

Modulated Structure of the Composite Crystal Urea/*n*-Heptadecane

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Abstract

The structure of the composite crystal urea/heptadecane was determined by single crystal X-ray diffraction. The lattice constants of the hexagonal substructures are $a = 8.218(2)$, $b = 8.218(3)$, $c_h = 11.017(3)$ Å for the urea (host) structure and $c_g = 23.713(1)$ Å for the heptadecane (guest) structure, respectively. The (3+1)-dimensional space group is $P6_122(00\rho)0\bar{1}\bar{1}$. Refinements on 786 reflections converged to $wR = 0.0232$ for 608 main host reflections, $wR = 0.1506$ for 10 main guest reflections, $wR = 0.0328$ for 49 common main reflections and $wR = 0.753$ for 119 pure satellite reflections. A comparison of the refinement of only the urea substructure and a refinement of the whole composite crystal, including the guest subsystem and the mutual modulations of both subsystems, shows that the main reflections, previously assigned to the urea host exclusively, are affected by a nonnegligible contribution of the heptadecane satellite scattering. The modulation of the guest structure has a maximum when the CH₂ groups of the heptadecane molecule are facing the channel walls at heights corresponding to troughs in this wall. Thus, the modulation of the guest structure can be interpreted by an adaptation of the guest molecules to the host structure. The modulation of the host structure was found to be very weak, as the satellite scattering of the host structure is low. ψ -scans of the $00l$ reflections revealed that the observed violation of the 6_1 screw axis extinction rule of the host structure and guest structure modulation can be explained by considerable *umweganregung*.

1. Introduction

Urea inclusion compounds consist of a hexagonal host structure of hydrogen-bonded urea molecules forming open channels along the *c* axis into which various long stretched molecules can be embedded. Generally, with alkane molecules as guests (here *n*-heptadecane C₁₇H₃₆), the *c* periods of the host (c_h) and of the guest substructures (c_g) are incommensurate, *i.e.* the ratio $|c_h/c_g| = n/m$ cannot be expressed by small integers *m* and *n*. While the host substructure exhibits a well defined three-dimensional long-range ordered structure, the guest substructure of alkane molecules is heavily disordered, as indicated by strong diffuse scattering (Forst,

Jagodzinski, Boysen & Frey, 1987; Fukao, 1994*a,b*; Weber, Boysen, Honal, Frey & Neder, 1996). At room temperature, both subsystems have hexagonal symmetry. The space groups are $P6_122$ and $P622$ for the host and the guest substructure, respectively. The hexagonal symmetry of the guest is due to a dynamic average of the alkane molecules rotating around their long axis, as found by incoherent quasielastic neutron scattering at ambient temperature (*e.g.* Boysen, Frey & Blank, 1988). Only weak lateral correlations exist between the alkane molecules in neighboring channels (Forst *et al.*, 1987; Fukao, 1994*a,b*; Weber, Boysen Honal *et al.*, 1996) and an approximate, but not perfect, long-range order along *c*, *i.e.* an almost one-dimensional lattice (Weber, Boysen, Honal *et al.*, 1996). Only the projection of the guest structure along the *c* axis is well ordered, since the alkane molecules are restricted to the centers of the tunnels. As a consequence, the related diffraction patterns show diffuse planes ('*s* layers'), which are almost sharp parallel to *c** and diffuse perpendicular to *c** and no diffuse *s* layer of zeroth order (Fig. 1). Nevertheless, some weak guest reflections can be observed on the first *s* layer. The *hk0* reflections of the guest substructure coincide with the *hk0* reflections of the host substructure. At room temperature the system urea/heptadecane shows a few very weak satellite reflections, which can be assigned to a mutual modulation of the host and guest substructures (Weber, Boysen, Honal *et al.*, 1996).

At lower temperatures the interaction of both subsystems, and with this the mutual modulations of both systems, increase giving rise to stronger satellite reflections. Further, the diffuse *s* layers decrease in intensity, while the intensities of the main reflections of the guest substructure become stronger. As a consequence of the increasing interaction of both subsystems, urea inclusion compounds undergo a phase transition from hexagonal to an orthorhombic phase (Forst, Boysen, Frey & Jagodzinski, 1986; Chatani, Taki & Tadokoro, 1977). This phase transition is combined with a static preferred orientation of the guest molecules forming a herringbone-like pattern in the projection along *c* and an at least sixfold twinning of the crystal (Forst, Jagodzinski, Boysen & Frey, 1990). New results have shown that there may be a 12-fold or even 24-fold twinning (Weber, 1996*b*).

Earlier structure investigations of urea inclusion compounds have considered only the host substructure (Smith, 1952, Forst *et al.*, 1990). However, there are some important drawbacks of such a simplification:

(i) No information about the guest structure can be acquired.

(ii) The mutual modulations of both subsystems are ignored.

(iii) The $hk0$ reflections of both subsystems cannot be included into a conventional refinement.

Different strategies have been reported to include the contribution of the guest scattering to the $hk0$ reflections. Fratz (1991) and Wegner (1991) modified their refinement program in such a way that the guest atoms were included in the refinement only for the calculation of the $hk0$ reflections, while Harris & Thomas (1990) took a smeared-out electron density for the guest structure by introducing large ADP's (atomic displacement parameters) parallel to the channel axis.

However, in order to obtain complete information on the real (modulated) structure it has to be refined as a composite crystal, *i.e.* in $(3+1)$ -dimensional space. Note that the three-dimensional structures of the subsystems are projections of the superspace.

2. Symmetry

The symmetry of urea inclusion compounds as composite crystals has been analysed by van Smaalen & Harris (1996). They have shown that the room-temperature phase of urea inclusion compounds with

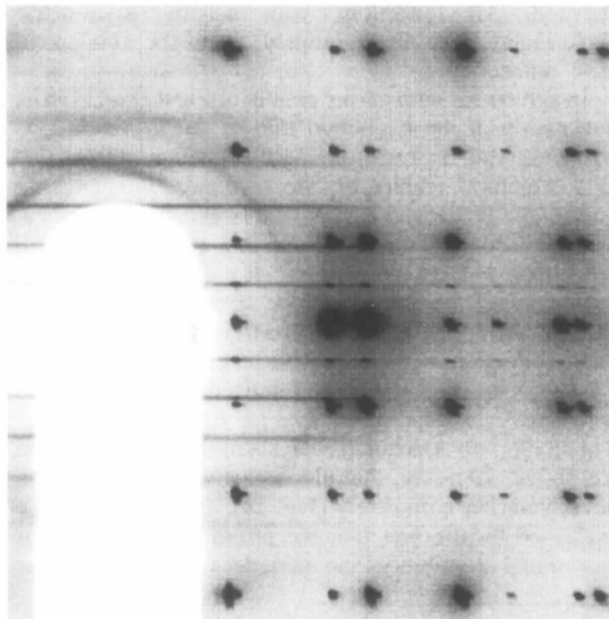


Fig. 1. Section of a rotating crystal X-ray photograph of urea/*n*-heptadecane at room temperature with rotation axis parallel to c^* (radiation: $\text{Cu K}\alpha_1$).

alkane molecules as guest molecules can be described by two equivalent $(3+1)$ -dimensional space groups: (i) $P6_122(00\rho)0\bar{1}\bar{1}$ and (ii) $P622(00\rho^{-1})h\bar{1}\bar{1}$, with $\rho = |q| = |c_g^*|/|c_h^*|$, depending on whether the host or the guest structure subsystem is chosen as subsystem (1). As the reflections due to the host are dominant in the diffraction patterns, superspace group (i) will be used in this paper. An important feature of composite crystals is that the subsystems may interact, leading to a mutual modulation of both. The modulation of subsystem (1) corresponds to the symmetry of subsystem (2) and *vice versa*. This holds for both the translational symmetry and the point-group symmetry.

According to the theory of modulated structures and composite crystals, four indices are required to describe the diffraction pattern of a one-dimensional modulated structure completely. Three indices are used for a three-dimensional approach to the individual host and guest subsystems, denoted by hkl_h and hkm_g , respectively, while four indices $hkml$ are used for the superspace approach. Generally, the intensities of $hkml$ reflections are composed of two parts:

(i) The m th satellite of a main host reflection hkl_h .

(ii) The l th satellite of the main guest reflection hkm_g .

In particular, the $hk0$ reflections indicate the main reflections of the host substructure, but they are also influenced by the l th satellite of the main guest reflection $hk0_g$. The interpretation of the $hk0m$ reflections is analogous, while the $hk00$ reflections are main reflections common for both systems. Reflections with $l \neq 0$ and $m \neq 0$ are pure satellite reflections, which are affected by the modulation of both subsystems. For the guest substructure only the $hk0_g$ reflections are of high intensity, while most hkl_g reflections are very weak. Thus, any modulation of the guest structure will at most affect the $hkml$ reflections with m equal to zero. On the other hand, many hkl_h reflections have high intensity, therefore, any significant modulation of the host structure should affect not only the main guest reflections, but also the pure satellites, *i.e.* the $hkml$ reflections ($l, m \neq 0$). Only satellite reflections with $hkl1$ and $hkl\bar{1}$ could be observed at room temperature with rotating crystal film techniques (Weber, Boysen, Honal *et al.*, 1996) and these reflections are very weak. From these arguments we can conclude that the pure satellite reflections must be interpreted mainly as a scattering from the modulation of the host structure. As these satellite reflections are of low intensity, it can be concluded that the host structure modulation must be very weak.

3. Experimental

Single crystals of urea/heptadecane were grown using a temperature difference method, as described by Weber, Boysen, Honal *et al.* (1996). A clear crystal was carefully ground to a sphere of *ca* 0.25 mm in diameter.

Details of the data collection are listed in Table 1.

Table 1. *Experimental details*Table 1 (*cont.*)

Crystal data	
Chemical formula	OC(NH ₂) ₂ /C ₁₇ H ₃₆
Superspace group	<i>P</i> 6 ₁ 22(00 <i>ρ</i>)011
<i>a</i> (Å)	8.218 (2)
<i>b</i> (Å)	8.218 (3)
<i>c_h</i> (Å)	11.017 (3)
<i>c_g</i> (Å)	23.713 (1)
α (°)	90.00 (3)
β (°)	89.99 (2)
γ (°)	119.99 (2)
Modulation vector	$\mathbf{q} = (00 c_g^* / c_h^*) = [000.4646(5)]$
μ (cm ⁻¹)	1.02
Temperature (K)	293
Crystal form	Sphere
Crystal size (mm ³)	8.83 × 10 ⁻³
Crystal color	Colorless
Data collection	
Diffractometer	Enraf-Nonius CAD-4
Monochromator	Graphite (002)
Radiation	Mo <i>K</i> α
Wavelength (Å)	0.71073
Data collection method	ω scans
θ range (°)	3.0–36.0
Index range of main host reflections	-13 ≤ <i>h</i> ≤ 0 0 ≤ <i>k</i> ≤ 13 1 ≤ <i>l</i> ≤ 18 <i>m</i> = 0
Index range of main guest reflections	-5 ≤ <i>h</i> ≤ -1 1 ≤ <i>k</i> ≤ 5 <i>l</i> = 0 <i>m</i> = 1
Index range of common main reflections	-13 ≤ <i>h</i> ≤ 0 0 ≤ <i>k</i> ≤ 13 <i>l</i> = 0 <i>m</i> = 0
Index range of pure satellite reflections	-5 ≤ <i>h</i> ≤ -1 1 ≤ <i>k</i> ≤ 5 1 ≤ <i>l</i> ≤ 6 <i>m</i> = -1, 1
No. of standard reflections	3
Frequency of standard reflections	Every 60 min
Absorption correction	None (see text)
Refinement general	
No. of measured reflections	2588
No. of independent reflections	786
No. of observed reflections	361
Criterion for observed reflections	<i>I</i> ≥ 3 σ (<i>I</i>)
Refinement on	<i>F</i>
Weighting scheme	$w = 1/[\sigma^2(F)]$
Extinction correction	None (see text)
Atomic scattering factors from	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
Refinement of the host structure	
No. of reflections used in refinement	608
<i>R</i> _{int} for all reflections	0.1329
<i>R</i> _{int} for observed reflections	0.0369
<i>R</i> _{all}	0.1104
<i>wR</i> _{all}	0.0483
<i>R</i> _{obs}	0.0448
<i>wR</i> _{obs}	0.0479
<i>S</i> _{all}	7.57
<i>S</i> _{obs}	10.97
Parameters	38

Refinement of the composite structure	
No. of reflections used in refinement	786
<i>R</i> _{int} for all reflections	0.1146
<i>R</i> _{int} for observed reflections	0.0201
<i>R</i> _{all}	0.1010
<i>wR</i> _{all}	0.0291
<i>R</i> _{obs}	0.0331
<i>wR</i> _{obs}	0.0274
<i>S</i> _{all}	4.53
<i>S</i> _{obs}	6.64
Parameters	57
Computer programs	
Data collection	CAD-4 EXPRESS (Enraf-Nonius, 1992)
Data reduction	MolEN (Fair, 1990)
Structure refinement	JANA94 (Petříček, 1994)
Structure presentation	XRSV (Weber, 1996a)

The modulus of the modulation vector $|\mathbf{q}| = |c_g^*|/|c_h^*| = 0.4646(5)$ is known from a previous synchrotron experiment (Weber, Boysen, Frey, Berar & Bley, 1996). Friedel pairs have been averaged, as no anomalous scattering of the atoms is expected. Since the linear absorption coefficient is very small ($\mu = 1.02$ cm⁻¹), the absorption correction is negligible. An attempt for extinction correction gave only marginal improvement of the fit and no reasonable parameters, *i.e.* negative extinction parameters, and has been omitted from the refinement. The reduction of the data gave some significantly negative intensities and discrepancies for some symmetrically equivalent satellite reflections. Thus, the profiles of all scans have been individually checked. All reflections with heavily asymmetric background have been omitted from the refinement (138 reflections).†

In agreement with earlier results of Forst *et al.* (1987), a violation of the extinction rule of the 6₁ screw axis was observed. In order to clarify whether this is due to a structural feature or due to *umweganregung*, ψ -scans were performed at 00*l*0 (*l* = 1–7) reflections and at some reflections with *h* ≠ 0 and/or *k* ≠ 0. For the 00*l*0 reflections a large number of strong *umweganregung* events could be found, which decrease in intensity with increasing *l*. The *umweganregung* peaks for the 0010 reflection are comparable even to the intensity of the relatively strong 0060 reflection (Fig. 2a). No *umweganregung* could be found for reflections with *h* ≠ 0 and/or *k* ≠ 0. A detailed analysis of the 0010 reflection has shown, however, that the intensity of this reflection never vanishes completely (Fig. 2b). This result may be explained by the fact that the terminal methyl groups have a higher mobility than the inner CH₂ groups. Thus,

† A list of structure factors has been deposited with the IUCr (Reference: SE0207). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the guest modulation does not perfectly follow the 6_1 screw axis.

4. Model

As only a few guest substructure main reflections could be observed, several restrictions had to be applied for the guest structure in order to reduce the number of refinable parameters. The rotational symmetry of the guest molecules (averaged in space and time) has been approximated by the sixfold symmetry of the guest molecules produced by the space group. This is sufficient, because the C atoms are very close to the rotation axis (ca 0.4 Å). Only the C atoms of the alkane molecule have been included in the model, as the refinement has shown that the H atoms are largely delocalized and have no significant influence on the Bragg intensities. The three-dimensional averaged structure of the guest molecules has been assumed to be in a stretched all-*trans* configuration with no intramolecular disorder apart from the modulation. As a consequence, the spacings between two C atoms along c_g are fixed at 1.28 Å. Moreover, an

isotropic atomic displacement parameter was taken and constrained to be equal for all guest atoms.

The modulation function of the guest structure was restricted to two features: a longitudinal displacive modulation parallel to c and a transverse displacive modulation perpendicular to the channel wall. Additional modulation parameters that would allow transverse modulations nonperpendicular to the channel wall did not improve the fit. The definition of the modulation function is given by

$$\mathbf{u} = \sum_j \mathbf{u}_j^s \sin(2\pi \cdot j \cdot \mathbf{q} \cdot \mathbf{r}) + \mathbf{u}_j^c \cos(2\pi \cdot j \cdot \mathbf{q} \cdot \mathbf{r}), \quad (1)$$

where \mathbf{r} is the positional vector of the given atom

and \mathbf{q} is the modulation vector $\begin{pmatrix} 0 \\ 0 \\ 0.4646 \end{pmatrix}$. A further

restriction in the description of the guest structure is that the modulation parameters are kept equal for all C atoms. The zigzag plane of the molecule is fixed within the \mathbf{a}, \mathbf{c} plane (and symmetric equivalent ones), such that the CH_2 groups of the heptadecane molecule are facing the channel walls. This orientation has not been chosen in order to suggest a preferred orientation of the alkane molecules (in the averaged three-dimensional structure they have rotational symmetry!), but to place the C atoms near the location of the maximum modulation of the guest structure (see §5).

In agreement with their fixed planar conformation, in the modulation of the host structure the urea molecules were treated as rigid bodies. Only one harmonic with no restrictions apart from those imposed by symmetry has been taken for the modulation of the host structure, as the qualitative interpretation of the diffraction pattern given above has shown that the satellite reflections, which are affected by the modulation of the host structure, are only few and very weak (see also Table 2). The modulation parameters [see equation (1)] of an individual atom i are calculated by

$$\mathbf{u}_i^s(i) = \mathbf{u}_{i,l}^s + \mathbf{u}_{r,l}^s \times (\mathbf{r}(i) - \mathbf{R}) \quad (2a)$$

and

$$\mathbf{u}_i^c(i) = \mathbf{u}_{i,l}^c + \mathbf{u}_{r,l}^c \times (\mathbf{r}(i) - \mathbf{R}), \quad (2b)$$

where $\mathbf{r}(i)$ is the positional vector of the i th atom and \mathbf{R} is the center of rotation of the rigid body as a weighted

centroid [here: $\mathbf{R} = \begin{pmatrix} 0.4115 \\ 0.8230 \\ 0.25 \end{pmatrix}$ (fractional coordinates)].

5. Results

5.1. Host structure

In a first step the nonmodulated three-dimensional host structure has been refined in a conventional way,

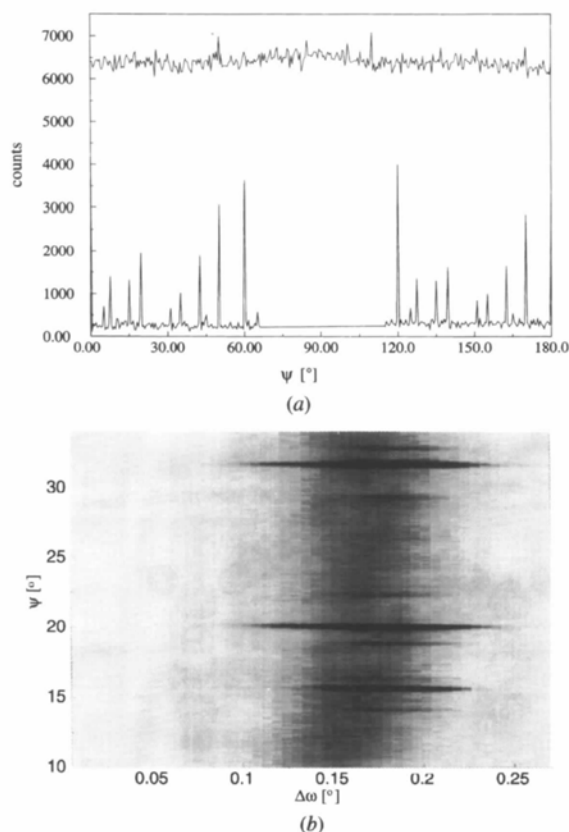


Fig. 2. (a) ψ -scans of the 0010 reflection (bottom) and the 0060 reflection (top). The ψ -values of 0010 between 66 and 114° were not accessible in the experiment. (b) Display of the 0010 reflection as a function of ψ (°) and the scan range $\Delta\omega$ (°). The background level is ca 200 counts, with the minimum value at the reflection position being ca 400 counts.

Table 2. Reflections used in the refinement of the complete composite structure

	Total	Observed	$\langle F \rangle$	$\langle F/\sigma(F) \rangle$
Main host reflections ($hkl0$) ($l \neq 0$)	608	305	67.9	44.0
Main guest reflections ($hk0m$) ($m \neq 0$)	10	9	27.3	47.1
Common main reflections ($hk00$)	49	26	141.5	75.5
Satellite reflections ($hk lm$) ($l, m \neq 0$)	119	19	4.2	2.2

i.e. only $hkl0$ reflections with $l \neq 0$ have been taken into account. The positional and atomic displacement parameters of urea/hexadecane given by Forst *et al.* (1990) were taken as starting values for the refinement.

The results of this conventional refinement are given in Table 3. A good agreement with the data of Forst *et al.* (1990) could be found. However, the high value of the goodness-of-fit ($S_{\text{all}} = 7.57$) indicates that the measured intensities cannot be completely explained by this model. In order to clarify this point, difference-Fourier maps have been calculated. Fig. 3 shows a difference-Fourier map in the section $x, y = -0.5$ to $0.5, z_h = 0.5$ of the host structure. A strong positive maximum at $(0.087, 0, 0.5)$, *i.e.* about 0.7 \AA away from the center of the channel, can be observed. The structural relations between host and guest structure are shown in Fig. 4. The orientation of the guest molecule chosen in this figure is that of its maximum modulation. Fig. 5 shows the difference-Fourier map of the a, c plane of the host cell in a section $x = -0.5$ to $0.5, y = 0$ and $z = 0-1$. Additionally to the same positive maximum at $x = 0.087, z_h = 0.5$, a strong negative maximum can be found at a distance of *ca* 0.5 \AA away from the center of the channel at $(0.076, 0, 0.85)$ and at symmetrically equivalent positions. These difference-Fourier maxima are close to the positions of the C atoms of an undistorted heptadecane molecule, which have a distance of *ca* 0.4 \AA from the center of the host channel. Thus, the difference map maxima may be interpreted as a consequence of the modulation of the guest structure with period $|c_l|$. All significant difference maxima of the guest structure are within the a, c plane and equivalent planes. Therefore, we can assume that the modulation of the guest structure has a maximum when the CH_2 groups of the alkane molecule are facing the tunnel walls. Trial refinements with additional atoms and an occupation of some tenths of an atom at the positions of positive difference-Fourier maxima gave a clearly improved fit. However, no further discussion of these results will be given, since a far more reliable interpretation of these phenomena can be obtained from the $(3+1)$ -dimensional approach.

The existence of maxima in the difference-Fourier plot near the position of the guest molecules has already been reported by Harris & Thomas (1990) for the compound urea/lauroyl peroxide. The authors concluded that

these maxima are due to an incommensurate modulation of the guest substructure, but no further interpretations on the properties of the guest structure modulation were given.

5.2. Composite structure

The results of the refinement of the composite structure using harmonics up to the 4th order with the restrictions mentioned above are listed in Tables 4, 5 and 6. Compared with the refinement of only the host structure, the S and R values of the $hkl0$ reflections have been clearly improved, although the ratio of included reflections and refined parameters is worse. No significant changes of the results compared with the refinement of only the host structure could be found in the averaged host structure.

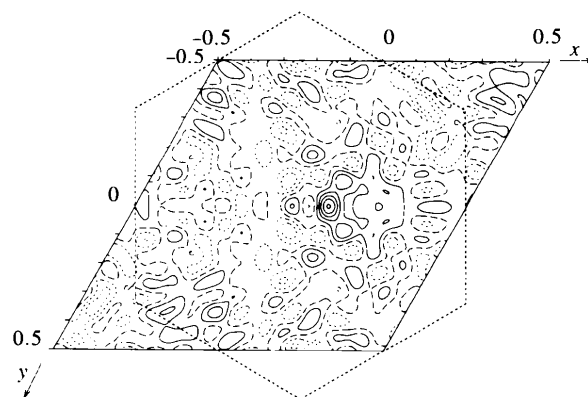


Fig. 3. x, y -section of the difference-Fourier map after refining only the host structure at $z_h = 0.5$. Contour lines are at intervals of 0.08 e \AA^{-3} . Positive and negative values are represented by solid and dashed lines, respectively, and the zero level by long dashed lines. The hexagon indicates the position of the channel walls.

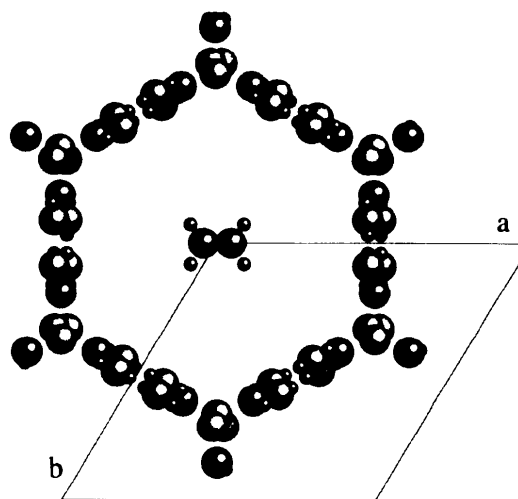


Fig. 4. View of the composite structure projected along $[001]$.

Table 3. Final values for the refinement of the host subsystem [only reflections ($hkl0$), $l \neq 0$]

The expression for the Debye-Waller factor is: $\exp(-2\pi^2 \sum_i \sum_j U^{ij} \mathbf{a}_i^* \mathbf{a}_j \mathbf{h}_i \mathbf{h}_j)$ with U^{ij} in \AA^2 .

	x	y	z	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C	0.4088 (2)	0.8176 (3)	1/4	0.040 (1)	0.040 (1)	0.034 (1)	0.0204 (7)	0.0023 (9)	0
O	0.3209 (1)	0.6418 (2)	1/4	0.0546 (9)	0.041 (1)	0.0297 (7)	0.0208 (5)	0.0003 (5)	0
N	0.4756 (4)	0.9129 (3)	0.3523 (1)	0.074 (1)	0.045 (1)	0.0329 (8)	0.019 (1)	-0.001 (1)	-0.0015 (9)
H(1)	0.532 (3)	0.034 (5)	0.355 (2)	0.01 (1)	0.21 (4)	0.02 (1)	0.06 (2)	0.002 (8)	0.04 (2)
H(2)	0.443 (2)	0.849 (3)	0.412 (2)	0.04 (1)	0.05 (2)	0.03 (1)	0.02 (1)	-0.02 (1)	-0.01 (1)

The refined occupation factor for the guest C atoms was 16.3 (2) carbons within one cell of the guest substructure. This is less than the expected value of 17. Thus, the nonincluded H atoms of the guest structure are not compensated by a higher occupation factor of the C atoms. This justifies the omission of H atoms from the refinement.

For the pure satellite reflections, which are mostly affected by the modulation of the host structure (see §2), the results are not satisfactory. Nevertheless, it was necessary to include the host modulation into the refinement, since the main guest reflections are expected to be influenced by satellite scattering of the host structure.

Hence, an accurate determination of the guest structure within the restrictions pointed out above is only possible by including the host structure modulation into the refinement.

6. Discussion

As the total scattering power of the guest structure is about $\frac{1}{3}$ of the total scattering power of the host structure, the low reliability factor for the $hk00$ reflections is evidence that the guest structure projected along c_g is well described by the selected model, in spite of the omission of the H atoms. On the other hand, a high reliability factor, $wR_{\text{obs}} = 0.1503$, for the $hk0m$ reflections shows that the three-dimensional averaged guest structure could only be obtained in a first approximation. This might be understood by the following consideration: the $hk0m$ reflections ($m \neq 0$) lie on diffuse planes. In order to minimize the contamination by the diffuse scattering underneath the peaks, only the strongest $hk0m$ reflections have been measured. Nevertheless, there is still some uncertainty about the contribution of diffuse scattering to their intensities. Furthermore, the only weak correlations between the z -coordinates of lateral neighboring heptadecane molecules cannot be described sufficiently by an isotropic ADP. The same argument holds for the nonperfect long-range order parallel c_g . An attempt to describe these features by anisotropic ADP's with U^{13} and U^{23} set to zero did, however, not improve the fit. Since the wR_{obs} value of the $hklm$ reflections ($l, m \neq 0$) is more than 50%, and thus unacceptably high, the host structure modulation could not be described satisfactorily. For this, the same arguments as above hold for the three-dimensional guest structure, as the host structure modulation is caused by the guest molecules. Additionally, the intensities of these reflections are very weak.

In contrast to the host structure modulation, the modulation of the guest structure could be obtained with sufficient confidence within the limits of the model. The fact that only the modulation of the projected guest structure could be determined indicates that the guest modulation could be obtained only as a function of z_h and not as a function of z_g . This has been taken into account by equalizing the modulation parameters for all guest atoms.

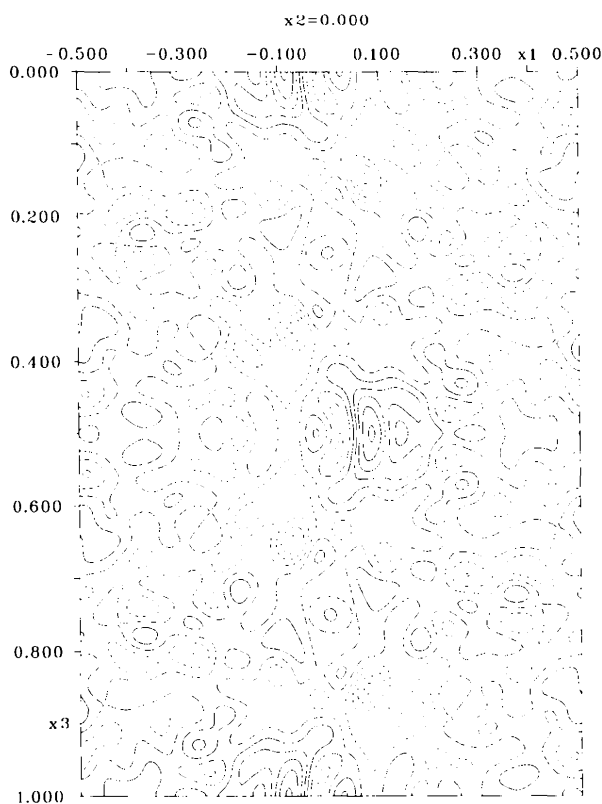


Fig. 5. x, z -section of the difference-Fourier map after refining only the host structure at $y = 0$. Contour lines are at intervals of 0.08 e \AA^{-1} . Positive and negative values are represented by solid and dashed lines, respectively, and the zero level by long dashed lines.

Table 4. Final values for the positional and atomic displacement parameters of the composite structure

The expression for the Debye–Waller factor is: $\exp(-2\pi^2 \sum_i \sum_j U^{ij} \mathbf{a}_i \cdot \mathbf{a}_j \cdot \mathbf{h}_i \cdot \mathbf{h}_j)$, with U^{ij} in \AA^2 . U_{iso} is defined by $\exp(-8\pi^2 U_{\text{iso}}[(\sin^2 \vartheta)/\lambda^2])$. The occupation factor of C(1) being on a special position is half the others.

(a) Host substructure									
	<i>x</i>	<i>y</i>	<i>z</i>	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C	0.40854 (9)	0.8170 (2)	1/4	0.0419 (5)	0.0443 (8)	0.0330 (7)	0.0221 (4)	0.0020 (5)	0
O	0.32039 (6)	0.6408 (1)	1/4	0.0532 (4)	0.0430 (6)	0.0306 (4)	0.0215 (3)	0.0003 (3)	0
N	0.4770 (2)	0.9130 (2)	0.35249 (9)	0.0722 (8)	0.0453 (6)	0.0332 (5)	0.0192 (6)	-0.0025 (5)	-0.0022 (5)
H(1)	0.537 (2)	0.035 (2)	0.3530 (8)	0.09 (1)	0.056 (8)	0.021 (6)	0.013 (8)	-0.001 (5)	0.007 (6)
H(2)	0.447 (2)	0.844 (2)	0.4171 (8)	0.11 (1)	0.063 (8)	0.040 (7)	0.041 (7)	-0.009 (8)	-0.021 (7)

(b) Guest substructure					
	Occupation	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
C(1)	0.0804 (8)	0.0525 (7)	0.0	1/2	0.111 (4)
C(2)	0.160 (2)	0.0525 (7)	0.0	0.554	0.111 (4)
C(3)	0.160 (2)	0.0525 (7)	0.0	0.607	0.111 (4)
C(4)	0.160 (2)	0.0525 (7)	0.0	0.661	0.111 (4)
C(5)	0.160 (2)	0.0525 (7)	0.0	0.715	0.111 (4)
C(6)	0.160 (2)	0.0525 (7)	0.0	0.768	0.111 (4)
C(7)	0.160 (2)	0.0525 (7)	0.0	0.822	0.111 (4)
C(8)	0.160 (2)	0.0525 (7)	0.0	0.876	0.111 (4)
C(9)	0.160 (2)	0.0525 (7)	0.0	0.929	0.111 (4)

Table 5. Final values of the amplitudes of the displacive modulation function

(a) Host substructure (rigid-body modulation)				
	$\mathbf{u}_{r,l}^x$	$\mathbf{u}_{r,l}^y$	$\mathbf{u}_{r,l}^z$	$\mathbf{u}_{r,l}^w$
	$\begin{pmatrix} 0.0015 (2) \\ 0 \\ 0.0005 (2) \end{pmatrix}$	$\begin{pmatrix} -0.0001 (2) \\ 0 \\ -0.0008 (2) \end{pmatrix}$	$\begin{pmatrix} -0.0015 (4) \\ -0.0018 (5) \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0.0016 (4) \\ 0.0034 (3) \\ 0 \end{pmatrix}$

(b) Guest substructure			
	<i>j</i>	\mathbf{u}_j^x	\mathbf{u}_j^z
C(1–9)	1	$\begin{pmatrix} 0 \\ 0 \\ 0.015 (2) \end{pmatrix}$	$\begin{pmatrix} -0.019 (1) \\ 0 \\ 0 \end{pmatrix}$
	2	$\begin{pmatrix} 0 \\ 0 \\ -0.012 (1) \end{pmatrix}$	$\begin{pmatrix} 0.005 (1) \\ 0 \\ 0 \end{pmatrix}$
	3	$\begin{pmatrix} 0 \\ 0 \\ 0.015 (1) \end{pmatrix}$	$\begin{pmatrix} 0.007 (3) \\ 0 \\ 0 \end{pmatrix}$
	4	$\begin{pmatrix} 0 \\ 0 \\ -0.019 (1) \end{pmatrix}$	$\begin{pmatrix} 0.017 (3) \\ 0 \\ 0 \end{pmatrix}$

Table 6. Final reliability factors of the refinement of the composite structure

	R_{all}	wR_{all}	R_{obs}	wR_{obs}
All reflections (<i>hklm</i>)	0.1010	0.0291	0.0331	0.0274
Main host reflections (<i>hkl0</i>) (<i>l</i> ≠ 0)	0.0968	0.0232	0.0296	0.0222
Main guest reflections (<i>hk0m</i>) (<i>m</i> ≠ 0)	0.1597	0.1506	0.1462	0.1503
Common main reflections (<i>hk00</i>)	0.0682	0.0328	0.0373	0.0324
Satellite reflections (<i>hklm</i>) (<i>l, m</i> ≠ 0)	1.0613	0.7530	0.4155	0.5197

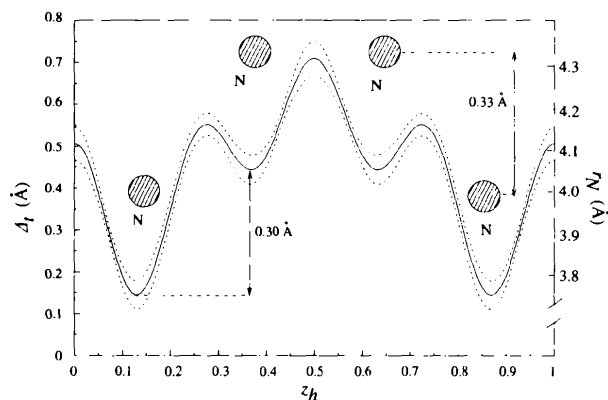


Fig. 6. Comparison of the transverse modulation of the guest C atoms as a function of z_h and the positions of the host N atoms. The dashed lines indicate the confidence interval of the guest modulation. The scale on the left-hand side belongs to the distance of the guest C atoms from the center of the channel, while the scale on the right-hand side corresponds to the distance of the N atoms from the center of the channel.

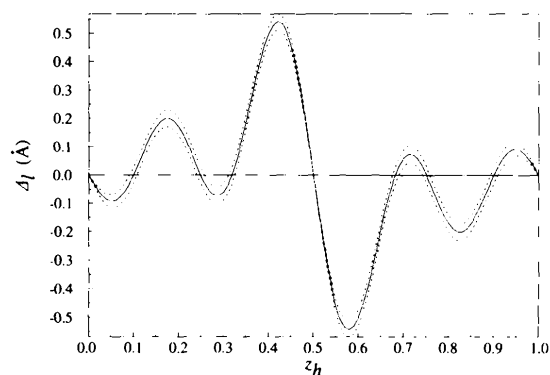


Fig. 7. Longitudinal modulation of the guest C atoms as a function of z_h . The dashed lines indicate the confidence interval.

Figs. 6 and 7 give the transverse and the longitudinal modulation of a guest carbon atom at the position ($x0z_h$) [$x = 0.0525$ (7), see Table 4b] as a function of z_h . The modulation of the other symmetrically equivalent orientations of the alkane molecules perpendicular to the channel walls can easily be obtained by applying the 6_1 screw axis. For the transverse modulation function, local maxima at $z_h = 0, 0.25, 0.5$ and 0.75 and local minima near $z_h = 0.1, 0.35, 0.65$ and 0.9 can be observed. These features can be related to the features of the host structure. Fig. 8(a) shows the projection of the tunnel structure along **a** (view from the center of a channel). It can be seen that there is a trough in the channel wall between the urea molecules at $z_h = 0$ and $z_h = 0.5$, leading to a shift of the guest atoms towards the channel walls. A smaller gap between the NH_2 groups of an urea molecule at $z_h = 0.25$ and $z_h = 0.75$ promotes a further shift away from the center of the channel.

Due to the small tilt of the urea molecules around their C—O axis, N atoms near $z_h = 0.35$ and $z_h = 0.65$ are 0.165 \AA 'outside' the channel walls and the nitrogens near $z_h = 0.1$ and $z_h = 0.9$ are 0.165 \AA 'inside' the channel walls (view along [100]), which means that an extrusion of the N atoms can be found at $z_h = 0.5$ and an intrusion near $z_h = 0$ (see Fig. 8b). Fig. 6 illustrates that the displacement of the N atoms from the channel walls is the origin for the local minima in the modulation function. Within the error limits, the minima have the same z_h coordinates as the N atoms. Even the distance between the local minima in the modulation function

parallel **a** (0.30 \AA) is in good agreement with the distance of the corresponding N atoms (0.33 \AA).

The longitudinal modulation of the guest structure can also be explained by the structure of the channel walls. The features of the longitudinal modulation (Fig. 7) are the following: the modulation function is mainly positive for the CH_2 groups at positions $z_h < 0.5$, while it is negative at $z_h > 0.5$. The maximum value of the longitudinal modulation is near $z_h = 0.5$. Thus, the components of the guest molecules tend to move towards the extrusion in the channel walls. Again the modulation function has maxima near the position of the host N atoms. The longitudinal modulation vanishes at $z_h = 0.25$ and $z_h = 0.75$, where the CH_2 groups of the heptadecane molecule are in the center between the NH_2 groups of the urea molecule.

It should be stressed that only the *averaged modulated* structure can be described by the model. Hence, the modulation function may not necessarily be interpreted as small shifts of individual CH_2 groups, as suggested by the modulation functions. Also, significant distortions in the guest structure may lead to similar results in the averaged modulated electron density of the guest structure. For example, a partial *gauche* conformation of the alkane molecules has already been observed for $\text{CH}_2\text{—CH}_2$ bonds near the ends of the alkanes by the NMR method (*e.g.* Imashiro, Kuwahara, Nakai & Terao, 1988) and by IR and Raman methods (Casal, 1990). Nevertheless, an adaptation of the guest atoms to the channel walls and a concentration of electron density at

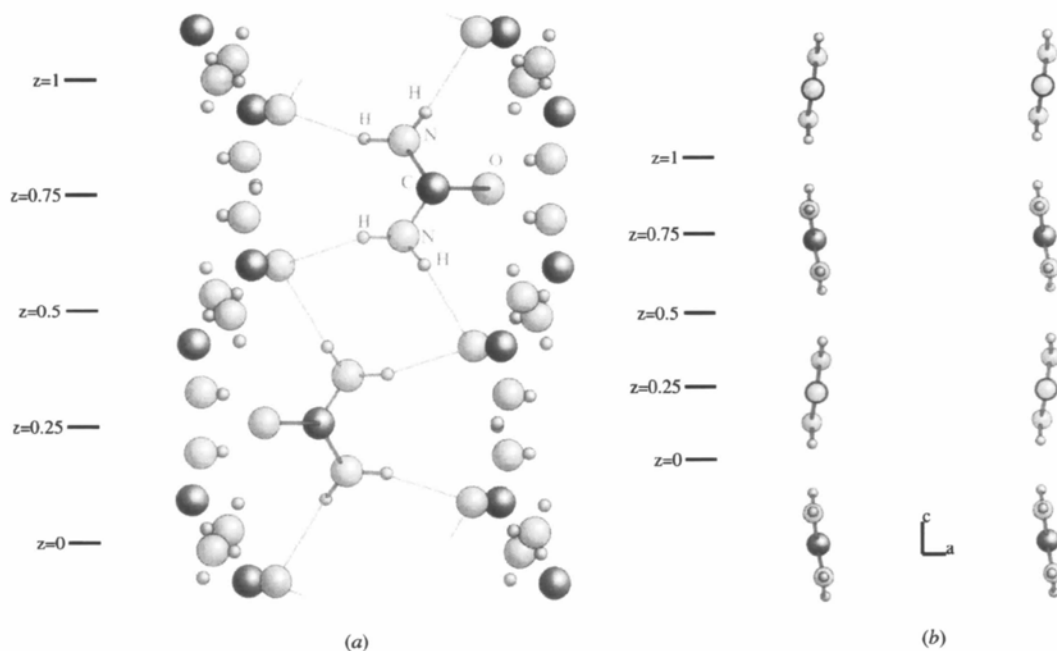


Fig. 8. (a) View of the host structure along [100] perpendicular to the channel walls. (b) Side view to the channel walls of the host structure.

the extrusion of the channel walls can be concluded from the experimental results. Thus, it can be deduced that the maximum of the modulation of a guest molecule occurs when the CH₂ groups are facing the channel walls. This result is important for the understanding of the phase transition at low temperatures, as the modulation of alkane molecules is energetically unfavorable and thus an orientation towards the channel walls will be avoided at low temperatures.

The high value of the goodness-of-fit ($S_{\text{all}} = 4.53$) indicates that the composite structure could not be completely solved. Also, the failing extinction correction which yielded negative values might be indicative for an incomplete description of the guest structure modulation in so far as too small F_{calc} values for the guest structure satellite scattering contribute to the $hkl0$ reflections. The current model does not include strong anharmonic modulation features, which may be the reason for the too low occupation factor of the guest carbons. The limited number of satellite reflections did not, however, allow higher harmonics to be included.

7. Conclusions

It has been shown that a reasonable structure determination of only one (main) subsystem of a composite crystal must always include the other subsystems, even if these subsystems are heavily disordered and therefore not satisfactorily refineable. In case that one subsystem is well ordered only along the projection parallel to the modulation vector, the satellite reflections of this subsystem will coincide with the main reflections of the other subsystem. No additional satellite reflections of the disordered structure will then be observed, although the satellite scattering of the projected structure may have a significant contribution to the main reflections of the other system.

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