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The Disordered Crystal Structure of Urea Inclusion Compounds $OC(NH_2)_2 + C_nH_{2n+2}$

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Abstract

Urea inclusion compounds, $OC(NH_2)_2 + C_nH_{2n+2}$, consist of two structural components, the urea framework and the included paraffin chains. Although the c-lattice constants of both are incommensurate and no satellite reflections are observed, independent structure determinations cannot be performed because of the contributions of the included chains and the framework to all of the observed reflections. For the compounds with dodecane and hexadecane, average structures and (001) projections, yielding the orientations of the included chains, have been determined at room temperature. Hydrogen (deuterium) positions (hexadecane) were determined using neutron data. Limitations of conventional refinement procedures are discussed. Using special arguments, the main features of the superstructure of the hexadecane compound have been revealed. X-ray diffraction of the low-temperature phase has been investigated for the same compound. Its structure could not be solved, because of the huge number of coincidences of inequivalent reflections caused by orientational twinning. Since separation of reflections was not performed in the structure determination by Chatani, Anraku & Taki [*Mol. Cryst. Liq. Cryst.* (1978), **48**, 219–231] their proposed structure cannot be correct.

1. Introduction

Urea inclusion compounds are framework structures of urea, $OC(NH_2)_2$, with n-paraffins, C_nH_{2n+2}. Their idealized structure is described in space group $P6_122$ ($a = 8{\cdot}22$, $c = 11{\cdot}02$ Å) and was originally suggested by Hermann (1949). This structure was confirmed by Smith (1952) for the compound with hexadecane, $C_{16}H_{34}$, as the inclusion. The framework represents a honeycomb-like structure with open channels occupied by the included chains. Since the 6_1-screw axis of the space group is only consistent with stretched paraffin chains rotating around their elongated axis, this structure can be no more than an average structure which may be generated by random orientational statistics or by dynamical rotation. Since the extinction rule of the 6_1-screw axis is not strictly obeyed below the transition at about 360 K, a free rotation of the paraffin chains seems to be improbable in this temperature range. Furthermore, the translation period of the paraffin molecules is incommensurate with the c-lattice constant of the urea framework structure. This is even true for the hexadecane inclusion compound, where the distances of neighbouring molecules are approximately twice the length of the c period of the urea framework structure. Surprisingly, the ordering of c distances of the paraffin chains is almost perfect, in spite of the nearly random orientational disorder of the molecules. As a consequence of this disorder no mutual modulations of the two incommensurate lattices could be observed. This fact favours the idea of two practically independent lattices, but it will be shown below that this assumption cannot be correct. There are several phase transitions which have been described by Forst, Boysen, Frey, Jagodzinski & Zeyen (1986). Compared with the other inclusion compounds, these are slightly different for the compound with hexadecane. Here additional reflections are observed in the room-temperature phase, indicating a doubled c period of the framework structure. They have been observed by other authors, *e.g.* Smith (1952), but no satisfactory explanation has been given so far. The disorder phenomena are accompanied by a strong diffuse scattering which has been explained by Forst, Jagodzinski, Boysen & Frey (1987). The quantitative interpretation revealed an orientational disorder of the stretched paraffin chains with negligible correlations between the chains in different channels at room temperature.

There are three phase transitions from the high-temperature phase I, to the low-temperature form IV. The study of these phase transformations (Forst *et al.*, 1986) and the diffuse scattering (Forst *et al.*, 1987) revealed that a full understanding can only be obtained if a renewed structure determination is performed taking into account the following:

(*a*) As shown in Forst *et al.* (1987), both structures cannot be independent; hence refinement methods

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must not be applied without a careful study of the contributions of the two structural elements (urea host and paraffin guest).

(*b*) A careful study of intensities for the compound with hexadecane revealed that the extinction rule of the 6_1-screw axis is violated. This observation is true specifically in the case of neutron data, but has also been confirmed by X-ray measurements using a synchrotron source (Boysen, Rieck, Schulz, Eichhorn & Haubold, 1989).

(*c*) The interactions between host and guest molecules are most probably due to hydrogen bonds and repulsive forces. Hence, determination of the hydrogen positions is necessary using neutron data of the deuterated compounds.

(*d*) Superstructure reflections indicate a doubled *c* period, caused by the corresponding *c* distance of the included paraffin chains. In spite of this the diffuse layers [called *s* layers by Forst *et al.* (1987)] remain almost sharp in the c^* direction, and are unaffected by this superstructure formation.

Since this compound does not belong to the normal type of modulated structures, characterized by main reflections and satellites, new methods of structure determination have to be applied which will be described in the following. Most emphasis will be placed on the room-temperature phase of the compound with hexadecane, which seems to represent a key structure in this group of compounds.

2. Experimental

Single crystals were synthesized according to the method described by Schlenk (1949). In the case of X-ray diffraction the dimensions of the needle-shaped crystals were about 5 mm in length and 1 mm in width. Great care was taken to obtain large needles of the compound with hexadecane for neutron measurements. In order to avoid incoherent background scattering, fully deuterated urea and paraffin have been used; the dimensions of the crystals were approximately 20 × 3 mm. Their mosaic spread did not exceed 6′ of arc. Intensities of sharp reflections were collected with an automatic single-crystal diffractometer (κ geometry), using Cu and Mo $K\alpha$ radiation. Neutron measurements were performed with the MAN II diffractometer ($\lambda = 1{\cdot}2$ Å) at the FRM reactor in Garching. Powder diffraction data with neutrons were obtained at 295, 70 and 4 K, using the MAN I diffractometer at FRM ($\lambda = 1{\cdot}078$ and 2·4 Å). The measurement and evaluation of the data have been extensively described by Forst (1984).

3. High-temperature phase

As has been shown in Forst *et al.* (1987), the low orders of diffuse *s* layers are completely sharp in the c^* direction for all of the compounds, but rather diffuse in the reciprocal plane perpendicular to c^*. Their *c*-lattice constant depends directly on the length of the included paraffin chains. For a detailed discussion see the papers by Laves, Nicolaides & Peng (1965) and Lenné (1961, 1963*a*,*b*). Because of the different maximum symmetries of paraffins with even or odd numbers of C atoms, we restricted our studies to the two even-numbered molecules dodecane and hexadecane, the inclusion compounds of which are called C12 and C16 in the following. A comparison showed that the collected data sets of both compounds are closely similar.† As mentioned above, the observation of superstructure reflections is restricted to C16. They vanish at elevated temperature (365 K). Here the diffraction patterns of sharp reflections are almost identical, hence the same framework structure may be assumed for both compounds. Even at room temperature a similar agreement is observed, the existence of superstructure reflections for C16 (doubled *c* constant) excepted. Their omission in structure refinement corresponds to a superposition of the two cells into a single one. Furthermore, the similarity of the diffraction patterns indicates that in the case of C16 a (small) part of the diffuse scattering concentrates into superstructure reflections, without changing the average structure of the cells significantly. A continuous decrease in intensities of the superstructure reflections with increasing temperature demonstrates the continuous transformation to the idealized average structure. Hence, in agreement with measurements of quasielastic neutron scattering by Boysen, Frey & Blank (1988), an initial free rotation of paraffins around their *c* axis may be excluded at least at lower temperatures. This is supported by the observation that the diffuse *s* layers are nearly unaffected by this transformation. Because of the one-dimensionality of the chain ordering, the almost strict periodicity of chain positions is not compatible with free rotation. This fact may be derived from the general proof by Gürsey (1950) that one-dimensional systems do not show long-range order, except for $T = 0$. This is an important point for all the structure determinations described below.

4. (001)-Projection of C16 and orientations of chains

The orientational disorder necessitates a careful study of the interdependence of Bragg and diffuse scattering. All previous papers have not taken this fact into account satisfactorily. Obviously, the pro-

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† Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52240 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

jection of structures on the basal plane (001) is exceptional in so far as both host and guest molecules contribute to the (*hk*0) reflections. Since all displacements parallel to *c* are meaningless, the diffraction patterns of both become 'commensurate'. Hence, the projection on (001) should provide the framework structure *and* the structure of the paraffin chains as well. As has been shown in Forst *et al.* (1987), the paraffin chain of C16 is at least nearly stretched. In the case of X-ray diffraction H atoms may be neglected in a first approximation. Hence we have to take into account two C positions only, separated by a small distance of about 0·9 Å. A major difficulty arises from the orientational disorder, involving at least six orientations of the paraffin chain. Fortunately, the diffraction patterns of a chain with six orientations, following hexagonal symmetry, and a rotating chain (cylinder symmetry) are not very different, as shown in Forst *et al.* (1987) (equations 3 and 4). This is particularly true for low diffraction angles. Hence the C atoms of the inclusion behave like heavy atoms in this projection. As a consequence, the Patterson function should show the chain and the projection of the framework very clearly. Fig. 1 gives this Patterson projection from which all distances of the known framework structure have been subtracted. The six orientations of the paraffin chain parallel to [$1\bar{1}0$] in the centre of the unit cell may easily be recognized, although six split pairs with orientations similar to these directions cannot safely be excluded. In the paper by Chatani, Anraku & Taki (1978) [110] is assumed to be the correct orientation. This different result was primarily concluded from energy calculations of chain–framework interactions. The present authors feel that these calculations, made without knowledge of H-atom positions, are not convincing. The fact that the partial Patterson function of the structure, shown in Fig. 1, yields a very clear indication of the orientations, may be easily understood by remembering that the distances of 'heavy' atoms appear as predominant maxima in this projection. In Fig. 1 the positions of the host atoms O, C and N are marked by small dots, their positional parameters having been taken from the final refinement using three-dimensional data. The framework structure, generated by the convolution with the chain, is well resolved. This is another indication that the chains of the inclusion are stretched and located in the centres of the channels.

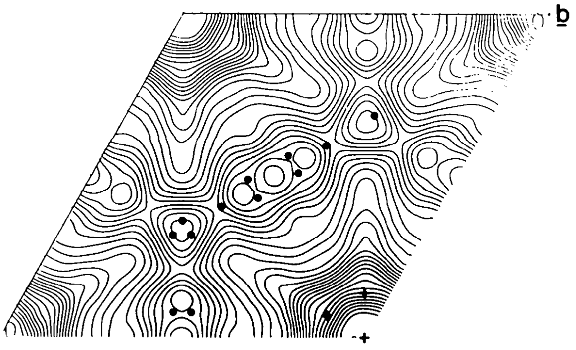


Fig. 1. Patterson projection along (00*l*) after subtracting intra-urea-framework distances. Dots represent distance vectors from the central inclusion to the urea framework, crosses indicate C—C distances of the chains.

Table 1. *Atomic parameters* (x, y) *in Cartesian coordinates for the hexadecane inclusion*

	C	D1	D2	*R* value
X-rays				
x (Å)	0·38 (2)	—	—	0·04
y (Å)	0·22 (2)			
B (Å^2)	8·6 (1·0)			
Neutrons				
x (Å)	0·36 (5)	0·46 (10)	1·36 (9)	0·07
y (Å)	0·18 (9)	1·36 (15)	−0·26 (10)	
B (Å^2)	8·0*	9·5*	9·5*	

* Fixed.

The (*hk*0) refinement was performed with X-ray and neutron data. For the inclusion both symmetry-adapted Bessel functions and positional parameters have been used for the intensity calculations. The refinement with X-ray data yielded no significant differences between the two models, while neutron data showed a small preference for the orientational model. This may be easily understood by considering the strong contribution of the D atoms with the largest off-centre distances from the chain axis. The unweighted *R* factor for X-rays (4%) was considerably better than that for neutrons (7%). Table 1 shows the parameters for the included paraffin chain in Cartesian coordinates (Å), as obtained from neutron data. In contrast to the X-ray refinement, a scaling factor of 0·78 had to be introduced for the chain in the neutron case. This fact and the higher *R* factor (7%) indicate that a considerable disorder of the H (D) atoms is involved. Unfortunately, a better solution of the chain structure with three-dimensional data can only be given if the diffuse *s* layers are included in refinement procedures. Since neither three-dimensional neutron data nor a special program were available, this part of structure determination could not be performed. Hence some uncertainties remain regarding the structure of the paraffin chain.

Another difficulty for the refinement with neutron data was caused by the fact that the D-atom positions of the two methyl end groups (six D atoms) could not be determined. This is due to their relatively small weight (1/7 in this projection), their large disorder, and the low number of neutron reflections available for the refinement. As has been pointed out in Forst *et al.* (1987), there is a nearly random distribution of orientations of the paraffin molecules within one channel. Looking at Fig. 1, we have to take into account six orientations (or six pairs with a small splitting angle). A typical diffuse scattering of the paraffin chains, called 'diffuse *d* layers' in Forst *et al.* (1987), is generated by these almost random orientational statistics. As will be shown in a forthcoming paper, important additional information on the orientational statistics may be drawn from the behaviour of line profiles of diffuse *d* layers and characteristic changes in intensities of *s* layers.

Table 2. *Atomic coordinates and thermal parameters* (Å^2) *of urea in* C12: *X-ray data*, Cu *Kα*

	O1	C1	N1	H1	H2
x	0·3207 (1)	0·4073 (2)	0·4781 (4)	0·5356 (32)	0·4386 (37)
y	0·6414 (3)	0·8146 (4)	0·9152 (3)	0·0598 (32)	0·8450 (40)
z	0·2500	0·2500	0·3527 (2)	0·3606 (14)	0·4045 (20)
U_{11}	0·0595 (12)	0·047 (13)	0·0737 (16)	—	—
U_{22}	0·0434 (13)	0·0406 (16)	0·0441 (13)	—	—
U_{33}	0·0313 (11)	0·0396 (17)	0·0324 (10)	—	—
U_{23}	0	0	− 0·0030 (9)	—	—
U_{13}	0	0	− 0·0014 (10)	-	—
U_{12}	0·0217 (6)	0·0203 (8)	0·0189 (13)	—	—
$U_{\rm iso}$	—	—	—	0·0329 (49)	0·0512 (78)

Table 3. *Atomic coordinates and thermal parameters* (Å^2) *of urea in* C16: *X-ray data*, Mo *Kα*

	O1	C1	N1	H1	H2
x	0·3205 (0)	0·4085 (1)	0·4772 (1)	0·5344 (11)	0·4512 (11)
y	0·6410 (1)	0·8171 (1)	0·9136 (1)	0·0348 (15)	0·8555 (11)
z	0·2500	0·2500	0·3527 (2)	0·3569 (5)	0·4036 (7)
U_{11}	0·0502 (3)	0·418 (3)	0·0715 (5)	0·0441 (59)	0·0343 (43)
U_{22}	0·0408 (3)	0·0423 (4)	0·0424 (3)	0·0953 (72)	0·0325 (49)
U_{33}	0·0270 (2)	0·0258 (2)	0·0296 (2)	0·0303 (41)	0·0642 (45)
U_{23}	0	0	− 0·0011 (2)	0·0386 (38)	− 0·0261 (41)
U_{13}	0	0	− 0·0018 (3)	0·0245 (30)	− 0·0088 (47)
U_{12}	0·0204 (1)	0·0211 (2)	0·0182 (4)	0·0395 (59)	0·0041 (35)

5. Average structure of C12 and C16 at room temperature

Coincidences other than (*hk*0) could be excluded by checking oscillation photographs (large inclination angles). Nevertheless, an independent refinement of the host structure is subject to the following restrictions:

(*a*) The superstructure reflections for C16 are neglected.

(*b*) (*hk*0) reflections have to be excluded from refinement.

(*c*) The coordinates of the guest molecule, as described in the unit cell of the host, are essentially continuous lines parallel to *c* (only in this case the structure factors of the inclusion become zero!). This condition only holds for an incommensurate structure that has no correlations between guest and host molecules.

Considering the result of the refinement for the guest molecule, given in the preceding section, restriction (*c*) is not really satisfied. Deviations have to be expected in parts of the framework structure that have a close contact with the guest molecule (hydrogen bonds, van der Waals and repulsive forces). Here systematic displacements take place, being large specifically for H atoms and their immediate neighbours. As a consequence, the atomic coordinates of the guest, described in the unit cell of the host (and *vice versa*), are no longer continuous lines. They show specific maxima which may be described with the aid of distribution functions, and have to be considered in the refinement of the host structure. The same discussion is valid for the structure determination of the guest molecule with the aid of the diffuse *s* and *d* layers, where the displacements of the host atoms have to be introduced in a similar way. Hence both the guest and the host have an unknown influence on the diffraction pattern ascribed to the corresponding partner. Obviously, many positions for the displaced atoms (or a distribution function with a corresponding large number of parameters) have to be introduced. Their contributions to structure factors are generally small, but they may become large occasionally, such that the observed intensities show substantial deviations from the calculated ones. These observations are important for a discussion of the various *R* factors.

The results of the refinement of C12 are given in Table 2. The unweighted and weighted *R* factors are satisfactory in this case, although the number of independent reflections (456) was not very large compared with 28 free parameters. The heavily disordered structure and the fact that the influence of the guest molecules could not be included are reasonable explanations for the values of 5·8 and 4·8%, respectively. The corresponding results for the refinement of the C16 structure are shown in Table 3. The large number of independent reflections (2680, Mo *Kα*) justifies the introduction of anisotropic temperature parameters for H atoms (38 free parameters). Compared with the results for C12, the unweighted *R* value is appreciably larger (16·1%), but a comparison with the weighted *R* (5·8%) reveals that the large number of weak reflections is responsible for this difference, which is most probably caused by the inclusion. Table 4 shows the results of the corresponding refinement using neutron data (910 independent reflections, 38 parameters). Although the agreements between the coordinates of O, C and N are satisfactory, the deviations for H (D) are far beyond the standard deviations. This may be explained by the large displacements caused by disorder and the influence of the guest molecules. This is particularly true for the large value of U_{11} for the two D atoms (*cf.* Table 4). Thermal ellipsoids are shown in Fig. 2, while Fig. 3 gives the hydrogen

Table 4. *Atomic coordinates and thermal parameters* (Å^2) *of urea in* C16: *neutron data*, λ = 1·2008 Å

	O1	C1	N1	H1	H2
x	0·3200 (4)	0·4080 (3)	0·4797 (4)	0·5483 (7)	0·4534 (7)
y	0·6400 (8)	0·8159 (6)	0·9130 (4)	0·0512 (6)	0·8383 (6)
z	0·2500	0·2500	0·3534 (2)	0·3559 (3)	0·4318 (3)
U_{11}	0·0473 (23)	0·462 (21)	0·0639 (20)	0·0918 (37)	0·0917 (36)
U_{22}	0·0513 (32)	0·0433 (26)	0·0463 (16)	0·0541 (25)	0·0601 (26)
U_{33}	0·0371 (22)	0·0340 (19)	0·0462 (12)	0·0589 (22)	0·0441 (17)
U_{23}	0	0	−0·0062 (12)	−0·0073 (19)	−0·0043 (18)
U_{13}	0	0	−0·0067 (12)	−0·0010 (21)	−0·0079 (20)
U_{12}	0·0256 (16)	0·0217 (13)	0·0183 (15)	0·0235 (23)	0·0344 (26)

(deuterium) bonds in the urea framework structure. The most important atomic distances and bond angles for C16 are shown in Table 5. The molecule is nearly planar; the maximum deviations from the best plane are given in Table 6.

Since the superstructure of C16 at room temperature is caused by small displacements, an accurate analysis of the thermal parameters is desirable. First of all, the extent to which the thermal ellipsoids may be interpreted in terms of a translated and rotated rigid urea molecule should be investigated. The result of this analysis is given in Table 7, which shows a satisfactory agreement with the independent motions of a rigid molecule. It should be pointed out, however, that not all displacements are due to thermal movements. According to the results published in Forst *et al.* (1986, 1987), there is a strong, nearly temperature-independent diffuse scattering, which has been found with the aid of the pure elastic part of diffuse neutron scattering. Hence we have to bear in mind that the thermal ellipsoids do contain information on the superstructure *and* on the additional disorder of the framework structure. Its separation will be treated in the following section.

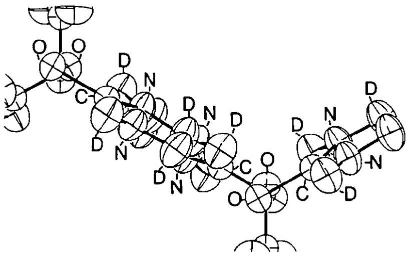


Fig. 2. Thermal ellipsoids of urea in C16 projected along [001].

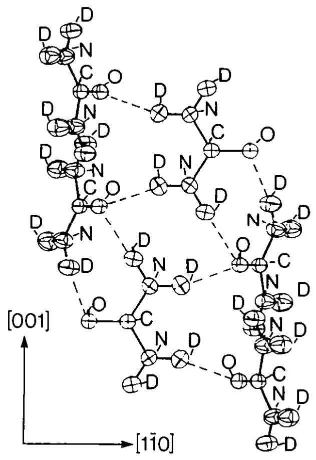


Fig. 3. Hydrogen bonds (broken lines) and thermal motion of the urea framework of C16 projected along [110].

Table 5. *Important distances* (Å) *and bond angles* (°)

	Dodecane, X-rays, Cu $K\alpha$	Hexadecane, X-rays, Mo $K\alpha$	Hexadecane, neutrons Uncorrected	Hexadecane, neutrons Corrected
O—C	1·239 (3)	1·253 (1)	1·255 (5)	1·263 (5)
C—N	1·354 (2)	1·334 (1)	1·343 (3)	1·353 (3)
N—D1	—	—	1·003 (3)	1.009 (3)
N—D2	—	—	1·003 (3)	1·011 (3)
O···D1—N	—	—	3·018 (4) (O—D 2·015)	
O′···D2—N	—	—	3·033 (4) (O—D 2·030)	
O—C—N	121·8 (2)	121·1 (1)	121·0 (2)	
N—C—N	116·4	117·8	118·0	
C—N—D1	—	—	122·7 (3)	
C—N—D2	—	—	117·5 (3)	
D1—N—D2	—	—	119·8 (4)	
O···D1—N	—	—	162·5	
O′···D2—N	—	—	170·7	

Table 6. *Deviations* (Å) *from the best plane of the urea molecule in* C16

Equation of the plane: $0{\cdot}989x - 0{\cdot}1452z = -0{\cdot}3989$.

	Deviation		Deviation
O	0·0000	D1	0·0042
C	0·0000	D1′	−0·0042
N	0·0152	D2	−0·0112
N′	−0·0152	D2′	0·0112

Table 7. *Tensor components of translations and librations in terms of a rigid molecule for the urea molecule in* C16

Coupling components between translations and librations vanish (standard deviations in parentheses).

L (rad^2)		
0·0030 (7)	0·0000 (10)	0·0000 (11)
0·0000 (0)	0·0128 (11)	0·0000 (12)
0·0000 (0)	0·0000 (0)	0·0098 (12)
S (rad Å)		
0·0000 (11)	0·0000 (5)	0·0009 (6)
0·0000 (15)	0·0003 (11)	0·0000 (15)
0·0009 (9)	0·0000 (12)	0·0003 (10)
T (Å^2)		
0·0559 (15)	0·0000 (13)	0·0016 (13)
0·0000 (0)	0·0494 (11)	0·0000 (10)
0·0000 (0)	0·0000 (0)	0·0414 (12)

6. Superstructure of C16

The simplest approach to the solution of the superstructure follows group-theoretical methods (Boysen & Forst, 1986), assuming the invariance of certain symmetry elements of the average structure. Two refinements have been tried, using space groups $P3_22_11$ and $C222_1$. The latter cannot account for the doubling of the c spacing and hence its validity is restricted to the projection on (001). The refinement in the former space group resulted in an improved R factor for X-rays (10·6%; 105 parameters), but there was no change in the weighted R factor in spite of the large number of parameters involved. For neutron data the results were even worse. The same behaviour was obtained for the refinements in space group $C222_1$. After these unsuccessful approaches to the solution of the superstructure we tried to analyze the observed intensities of the additional reflections in a statistical way: as has been pointed out above, the omission of superstructure reflections in structure analysis superposes two adjacent cells in the c direction into a single one. Therefore, it seems reasonable to expand the structure factor of the two cells by introducing average and displacement vectors for the two positions $\mathbf{r}_{\nu_1}$; $\mathbf{r}_{\nu_2} + \mathbf{c}/2$:

$$\bar{\mathbf{r}}_\nu = (\mathbf{r}_{\nu_1} + \mathbf{r}_{\nu_2})/2;\ \Delta\mathbf{r}_\nu = (\mathbf{r}_{\nu_1} - \mathbf{r}_{\nu_2})/2;$$

$$\mathbf{r}_{\nu_1} = \bar{\mathbf{r}}_\nu + \Delta\mathbf{r}_\nu;\ \mathbf{r}_{\nu_2} = \bar{\mathbf{r}}_\nu - \Delta\mathbf{r}_\nu.$$

With these definitions we get the following expression for the structure factor (small $\Delta\mathbf{r}_\nu$)

$$F(\mathbf{h}) = (1 + \exp\{\pi i l\}) \sum_\nu f_\nu \exp\{2\pi i \mathbf{h}\bar{\mathbf{r}}_\nu\}$$
$$+ 2\pi i(1 - \exp\{\pi i l\}) \sum_\nu f_\nu \exp\{2\pi i \mathbf{h}\bar{\mathbf{r}}_\nu\} \mathbf{h}.\Delta\mathbf{r}_\nu. \quad (1)$$

The first term in (1) describes normal reflections and the second term superstructure reflections. Now we define the average displacements in the first cell:

$$\langle\Delta\mathbf{r}\rangle = \tfrac{1}{m} \sum_{\nu=1}^{m} \Delta\mathbf{r}_\nu; \quad \Delta\mathbf{r}'_\nu = \Delta\mathbf{r}_\nu - \langle\Delta\mathbf{r}\rangle.$$

Introducing these definitions into (1), we get for the second term:

$$F(\mathbf{h}) = 4\pi i \mathbf{h}\langle\Delta\mathbf{r}\rangle \sum_\nu f_\nu \exp\{2\pi i \mathbf{h}.\bar{\mathbf{r}}_\nu\}$$
$$+ 4\pi i \sum_\nu \mathbf{h}.\Delta\mathbf{r}'_\nu f_\nu \exp\{2\pi i \mathbf{h}.\bar{\mathbf{r}}_\nu\}. \quad (2)$$

Equation (2) can be interpreted as follows:

(*a*) Let us assume that transformation from the room-temperature to the high-temperature phase follows group-theoretical considerations. Then all displacements are correlated by one of the symmetry operations 6_1,2_1,2. This means that the sum of all displacement vectors $\Delta\mathbf{r}_\nu$ and $\langle\Delta\mathbf{r}\rangle$ vanishes. According to (2), no direct relationship between superstructure reflections and structure factors of the host exists.

(*b*) In the case of non-vanishing $\mathbf{h}\langle\Delta\mathbf{r}\rangle$ we may observe reflections whose intensities are roughly proportional to the squared structure factors, but according to (2), the major part of displacement vectors must have similar components in this case, and the term $\mathbf{h}\langle\Delta\mathbf{r}\rangle$ must not be small. This property has been confirmed for most (32) of the intense superstructure reflections. The result is shown in Fig. 4 [best and worst (*hkl*) layers]. This verifies the statement that the displacement vectors are equal for most of the atoms to a first approximation. Hence the transformation cannot be explained in terms of invariant symmetries. It should be noted, however, that the number of weak reflections is small at room temperature, even for large l. But there is a continuous increase of their average intensities with decreasing temperature.

The next step in our investigation was a study of displacement vectors using only superstructure reflections. In this case a difference Fourier or its convolution (here defined as a difference Patterson) is obtained which contains information on displaced atoms only. Let us first discuss the effect of displaced atoms. It is well known that the convolution of a pair of 'difference' atoms, roughly displaced in the same direction, shows a fairly sharp positive peak. Its location coincides with the distance vector of the pair in question. The positive peak is surrounded by two negative broader ones, such that the integral over all three maxima is zero. If the two atoms are displaced in opposite directions the signs of densities are reversed. For a pair of displacement vectors perpendicular to each other a more complicated density distribution is realized: two negative and two positive diffuse maxima result in the plane of the two displacement vectors, but the rule of zero integrated density remains unchanged. Keeping these facts in mind, we started our analysis with the most important section of the difference Patterson at $z' = \frac{1}{12}$ which corresponds to a Harker section for the average structure. Figs. 5(*a*) and 5(*b*) show the two sections for the average and the difference structure, obtained with normal (l = even) and superstructure (l = odd) reflections. At the corners and the

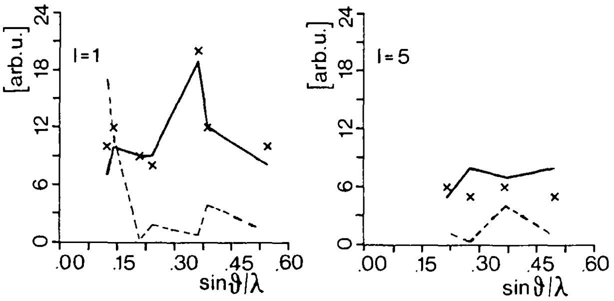
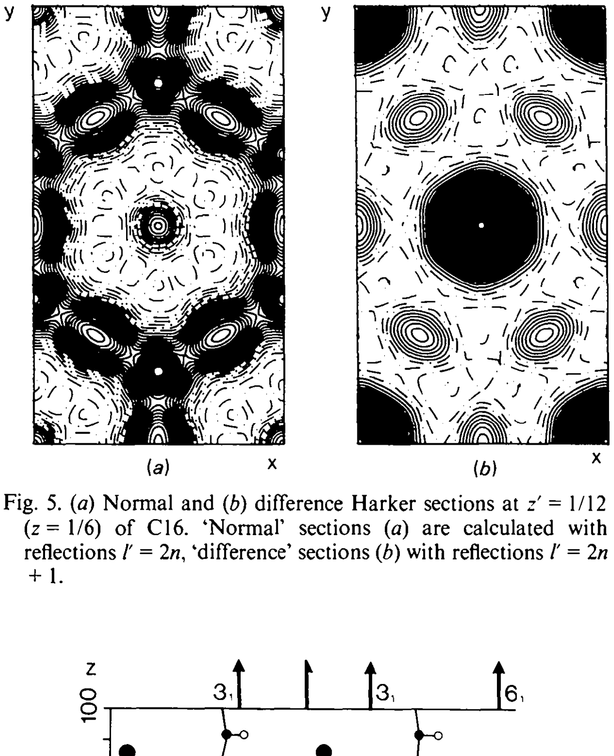


Fig. 4. Correlations between superstructure reflections of C16 (broken lines) and urea-framework structure factors (full lines). Measured intensities are indicated by crosses.

edges of the well-resolved hexagon, the O—O, C—C and N—N distances of the pairs correlated by the 6_1-screw axis may easily be seen. Two C—O distances in the neighbourhood of the said O—O distance are not well resolved. At the centre we find contributions of N—N distances which are caused by accidental values of the N parameters. This is demonstrated in Fig. 6, which shows that all N atoms lie near to a set of planes displaced by a multiple of $\frac{1}{6}$.

In the light of the comments given above, Fig. 5(*b*) is surprising in so far as the densities are essentially positive. Hence, the majority of atoms are displaced in the same direction. This is true specifically for the N—N atoms at the centre of the hexagon, originating from N atoms at different heights in the unit cell (*cf.* Fig. 6). The positive elliptical maxima on the edges of the hexagon indicate (nearly) equal displacements of N and C. Since the O—O distances lie in the centre of three such positive peaks, it should not be concluded that O atoms are not displaced. The possible positive peak might be suppressed by the negative maxima, adjacent to the positive ones. Otherwise the predominant positive integrated squared electron density cannot be understood. In agreement with the experimental observation that the intensities of superstructure reflections are roughly proportional to the squared structure factors of the framework structure, we may state here again that all atoms contributing to this section are displaced in the same direction. This observation is confirmed by the difference Patterson projection, calculated from the superstructure reflections (0*kl*). Fig. 7 shows the continuation of the positive peaks in the *c* direction.



(*a*) (*b*)

Fig. 5. (*a*) Normal and (*b*) difference Harker sections at $z' = 1/12$ ($z = 1/6$) of C16. 'Normal' sections (*a*) are calculated with reflections $l' = 2n$, 'difference' sections (*b*) with reflections $l' = 2n + 1$.

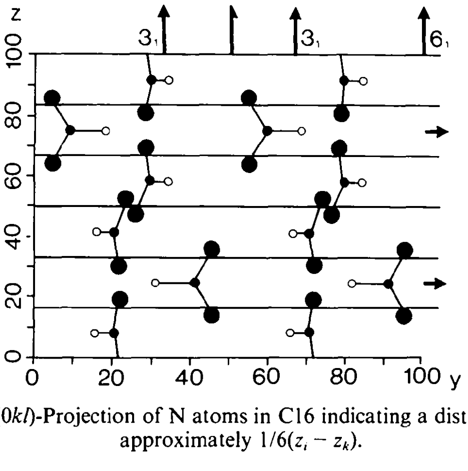


Fig. 6. (0*kl*)-Projection of N atoms in C16 indicating a distance of approximately $1/6(z_i - z_k)$.

7. Low-temperature phase III

Chatani, Taki & Tadokoro (1977) have published a provisional structure determination of phase III. The only experimental result given in this paper is a Fourier projection on the (001) plane. The authors assume domains with the rhombic space-group symmetry $P2_12_12_1$, twinned according to the three orientations of the lost 6_1 axis. This picture cannot be fully correct. The transition is accompanied by the observation of superstructure reflections, caused by the transition from the *C*-centered to the primitive space group. The extinction rules of the space group $P2_12_12_1$ could only be verified for reflections (*h*00) and (0*k*0) (*cf.* Figs. 8*a*,*b*), while the corresponding rule for (00*l*) reflections is violated. The study of diffuse scattering (Forst *et al.*, 1987) disagrees strongly with the chain orientations shown in the

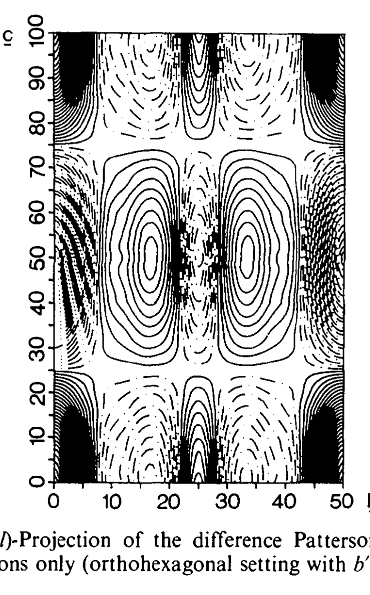


Fig. 7. (0*kl*)-Projection of the difference Patterson using super reflections only (orthohexagonal setting with $b' = 14{\cdot}25$ Å).

paper by Chatani *et al.* (1977). The three-dimensional interpretation of the Fourier projection in this paper allows only two (rotated by 180°) of the original six orientations. It will be shown in our forthcoming paper that this model cannot account for the diffuse scattering observed. Intensities and line profiles of *s* and *d* layers show that the number of orientations is invariant in this transition, although their hexagonal symmetry is lost.

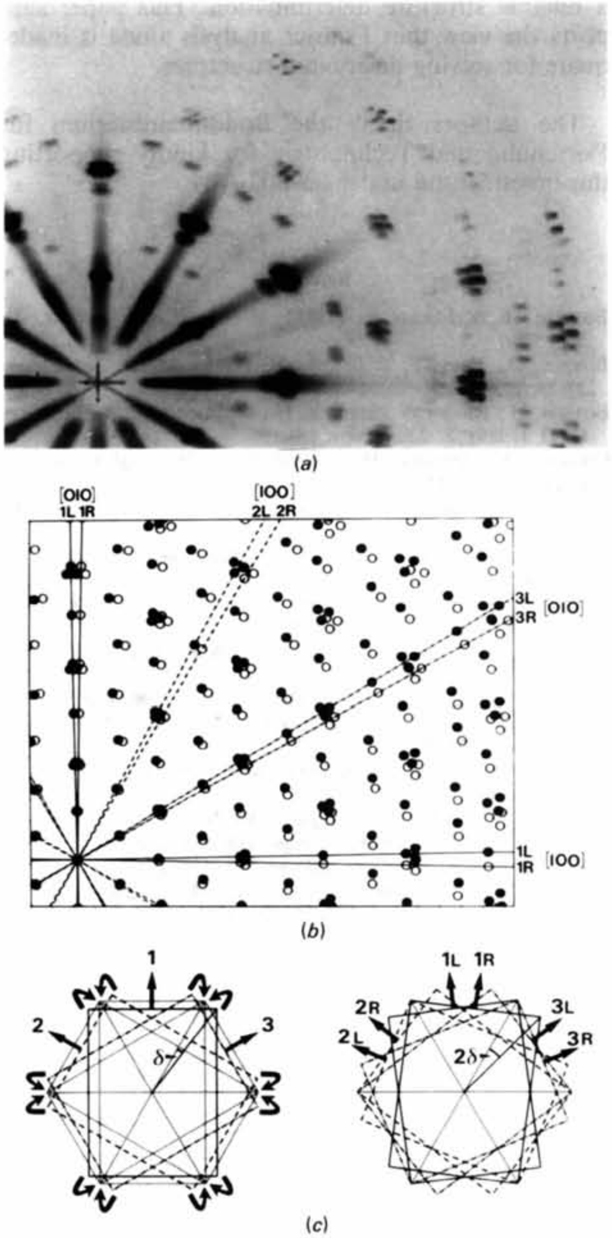


Fig. 8. Interpretation of the domain structure of phase III at 70 K. (*a*) Precession photograph of the (*hk*0) plane at 78 K (Cu $K\alpha$ with some $K\beta$ contamination). (*b*) Interpretation of (*a*) in terms of three slightly rotated pairs of domains. The directions [100] and [010] are indicated, where the solid, dashed and dashed-dotted lines correspond to the pairs 1, 2 and 3, respectively, in (*c*). (*c*) Generation (left) and final orientation (right) of domains in phase III. The original orthohexagonal cells (left) and the plane of intergrowth are indicated by dotted lines. The orthorhombic distortion and the corresponding split angle δ have been exaggerated for clarity.

Moreover, as shown in Fig. 8(*a*), there are more than three different orientations of domains. A careful analysis of this diffraction pattern revealed six orientations, characterized by a small angular deviation of the rhombic *x*, *y* axes from the corresponding orthohexagonal axes. An interpretation of the diffraction pattern is shown in Fig. 8(*b*). It should be mentioned that the small angle is temperature dependent; at 78 K an angle of about 1° is realized. This may be explained by assuming that the basic planes (100), (010) and $(1\bar{1}0)$ (hexagonal indices) are planes of intergrowth of the relevant pairs. This is illustrated in Fig. 8(*c*), which shows that the angle can be calculated from $\delta = -\arctan(b_o/a_o) + 60°$, in full agreement with the observed values (b_o, a_o, orthorhombic lattice constants). Note that the planes of intergrowth are free of strain. These facts emphasize that we either have to separate the overlapping reflections by high-resolution methods, or have to use high-resolution powder techniques for the refinements.

A comparison of neutron powder diffraction patterns with calculations, using approximate parameters as derived from the Fourier projection published by Chatani *et al.* (1977), showed that only (*hk*0) reflections can be roughly explained with this model. Obviously, the experimental work involved in a renewed structure determination is by far too large when compared with the results to be expected. Hence we did not trace this problem any further. This is justified by a successful semiquantitative study of the diffuse scattering from *s* and *d* layers, which yields very interesting information on the correlations between chain and framework ordering.

8. Concluding remarks

With the aid of neutron diffraction data a reliable determination of hydrogen bridges in the framework structure of urea inclusion compounds was possible. The whole framework is stabilized by these bridges. Although the doubling of the *c*-lattice constant of C16 is caused by the inclusion, the intensities of the superstructure reflections are primarily determined by the urea molecule. This contrasts with incorrect conclusions published in literature. The superstructure formation, which indicates a kind of domain structure of a single unit cell is of minor importance, as far as the displacements involved are concerned. This may be demonstrated by comparing the ellipsoids of thermal motion (Fig. 2) with the displacements, as demanded by the superstructure reflections. Table 7 shows the static and dynamic displacements of urea which may well be interpreted in terms of a rigid molecule. Since there is only one predominant rotation around the *a* axis, which generates positive and negative displacements of neighbouring atoms, this rotation cannot be considered as the relevant rotation, as demanded for the domain structures. A predominant displacement of the urea molecule in a particular direction is not realized. Hence we cannot determine the displacements responsible for superstructure formation by analyzing the ellipsoids of thermal motion in the average structure. Owing to the influence of the paraffin chains a structure analysis with the superstructure reflections alone seems to be hopeless. Here a careful study of diffuse scattering can help to overcome this difficulty. Special refinement programs have to be developed for this purpose.

The same arguments may be applied to the structure determination of the inclusion. Since the *s* layers are diffuse in two dimensions, with some diffuse maxima caused by short-range order in the corresponding two directions, we have to face the difficulty that the framework also contributes to the diffuse scattering. It has been shown by Forst *et al.* (1987), however, that the main influence is from the inclusion. Hence a solution of the structure may be found by beginning with the inclusion and a stepwise consideration of the displacements of the framework. This is a tedious procedure which has been tried in a provisional, semi-quantitative way by considering line profiles and intensities of diffuse *s* and *d* layers. It could be shown that there are correlations between orientations and distances of adjacent molecules. This will be discussed in a separate paper.

The orientational disorder in urea inclusion compounds with paraffins causes the essential incoherence of the two patterns of the framework and its inclusion. The observed intensities, however, are not independent. This fact hampers structure analysis by classical methods considerably. The interpretation of elastic and inelastic diffuse scattering is necessary for a reliable structure determination. This paper supports the view that Fourier analysis alone is inadequate for solving disordered structures.

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