mathbf{a}_h^* + k\mathbf{b}_h^* + l\mathbf{c}_h^* + m\mathbf{c}_g^*$$

with integer coefficients h , k , l , and m . The subset ($hkl0$) of the complete diffraction pattern has been described previously as the “h” diffraction pattern, and the subset ($hk0m$) has been described previously as the “g” diffraction pattern. Genuine satellite reflections ($hklm$) with $l \neq 0$ and $m \neq 0$ have been

observed for the first time for a urea inclusion compound only very recently.²¹

The h diffraction pattern arises from diffraction by the basic host structure (and by the incommensurate modulation to the basic guest structure), whereas the g diffraction pattern arises from diffraction by the basic guest structure (and by the incommensurate modulation to the basic host structure). The h diffraction pattern is generally much more intense than the g diffraction pattern, and virtually all significant peaks in the X-ray powder diffractogram of a urea inclusion compound represent h reflections. In general, g reflections are present in the X-ray powder diffractogram only as extremely low-intensity peaks at low diffraction angles. As described previously,⁴ structure determination calculations using the h diffraction data allow the basic host structure to be determined but also require the introduction of some electron density within the tunnel, as now described. First, the ($hk00$) reflections, which are common to both the h and g diffraction patterns, provide two-dimensional information on the basic guest structure projected on to the plane perpendicular to the tunnel axis. Second, the h reflections ($hkl0$) with $l \neq 0$ convey information on the incommensurate perturbations to the basic guest structure (these perturbations, which arise from host–guest interaction, have the same periodicity as the basic host structure). At the level considered in the present work, no direct physical interpretation can be assigned to the electron density distribution determined within the tunnel from analysis of the h diffraction data, except perhaps when projected on to the plane perpendicular to the tunnel axis. In summary, the X-ray powder diffractogram essentially represents h diffraction data, analysis of which allows the basic host structure to be determined; analysis of the h diffraction data also requires some electron density to be introduced into the host tunnel, although physical interpretation can be assigned to this electron density only with extreme caution.

3. Experimental Section

3.1. Sample Preparation. Crystals of the hexadecane/urea inclusion compound were prepared from commercially available reagents using the following method. An excess amount of hexadecane (excess with respect to the expected guest/host molar ratio in the inclusion compound) was added to a saturated solution of urea in methanol in a conical flask under ultrasonic agitation at ca. 55 °C. A sufficient amount of 2-methylbutan-2-ol was then added to render the liquid hexadecane completely miscible with the methanol. At this stage, crystals of the hexadecane/urea inclusion compound precipitated immediately; these crystals were then dissolved by addition of a sufficient amount of methanol to establish a homogeneous solution. The flask was then transferred to an incubator, in which it was cooled systematically from 55 to 15 °C over a period of 24 h. When sufficiently large crystals had grown (generally after a few days), they were collected and washed with 2,2,4-trimethylpentane. The crystals were long hexagonal needles, and their behavior in the polarizing microscope was consistent with their assignment to the hexagonal crystal system. X-ray powder diffraction indicated that these crystals had the conventional urea tunnel structure and that there were no significant amounts of the “pure” crystalline phase of urea (the crystal structure of which differs substantially from the urea host structure in urea inclusion compounds).

3.2. X-ray Powder Diffraction. X-ray powder diffractograms of the hexadecane/urea inclusion compound were recorded in transmission geometry on station 2.3 at the Synchrotron Radiation Source, Daresbury Laboratory, using a finely ground sample loaded in a capillary sample holder (1.0 mm

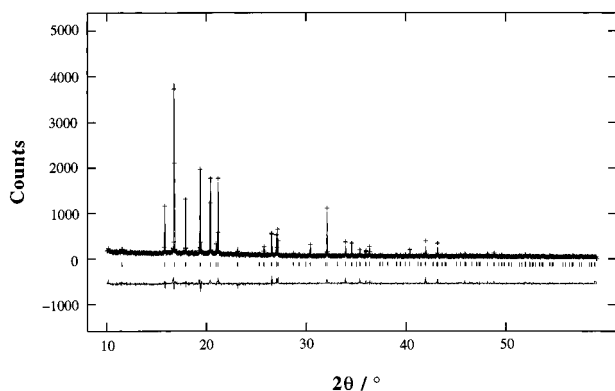


Figure 1. Comparison of experimental and calculated X-ray powder diffraction profiles ($\lambda = 1.200$ Å) for the Rietveld refinement calculations for hexadecane/urea at ambient temperature. The calculated powder diffraction profile is for the structure reported in Table 1. Experimental diffractogram (+ marks), calculated diffractogram (solid line), difference diffractogram (bottom trace); marks below the upper trace indicate the predicted positions of reflections.

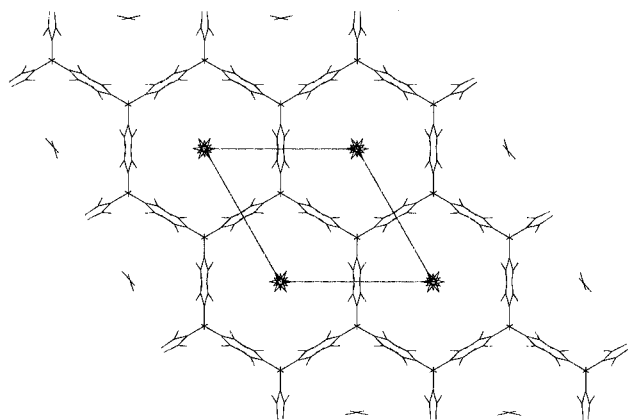


Figure 2. Structure of the hexadecane/urea inclusion compound determined from the "h" diffraction data in the X-ray powder diffractogram recorded at ambient temperature (high-temperature phase; structural parameters specified in Table 1). The structure is viewed along the tunnel axis (c_h direction). The extent to which physical interpretation can be given to the refined positions of atoms within the tunnel is discussed in the text.

diameter). The data were recorded at $\lambda = 1.200$ Å in the range $2\theta = 3$ – 60° for a period of 75 min at ambient temperature (high-temperature phase) and for a period of 150 min at 120 K (low-temperature phase). A commercial cryostat (Oxford Instruments) was used for the experiment at 120 K, and was stable to within ± 2 K during the data collection.

The experimental X-ray powder diffractograms (see section 5, Figures 1 and 3, and ref 8) demonstrate clearly that a structural change occurs between the high-temperature phase and the low-temperature phase. At a qualitative level, this structural change can be interpreted in terms of a small hexagonal-to-orthorhombic distortion, as rationalized previously.⁸ Indexed X-ray powder diffractograms for the high-temperature and low-temperature phases are given in ref 8.

4. General Approach for Rietveld Refinement Calculations

All Rietveld refinement calculations were carried out using the General Structure Analysis System (GSAS) program package.²² The pseudo-Voigt line-shape function was used, and the background was determined by linear interpolation between manually selected points.

In our strategy for structure determination of the host structure in the low-temperature phase from powder diffraction data, we

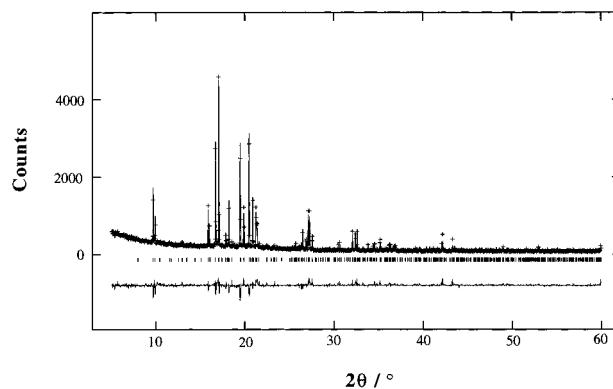


Figure 3. Comparison of experimental and calculated X-ray powder diffraction profiles ($\lambda = 1.200$ Å) for the Rietveld refinement calculations for hexadecane/urea at 120 K. The calculated powder diffraction profile is for the structure reported in Table 2. Experimental diffractogram (+ marks), calculated diffractogram (solid line), difference diffractogram (bottom trace); marks below the upper trace indicate the predicted positions of reflections.

recognize⁸ that the host structure in the low-temperature phase is substantially similar to that in the high-temperature phase (although of lower symmetry). On this basis, the known host structure in the high-temperature phase should represent an adequate initial structural model for Rietveld refinement of the low-temperature phase. Nevertheless, more substantial differences may be expected in the guest substructure between the low-temperature and high-temperature phases, and the way of handling the electron density within the tunnel in the Rietveld refinement calculations for the low-temperature phase requires careful consideration. Several strategies were considered in this regard, and only the optimum strategy is described (see section 5.2).

5. Results and Discussion

5.1. High-Temperature Phase. The X-ray powder diffractogram recorded at ambient temperature can be indexed (h diffraction data) on the basis of the hexagonal lattice parameters ($a_h = b_h = 8.227$ Å, $c_h = 11.017$ Å) of the basic host structure, determined previously from single-crystal X-ray diffraction data.^{3,4} The direction of the tunnel is defined by the c_h axis. The Rietveld refinement calculations for the data recorded at ambient temperature were carried out using the 2θ range 10– 60° .

The initial structural model used for the Rietveld refinement calculations comprised all the structural parameters determined from single-crystal X-ray diffraction data recorded at ambient temperature.²³ Thus, in addition to atoms of the basic host structure, this model also contains discrete atomic positions (with high atomic displacement parameters) within the tunnel to represent the contribution to the h diffraction pattern from scattering by the guest substructure. We emphasize that no physical significance should be assigned to these discrete atomic positions (except, perhaps, in the case of high-quality diffraction data, to the projection of this electron density on to the plane perpendicular to the tunnel axis). The isotropic atomic displacement parameters for atoms of the urea molecule were not refined but were fixed at a common value (0.044 Å²), taken as the average of the isotropic atomic displacement parameters determined previously from single-crystal X-ray diffraction data. Hydrogen atoms were added to the urea molecules according to standard geometries, and restraints (based on standard molecular geometry) were applied to the bond lengths and bond angles of the urea molecule. Rietveld refinement using this initial structural model was well-behaved, although attempts to

TABLE 1: Refined Structural Parameters for the High-Temperature Phase of the Hexadecane/Urea Inclusion Compound at Ambient Temperature^a

atom	x/a_h	y/b_h	z/c_h	$U_{iso}/\text{\AA}^2$
Host				
O1	0.640(1)	0.320(1)	$7/12$	0.044 [F]
N1	0.913(1)	0.480(2)	0.481(1)	0.044 [F]
C1	0.816(1)	0.408(1)	$7/12$	0.044 [F]
H1	0.855(2)	0.484(2)	0.414(2)	0.066 [F]
H2	1.033(1)	0.533(2)	0.481(1)	0.066 [F]
Atoms in Tunnel				
C2	0.073(5)	0	0	0.36(1)
C3	-0.058(5)	-0.029(5)	$1/12$	0.36(1)

^a $P6_122$; $a_h = b_h = 8.221(1)$ Å; $c_h = 11.014(1)$ Å. Goodness-of-fit indices: $R_p = 0.113$; $R_{wp} = 0.172$. Parameters labeled [F] were fixed (at standard values) in the Rietveld refinement calculations.

refine the common isotropic atomic displacement parameter for atoms of the urea molecule led to an unreasonably low value; on the other hand, a common isotropic atomic displacement parameter for the atoms within the tunnel could be refined in a satisfactory manner. The crystallites of the hexadecane/urea inclusion compound have a needle morphology and may be expected to show some degree of preferred orientation with respect to the needle axis, and for this reason, a preferred orientation parameter was refined in the later stages of the Rietveld refinement calculations. However, the refined value of the preferred orientation parameter was close to unity, indicating that the effects of preferred orientation on the experimental data were negligible. The final refined structural parameters at ambient temperature are reported in Table 1, and the experimental and calculated X-ray powder diffractograms are compared in Figure 1. The final refined structure, viewed along the tunnel axis (c_h axis), is shown in Figure 2.

The final Rietveld refinement calculations for the high-temperature phase described above were carried out for the 2θ range 10–60°, as the refinement calculations were found to be better behaved with the peak at $2\theta \approx 9.5^\circ$ excluded. It is interesting to note that this peak, which is indexed as (1000), is common to both the h and g diffraction patterns, and its intensity is known (from experimental observations for other urea inclusion compounds) to depend strongly on the identity of the guest molecule. The fact that inclusion of the (1000) peak has an adverse effect on the quality of the refinement calculations may be a consequence of the approximate manner with which the contributions from the guest substructure to the h diffraction pattern are represented in the approach adopted here. Due consideration of this issue must also be given in the analysis of the data for the low-temperature phase.

5.2. Low-Temperature Phase. The X-ray powder diffractogram recorded at 120 K (low-temperature phase) can be indexed (h diffraction pattern) by a lattice ($a_h = 10.975$ Å, $b_h = 13.892$ Å, $c_h = 8.252$ Å) with orthorhombic metric symmetry. The direction of the tunnel is now defined by the a_h axis. This orthorhombic lattice represents only a small distortion from the orthohexagonal description of the hexagonal lattice that describes the periodicity of the basic host structure in the high-temperature phase. The peak intensities (for the h diffraction pattern) are consistent with the space group $P2_12_12_1$ assigned previously^{10,24,8} to the low-temperature phase. Thus, the 6_1 screw axis (parallel to the tunnel axis) is lost following the hexagonal-to-orthorhombic transition, with the urea tunnel distorting to a symmetry that is closer to the symmetry of the guest molecule (note that the C center that characterizes the orthohexagonal description of the high-temperature phase is also lost).

The initial structural model for Rietveld refinement using the data recorded at 120 K comprised the fractional coordinates of the atoms of the urea molecules in the high-temperature phase transformed as fractional coordinates within the orthohexagonal unit cell. These fractional coordinates were then combined with the true orthorhombic unit cell of the basic host structure in the low-temperature phase, and the set of three molecules defining the asymmetric unit within the $P2_12_12_1$ description was considered. Initial Rietveld refinement calculations were carried out using this “host-only” structural model, with 2θ in the range 10–60° (based on the experience gained for the high-temperature phase (see above), it was considered desirable to omit the peaks at $2\theta \approx 9.5^\circ$ in the initial refinement calculations). The refinement was well-behaved, and the difference Fourier map calculated for the refined host-only structural model had several significant maxima located within the tunnel, clearly representing the contributions of the guest substructure to the h diffraction data. A carbon atom was added (with isotropic atomic displacement parameter fixed at 0.4 Å²) in the position of the highest maximum in the difference Fourier map, and only the scale factor was then refined. The agreement between the experimental and calculated powder diffraction patterns improved significantly with the addition of this electron density within the tunnel. This procedure was repeated, adding one carbon atom at a time, until the agreement between the experimental and calculated powder diffraction patterns became worse upon adding an additional carbon atom. In the best model, five carbon atoms were added within the tunnel. The positions of the urea molecules were then refined in an iterative manner, with only one urea molecule allowed to refine at a time; in these refinements, restraints (based on standard molecular geometry) were applied to the bond lengths and bond angles of the urea molecules. Next, the positions of the atoms within the tunnel were allowed to refine (one or two atoms at a time, but never all together), with the urea molecules fixed. Following this, the common isotropic atomic displacement parameter for the atoms within the tunnel was refined. As for the high-temperature structure, attempts to refine a common isotropic atomic displacement parameter for the atoms of the urea molecules led to an unreasonably low value. Hence, the common isotropic atomic displacement parameter of the atoms of the urea molecules was fixed at 0.02 Å².

After a satisfactory fit was achieved, the atoms within the tunnel were omitted and the difference Fourier map was recalculated for a structural model comprising only the refined host structure (as determined above). Importantly, the wider 2θ range of 5–60° was used at this stage (i.e., with the peaks at $2\theta \approx 9.5^\circ$ included). From the difference Fourier map, atoms were reintroduced into the tunnel, adding one carbon atom at a time, following the same refinement strategy described above, until the optimal agreement between the experimental and calculated powder diffraction data was obtained. Finally, hydrogen atoms were added to the urea molecules according to standard geometries. As discussed in section 5.1 for the high-temperature phase, a preferred orientation parameter was refined in the later stages of the Rietveld refinement calculations; again, the refined value of the preferred orientation parameter was close to unity, indicating that the effects of preferred orientation on the experimental data were negligible. The parameters for the best structural model obtained at 120 K are reported in Table 2, and the experimental and calculated X-ray powder diffractograms are compared in Figure 3. The final structure is shown, viewed along the tunnel axis (a_h axis), in Figure 4.

The basic host structure (Figure 4) in the low-temperature phase is clearly a distorted form of the basic host structure in

TABLE 2: Refined Structural Parameters for the Low-Temperature Phase of the Hexadecane/Urea Inclusion Compound at 120 K^a

atom	x/a_h	y/b_h	z/c_h	$U_{iso}/\text{\AA}^2$
Host				
O1	0.335(1)	0.088(1)	0.022(1)	0.020 [F]
O2	0.998(4)	0.066(1)	0.013(6)	0.020 [F]
O3	0.665(1)	0.088(1)	-0.024(1)	0.020 [F]
N11	0.233(1)	0.010(1)	-0.177(1)	0.020 [F]
N12	0.439(1)	0.036(1)	-0.197(1)	0.020 [F]
N21	1.101(3)	0.207(2)	0.025(9)	0.020 [F]
N22	0.895(3)	0.204(2)	-0.022(9)	0.020 [F]
N31	0.565(1)	0.035(1)	0.198(1)	0.020 [F]
N32	0.771(1)	0.010(1)	0.171(1)	0.020 [F]
C1	0.336(1)	0.044(1)	-0.112(1)	0.020 [F]
C2	0.999(3)	0.156(1)	-0.024(2)	0.020 [F]
C3	0.666(1)	0.043(1)	0.109(1)	0.020 [F]
Atoms in Tunnel				
C4	0.039(6)	0.243(2)	0.499(6)	0.34(1)
C5	0.020(9)	0.246(2)	0.498(7)	0.34(1)
C6	0.326(4)	0.252(3)	0.521(3)	0.34(1)
C7	0.174(4)	0.248(3)	0.523(3)	0.34(1)
C8	0.325(4)	0.251(3)	0.509(3)	0.34(1)

^a $P2_12_12_1$; $a_h = 10.975(1)$ Å; $b_h = 13.894(1)$ Å; $c_h = 8.253(1)$ Å. Goodness-of-fit indices: $R_p = 0.090$; $R_{wp} = 0.134$. Parameters labeled [F] were fixed (at standard values) in the Rietveld refinement calculations.

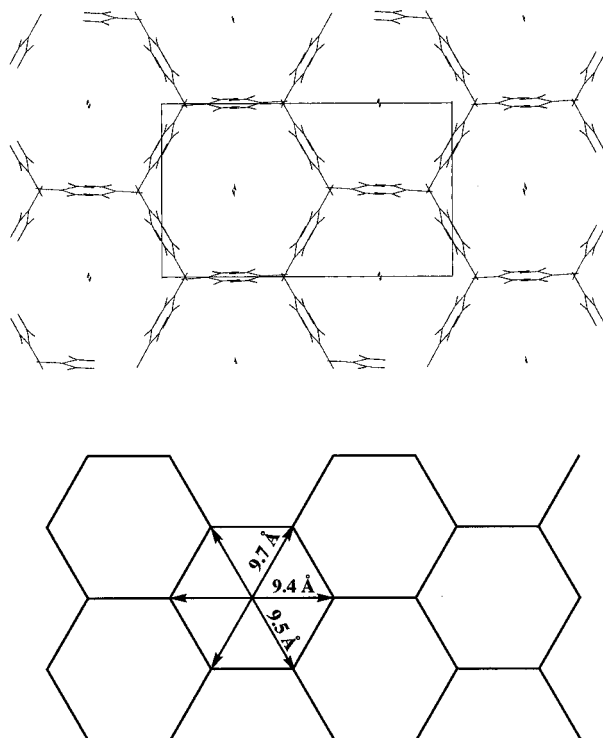


Figure 4. Structure of the hexadecane/urea inclusion compound determined from the h diffraction data in the X-ray powder diffractogram recorded at 120 K (low-temperature phase; structural parameters specified in Table 2). The structure is viewed along the tunnel axis (a_h direction). The extent to which physical interpretation can be given to the refined positions of atoms within the tunnel is discussed in the text. The schematic diagram of the host structure illustrates the distortion of the tunnel from hexagonal symmetry.

the high-temperature phase (compare Figures 2 and 4) and is based approximately on the orthohexagonal lattice of the high-temperature phase. The two tunnels running through the unit cell in the low-temperature phase are identical (related by a 2_1 screw axis perpendicular to the tunnel axis). The projection of the tunnel on to the plane perpendicular to the tunnel axis is a distorted hexagon with one "diameter" between opposite corners

of the hexagon longer than the other two diameters (Figure 4). Unlike single-crystal X-ray diffraction experiments, from which important insights into the average orientational characteristics of the guest molecules with respect to the urea tunnel structure may sometimes be derived^{25,26} by projecting the structure onto the plane perpendicular to the tunnel axis, an accurate physical interpretation of the electron density introduced into the tunnel in the refinement calculations is not considered justified from the X-ray powder diffraction data considered here. For this reason, we make no attempt to reach any structural conclusions from the refined positions of the atoms inside the tunnel, even with regard to the projection of this electron density onto the plane perpendicular to the tunnel axis. Nevertheless, it is important to recognize that introduction of this electron density into the tunnel is crucial for obtaining a good quality fit to the h diffraction data and, hence, for obtaining a good quality determination of the basic host structure.

6. Concluding Remarks

High-resolution synchrotron X-ray powder diffraction data have been used to elucidate structural properties of the low-temperature phase of the hexadecane/urea inclusion compound. To our knowledge, this represents the first time that Rietveld refinement has been applied successfully to determine the structural properties of an incommensurate solid inclusion compound. Importantly, the research reported here validates an approach for structure determination of the low-temperature phases of inclusion compounds for which the transition from the high-temperature phase to the low-temperature phase is accompanied by crystal twinning (thus limiting the prospects for obtaining accurate and reliable structural information from single-crystal diffraction data). Although this approach was proposed several years ago,⁸ extensive attempts to apply this approach for urea inclusion compounds were unsuccessful, mainly as a consequence of the inferior quality of powder diffraction data used in the previous study. The strategy adopted here for structure refinement of the low-temperature phase is appropriate provided the low-temperature and high-temperature structures are sufficiently similar that the atomic coordinates of the high-temperature structure (transformed appropriately to the low-temperature unit cell and space group) can be used as the initial structural model for structure refinement of the low-temperature phase. Importantly, the present work has demonstrated that the subtleties and complexities associated⁴ with determination of the basic host structure of an incommensurate inclusion compound do not represent insurmountable difficulties in the case of structure determination from powder diffraction data. In view of the success of this approach, the future exploitation of powder diffraction techniques for structural characterization of low-temperature phase transitions in incommensurate solid inclusion compounds should be strongly encouraged.

Now that reliable knowledge of the conventional low-temperature structure of the alkane/urea inclusion compounds is available, we are confident that future theoretical and computational studies will lead to significant progress in deriving a fundamental understanding of the low-temperature phase transition in these solids.

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