

# Superspace description of the structure of the composite crystal urea/*n*-octane at room temperature

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A structural model for the composite crystal urea/*n*-octane is proposed. Despite the lack of information from the largely disordered guest substructure, the final model is consistent with the collected diffraction pattern. The use of the superspace approach stresses the composite character of the inclusion compounds and makes easier a unified view of the whole urea/*n*-alkane family. In particular, a comparison between the octane and heptadecane derivatives shows a common pattern for the origin of the modulation of the guest chains based on the distribution of the NH<sub>2</sub> groups within each tunnel wall.

## 1. Introduction

The urea inclusion compounds belong to the type of composite materials in which guest molecules are spatially confined within tunnelar cavities in a crystalline host material. In many cases the guest components are structurally disordered within the space they are constrained to occupy, whereas in other cases guest molecules form an arrangement which is sufficiently well ordered to allow a three-dimensional lattice periodicity to be defined.

In particular, in the urea inclusion compounds the guest molecules are located in a structure of linear and parallel tunnels formed by an extensively hydrogen-bonded arrangement of urea molecules (Harris & Thomas, 1990). The structural periodicities of the guest components are not in structural registry along one crystallographic direction. Thus, these materials can be considered as an intergrowth of two translationally symmetric subsystems. If the periodicities along the channels of the host and guest molecules are denoted by  $c_h$  and  $c_g$ , respectively, there is, in general, an incommensurate relationship between them. In other directions within the crystal such lattice relations are commensurate (van Smaalen & Harris, 1996).

Structural compatibility between host and guest components is fundamental to most inclusion phenomena. If these compatibility conditions are not fulfilled, no inclusion compound is formed. In this particular case the approximate tunnel diameter is *ca* 5.5 Å (George & Harris, 1995) and guest

molecules for which the minimum molecular dimension is of this order can, in principle, be accommodated within these tunnels. In practice, guest molecules based on a sufficiently long  $n$ -alkane chain will form inclusion compounds with urea. Furthermore, some degree of substitution of the  $n$ -alkane chain can be tolerated (Hollingsworth & Harris, 1996). When lowering the temperature most of the urea inclusion compounds undergo phase transitions into less symmetric structures which normally involve a volume multiplication of the host structure and a partial ordering of the guest molecules. At room temperature the basic host structure is hexagonal (or strongly pseudohexagonal), with average space group  $P6_122$  ( $Z_h = 6$ ) and lattice parameters  $a_h = b_h \simeq 8.2$ ,  $c_h \simeq 11.0$  Å. This hexagonal basic structure is the structural limit of the host structure in the absence of any host–guest interaction since the hexagonal arrangement of the urea molecules is stabilized by the guest subsystem. The packing of the guest molecules in the basic guest structure can be described by two parameters,  $c_g$ , determined by the chain length, and  $\Delta_g$  (the minimum offset along the tunnel axis, between the positions of the guest molecules in any pair of adjacent tunnels). Steric restrictions force the  $\mathbf{c}_g$  projection of the guest molecules onto the  $\mathbf{a}_h$ ,  $\mathbf{b}_h$  plane to be ordered. The basic host and guest substructures are modulated along the common direction parallel to both  $\mathbf{c}_g$  and  $\mathbf{c}_h$  axes, which are eventually the respective modulation wavevectors.

Guest molecules in urea inclusion compounds can be divided into families which share a given guest packing in the urea tunnels. This packing determines the symmetry of the guest substructure and therefore the global symmetry of the composite, which strictly speaking must be described by a superspace group. Symmetry compatibility leads normally to both a configurational disorder of the guest (which has attracted considerable interest: Forst *et al.*, 1986; Harris & Thomas, 1990; Fukao, 1994*a,b*; El Baghdadi *et al.*, 1996; Boysen *et al.*, 1988) and the presence of several twin domains. The list of all possible superspace groups for the urea inclusion compounds at room temperature was given by van Smaalen & Harris (1996). A list of the possible superspace groups for the low-temperature phases consistent with the available (and scarce) diffraction patterns can be found in van Smaalen & Harris (1996).

Owing to the commensurate relation between the periodicities of the  $\mathbf{c}_g$  projections of both subsystems there is a common  $(\mathbf{a}^*, \mathbf{b}^*)$  reciprocal plane. The whole reciprocal lattice can be indexed with integer indices using a reciprocal basis of four vectors:  $\{\mathbf{a}_h^*, \mathbf{b}_h^*, \mathbf{c}_h^*, \mathbf{c}_g^*\}$  being the usual choice. On this basis the reflections  $(h,k,0,0)$  are common to both subsystems, whereas those with indices  $(h,k,\ell,0)$  and  $(h,k,0,m)$  are the main reflections of the host and guest, respectively. Satellites are indexed with four non-zero Miller indices. Notice that the  $(hk10)$  reflections have some information concerning the modulation of the guest. However, in urea inclusion compounds the reciprocal space shows sharp  $(h,k,\ell,0)$  reflections (in particular it means that the projection of the guest is ordered) and diffuse planes perpendicular to  $\mathbf{c}_h^*$ , whose periodicity is  $\mathbf{c}_g^*$ , *i.e.* guest molecules are not perfectly ordered

along  $\mathbf{c}_g$ . Satellites are rarely detected and therefore the modulation parameters cannot be determined with accuracy. Even the main reflections of the guest subsystem are difficult to locate within the diffuse planes and as a consequence a full structure solution of the guest basic structure is precluded. On many occasions the structure of some urea inclusion compounds has been described by the host structure plus an additional atom, centred in the tunnels, mimicking the average effect of the guest molecules. The superspace description of these structures will require a very constrained model for the guest molecules that are assumed to be in an ideal *trans* configuration.

One of the most studied families is the one in which urea tunnels are filled with  $n$ -alkane chains. They show the highest symmetry within the urea inclusion family. In particular,  $\Delta_g = 0$  and therefore  $\mathbf{a}_h = \mathbf{a}_g$ ,  $\mathbf{b}_h = \mathbf{b}_g$  and  $Z_g = 1$ . The hexagonal symmetry of the guest subsystem implies a high degree of configurational disorder (rotational and up/down; van Smaalen & Harris, 1996) for the  $n$ -alkane chains. Long-range order along  $\mathbf{c}_g$  seems to be related to the length of the  $n$ -alkane chains (Frey & Boysen, 1998). The shorter this length, the lower the chemical stability of the composite urea/ $n$ -alkane and therefore the weaker the order along the tunnels. The reported shorter  $n$ -alkane molecule that forms urea inclusion compounds is hexane (Takemoto & Sonoda, 1984).

The aim of this work is the study of the structure of the urea/octane inclusion compound. As shown in §3 octane molecules show a fluid-like character and do not contribute [excluding the common  $(\mathbf{a}^*, \mathbf{b}^*)$  plane] with sharp Bragg peaks to the diffraction pattern. Despite this unfavourable situation a superspace ideal structural model congruent with the experimental data can be achieved. The superspace formalism again plays a unifying role, allowing an easy comparison with the known structure of the composite crystal urea/heptadecane (Weber *et al.*, 1997) at room temperature.

## 2. Experimental

Crystals of urea/octane were grown by the slow cooling method (Sarig, 1994) from a saturated solution of chemically pure urea and octane in a 50% methanol and 50% 2-propanol mixture. The saturated solution was prepared at 323 K in excess (with respect to the expected molar guest/host ratio; Takemoto & Sonoda, 1984) octane and then cooled from 328 to 278 K at  $0.1^\circ \text{ h}^{-1}$ . Single crystals have been studied with a Stoe IPDS using monochromated Mo  $K\alpha$  radiation. Monochromatic Cu  $K\alpha_1$  X-ray powder measurements were carried out on a Stoe focusing beam transmission diffractometer equipped with a linear position-sensitive detector. Samples were prepared by pulverization of the synthesized single crystals. Powder diffraction patterns were collected using the Debye–Scherrer geometry. The scanned region of reciprocal space was  $[5\text{--}110^\circ]$  in  $2\theta$ .

At room temperature the urea/octane crystal is not stable, but a decomposition mechanism exists which can be described as follows:

urea/octane(solid) → urea(solid) + octane(gas)

After 24 h the crystals lose their transparency and the hexagonal X-ray diffraction diagrams turn on that corresponding to a low-quality urea tetragonal crystal, plus the contribution of an amorphous phase. Powder X-ray diffraction patterns only show peaks belonging to tetragonal urea without any octane contribution, which probably evaporates when the sample is ground. This behaviour is also shown by other urea/*n*-alkane inclusion compounds with *n* > 10 (White, 1998).

The stability of the crystal can be achieved if it is encapsulated in octane atmosphere or if the crystal is cooled below the octane melting temperature.

### 3. Analysis of the reciprocal space

During the data collection, a single crystal was encapsulated in a capillary containing liquid octane to prevent the decomposition mechanism. To minimize the intensity of the halo diffracted by the liquid the amount of octane was reduced to a minimum. Details on the experimental conditions are given in Table 1.<sup>1</sup> The X-ray diffraction diagrams show the typical distribution of intensities from the host subsystem and some low-angle contribution from the liquid octane (see Fig. 1). However, neither diffraction peaks nor diffuse planes belonging to the guest subsystem can be detected. This implies a fluid-like character of the octane molecules within the tunnels, which is related to the length of the molecule (Frey & Boysen, 1998). Only after cooling<sup>2</sup> the sample can one diffuse layer be observed (Fig. 2), whose position agrees with the reported value for *c<sub>g</sub>* (Weber *et al.*, 1996). Nevertheless, the position of this layer also coincides with one *d* band corresponding to the internal periodicity of the alkane molecules (Weber *et al.*, 1996; Rabiller *et al.*, 2000). This lack of structural information about the guest along the *c<sub>g</sub>* axis implies that only the basal (*x,y*) coordinates of the octane molecules can be determined.

#### 3.1. Superspace-group assignment

The lack of guest main reflections and satellites other than those belonging to the (*hk*00) and (*hk*10) reciprocal planes makes impossible the experimental determination of the superspace group. Nevertheless, it is accepted that the whole family of the urea/*n*-alkane inclusion compounds are isostructural at room temperature. Therefore, Δ<sub>g</sub> = 0, the (**a**,**b**) periodicities are identical and there is an octane molecule in the basic guest unit cell. Under these assumptions the super-

<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0114). Services for accessing these data are described at the back of the journal.

<sup>2</sup> The composite urea/octane suffers a phase transition very difficult to detect by Differential Scanning Calorimetry (DSC). The phase transition temperature [112 (1) K] has been estimated by following the evolution of the X-ray diffraction diagram as a function of temperature. However, the diffuse layer shown in Fig. 2 could only be measured at lower temperatures (90 K). Notice that below the phase transition temperature the structure is orthorhombic (C222<sub>1</sub>) and the orthohexagonal axes **a** and **b** are doubled. Therefore, additional spots appear in Fig. 2 which are not present in the room-temperature phase.

**Table 1**

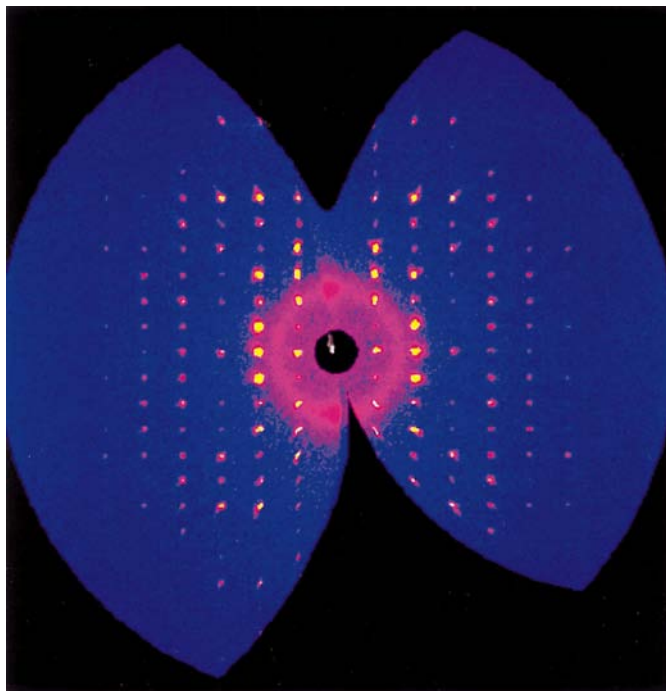
Experimental conditions and structure refinement details.

Crystal data	
Chemical formula	OC(NH <sub>2</sub> ) <sub>2</sub> ·C <sub>8</sub> H <sub>18</sub>
Crystal habit	Hexagonal prism
Crystal colour	Colourless
Superspace group	<i>P</i> 6 <sub>1</sub> 22(00γ)1̄10
Temperature (K)	293
<i>a<sub>h</sub></i> (Å)	8.2259 (35)
<i>c<sub>h</sub></i> (Å)	11.0188 (38)
<i>c<sub>g</sub></i> (Å) (see text)	12.419
<b>q</b> (see text)	1/γ <i>c<sub>g</sub></i> * = 1.12 <i>c<sub>g</sub></i> *
Lattice parameters (host) from	608 reflections
Volume (host) (Å <sup>3</sup> )	645.7 (5)
μ (mm <sup>-1</sup> )	0.09
Data collection	
Diffractometer	Stoe IPDS
Wavelength (Å)	0.71073
Distance IPDS (mm)	70
2θ range (°)	3.3/52.1
Number of exposures	100
Phi movement mode	Rotation
Phi range (°)	0–200
Phi increment (°)	2
Irradiation/exposure (min)	3
Profile function	Dynamic
Smallest profile diameter (pixel)	15
Largest profile diameter (pixel)	19
Effective mosaic spread	0.024
Data set completeness (%)	100
Date set redundancy	6.02
<i>h, k, l</i> limits	–10/10, –10/10, –12/12
Absorption correction	None
Refinement	
Unique reflections	418 ( <i>l, m</i> = 0: 30)
Observed independent reflections, <i>I</i> > 3σ( <i>I</i> )	278 ( <i>l, m</i> = 0: 22)
Number of refined parameters	28
Refinement based on	<i>F</i>
Weighting scheme	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> ) + 0.0001 <i>F</i> <sup>2</sup> ]
Extinction correction	None
Δρ (e Å <sup>-3</sup> ) (max, min)	1.27, –0.19
<i>R</i> <sub>int</sub>	0.0847
<i>R</i> <sub>obs</sub> (%) (with/without) modulation:	
( <i>hkℓ</i> 0)	0.0551/0.0560
( <i>hkℓ</i> 0) ( <i>ℓ</i> ≠ 0)	0.0482/0.0491
( <i>hk</i> 00)	0.0951/0.0953
( <i>hk</i> 10)	0.0651/0.0670
<i>R</i> <sub>all</sub> (%)	8.07 ( <i>l, m</i> = 0: 10.60)
<i>wR</i> <sub>all</sub> (%)	6.33 ( <i>l, m</i> = 0: 9.50)
<i>S</i> <sub>obs</sub>	2.54
<i>S</i> <sub>all</sub>	3.14

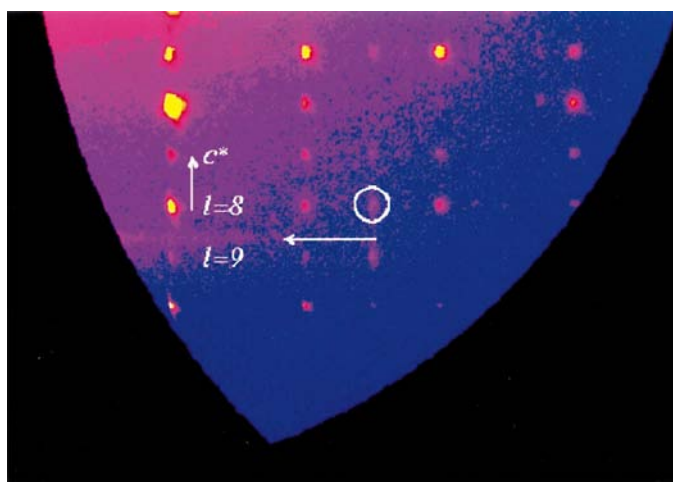
Computer programs used: *IPDS Stoe Software* (Stoe & Cie, 1998), *JANA2000* (Petricek & Dusek, 2000), *ORTEP3* (Farrugia, 1996).

space group is *P*6<sub>1</sub>22(00γ)1̄10 (van Smaalen & Harris, 1996), provided the diffraction pattern is indexed with the reciprocal basis {**a<sub>h</sub>**\*, **b<sub>h</sub>**\*, **c<sub>h</sub>**\*, **c<sub>g</sub>**\*}. This superspace group determines the superspace groups for both the host and guest substructures. In particular, the guest superspace group is hexagonal and causes the octane molecule to be configurationally disordered. Obviously in this case in which the information is very limited the superspace group could be a subgroup of *P*6<sub>1</sub>22(00γ)1̄10 and the sample could be twinned. Nevertheless, choosing the highest symmetry superspace group allows a reduction in the number of structural parameters and a unified description of

the urea/*n*-alkane family. The value of  $\gamma$  cannot be determined empirically and has been calculated from  $c_g = (n - 1)1.277 + 3.48 \text{ \AA}$  (Lenné *et al.*, 1970; El Baghdadi, 1993).  $\gamma = c_g^*/c_h^* = 11.088/12.419 = 0.893$ .



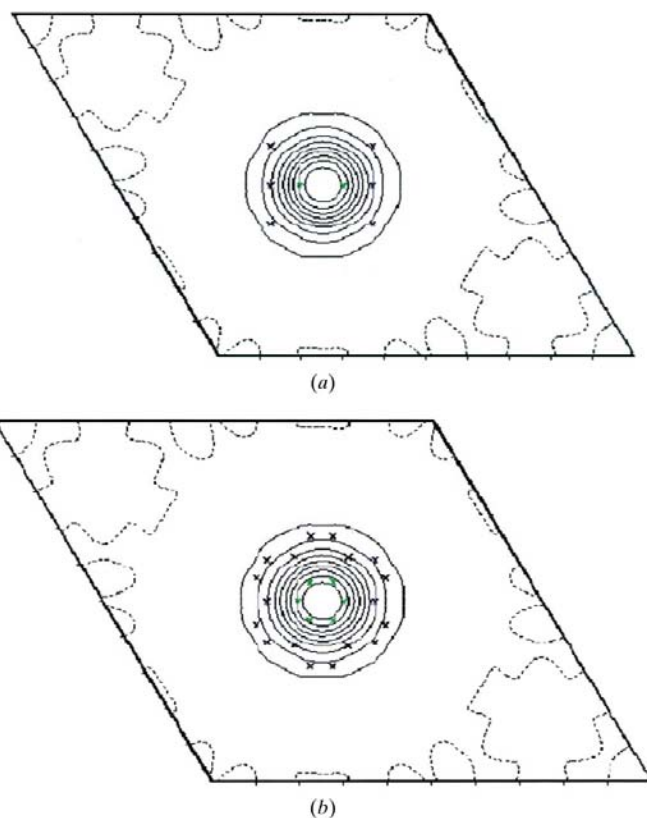
**Figure 1**  
The  $(h0lm)$  reciprocal plane of urea/octane. The reflections can be indexed with the urea reciprocal lattice. Neither main guest diffuse layers nor pure satellite can be detected. The octane liquid contribution to the X-ray diffraction diagram is observed at the centre of the figure.



**Figure 2**  
A selected part of the  $(h0lm)$  reciprocal plane of urea–octane at 90 K. The weak diffuse layer marked with the horizontal arrow can be indexed with  $l = 0$ ;  $m = -10$ . However, it could also correspond to a  $d$ -band arising from the internal periodicity of the alkane chains. The circled spot belongs to the low-temperature orthorhombic reciprocal lattice, whose orthohexagonal axes **a** and **b** are doubled with respect to those of the room-temperature structure.

#### 4. Structure refinement

Assuming  $P6_122(00\gamma)\bar{1}\bar{1}0$  as the superspace group and using only the  $(h,k,\ell,0)$  reflections, the basic host structure can be refined starting from the positions of the C, N and O atoms belonging to the urea subsystem already published. The  $R_{\text{obs}}$  factor achieved after this refinement is 15% for all reflections and 39% for the common  $(h,k,0,0)$  reflections which contain structural information about the **c** projection of the octane subsystem. Assuming the octane molecules to be rigid units in the *trans* configuration and aligned parallel to  $c_g$  (or  $c_h$ ), three possible models exist for the disposition of the guest in the urea tunnels. In two of them the twofold axis of the octane coincides with a twofold axis (along  $[120]$  or  $[010]$ ) of the guest superspace group. In both cases six different orientations for the guest molecules in the tunnels (related by the sixfold axis along the **c** axis) are produced. A different possibility would be to locate the octane molecule with no coincidence between the symmetry elements of the site and molecular point groups. In this case there are 12 different orientations for the molecule. A difference Fourier map calculated with the common reflections is shown in Fig. 3. Owing to the isotropic distribution of the electronic density in the centre of the tunnels it is not possible to distinguish a preferable (symmetry-independent) orientation for the octane molecules.



**Figure 3**  
Electron density maps of the **(a,b)** plane showing the electronic density in the centre of the urea tunnels. **(a)** The octane atoms in one of the six possible configurations (see text) are denoted by green and blue crosses for C and H atoms, respectively. **(b)** The same octane molecule after applying the site symmetry operations.

**Table 2**

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

The expression of 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  $\text{\AA}^2$ .  $U^{\text{iso}}$  is defined by  $\exp(-8\pi^2 U_{\text{iso}} [(\sin^2 \theta)/\lambda^2])$ . The occupation factor of the octane atoms is 1/6. The elements  $U^{13}$  and  $U^{23}$  corresponding to the octane molecule are zero.

(a) Host substructure

	<i>x</i>	<i>y</i>	<i>z</i>	$U^{11}/U_{\text{iso}}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C	0.8164 (4)	0.4082 (2)	1/12	0.045 (2)	0.036 (1)	0.028 (2)	0.0223 (9)	0	-0.006 (1)
O	0.6404 (2)	0.3202 (1)	1/12	0.033 (1)	0.0464 (9)	0.028 (1)	0.0167 (6)	0	-0.0020 (8)
N	0.9128 (3)	0.4340 (3)	0.1854 (2)	0.036 (1)	0.075 (2)	0.027 (1)	0.021 (1)	-0.001 (1)	0.005 (1)
H(1)	0.858 (3)	0.392 (3)	0.245 (2)	0.043 (5)					
H(2)	1.029 (3)	0.481 (3)	0.187 (2)	0.043 (5)					

(b) Guest substructure

	<i>x</i>	<i>y</i>	<i>z</i>	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$
C(1)	-0.052638	0	0.050025	0.1	0.1	0.3	0.05
H(11)	-0.06551	0.114544	0.050025	0.1	0.1	0.3	0.05
H(21)	-0.180053	-0.114544	0.050025	0.1	0.1	0.3	0.05
C(2)	0.052638	0	0.150076	0.1	0.1	0.3	0.05
H(12)	0.180053	0.114544	0.150076	0.1	0.1	0.3	0.05
H(22)	0.06551	-0.114544	0.150076	0.1	0.1	0.3	0.05
C(3)	-0.052638	0	0.250127	0.1	0.1	0.3	0.05
H(13)	-0.06551	0.114544	0.250127	0.1	0.1	0.3	0.05
H(23)	-0.180053	-0.114544	0.250127	0.1	0.1	0.3	0.05
C(4)	0.052638	0	0.350178	0.1	0.1	0.3	0.05
H(14)	0.180053	0.114544	0.350178	0.1	0.1	0.3	0.05
H(24)	0.06551	-0.114544	0.350178	0.1	0.1	0.3	0.05
H(34)	0.122781	0	0.416824	0.1	0.1	0.3	0.05

The only possible positional parameters to be refined are the rotation angle along the tunnel axis and the (*x*,*y*) position of the molecular centre in the common (**a**, **b**) plane. Preliminary refinements showed that the above orientational models are totally equivalent for the intensity data set and that the best position for the molecular centre is the centre of the tunnels. Therefore, the molecular orientation was chosen (and fixed) to be the same as for the urea/*n*-heptadecane crystals (Weber *et al.*, 1997), in which the guest molecular planes are perpendicular to the walls of the urea tunnels. The twofold axis of the octane is parallel to the crystallographic direction [120]. Owing to the superspace group of the guest subsystem only half of the octane molecule has to be specified. The atomic coordinates of the independent atoms were calculated from geometrical considerations and kept fixed. Only a molecular isotropic thermal displacement parameter was refined. After refining the guest structure the urea H atoms can be found in a difference Fourier map. Their thermal displacement parameters have been restricted to be identical (see Table 2). The guest molecule and the urea H atoms particularly improve the agreement of the common (*hk00*) reflections reaching a value for  $R_{\text{obs}} = 0.096$ . The agreement factor for the main reflections of the host subsystem is  $R_{\text{obs}} =$

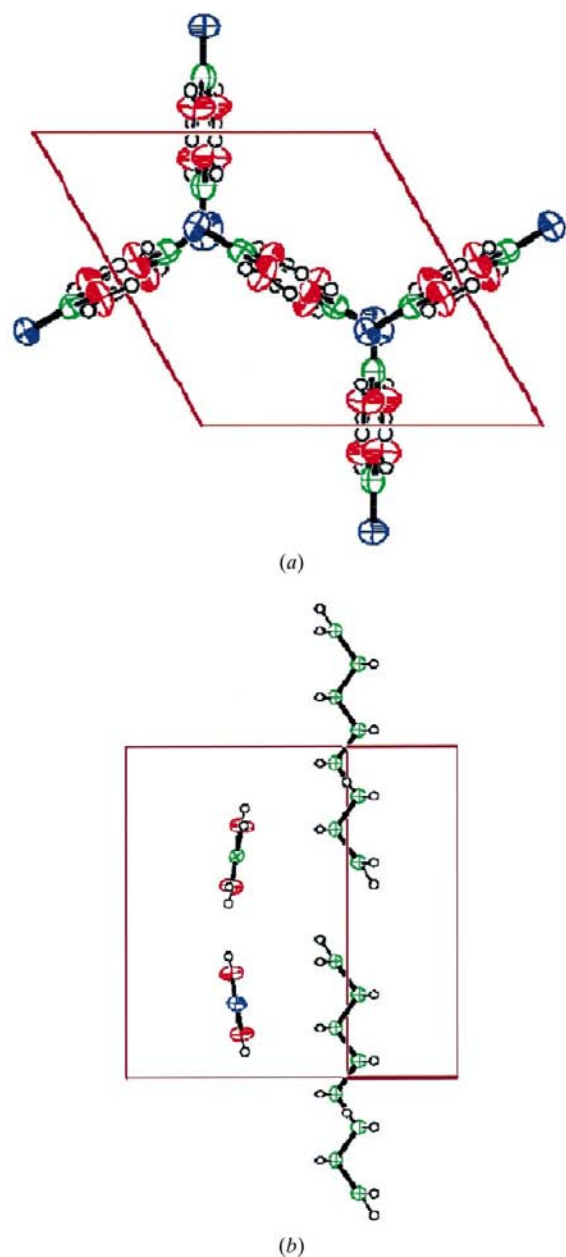
0.048. In particular, the agreement factor for (*hk10*) (which contain the influence of the guest first-order satellites corresponding to the common reflections) is  $R_{\text{obs}} = 0.067$ . Two projections of the host and guest structures are shown in Fig. 4.

A comparison of the electronic density in the (**b**, **c<sub>g</sub>**) plane calculated using the full intensity data set with and without the (*hk10*) reflections (see Fig. 5) shows that the guest modulation is very small. It can be appreciated with difficulty that the tube of electronic density calculated without the (*hk10*) reflections is less wavy along the **c** axis. Given this subtle hint and despite the strong disorder of the octane molecules, a transversal sinusoidal modulation of the molecular centre of mass was tested. Given the special position it occupies, not all the relevant modulations are independent. In particular, the following restrictions apply:  $u_y^s = 2u_x^s$ ,  $u_x^c = 3^{1/2}u_x^s$ ,  $u_y^c = u_z^c = u_z^s = 0$ , where the superscripts *s* and *c* refer to the cosine and sine parts of the modulation function, respectively (see Table 3). The strong correlations between the modulation amplitudes and thermal parameters make the refinement unstable. Therefore, the only symmetry-independent molecular thermal tensor element  $U^{11}$  corresponding to the (*a*,*b*) plane was fixed to a value close to the one refined without modulation, but allowing displacive modulation consistent

with the Fourier map shown in Fig. 5(b).  $U^{33}$  was deliberately enlarged to simulate the strong disorder along  $c_g$  present in the structure.

The result of this (perhaps a bit daring) refinement (Tables 2 and 3) improves a little the global  $R_{\text{obs}}$  factor (see Table 1). As expected, the improvement is a little higher for the  $(hk10)$  reflections for which  $R_{\text{obs}}$  is reduced to 0.0615.

The origin of the octane modulation can be attributed to the distribution of the N atoms ( $\text{NH}_2$  groups), which are located at two different distances of the tunnel axis within each urea



**Figure 4**  
(a) Projection along  $c_h$  of the urea substructure. (b) Projection along  $[120]$  of the guest unit cell, showing two octane molecules and two urea molecules that belong to the same tunnel wall. O, C, N and H atoms have been drawn in blue, green, red and white, respectively.

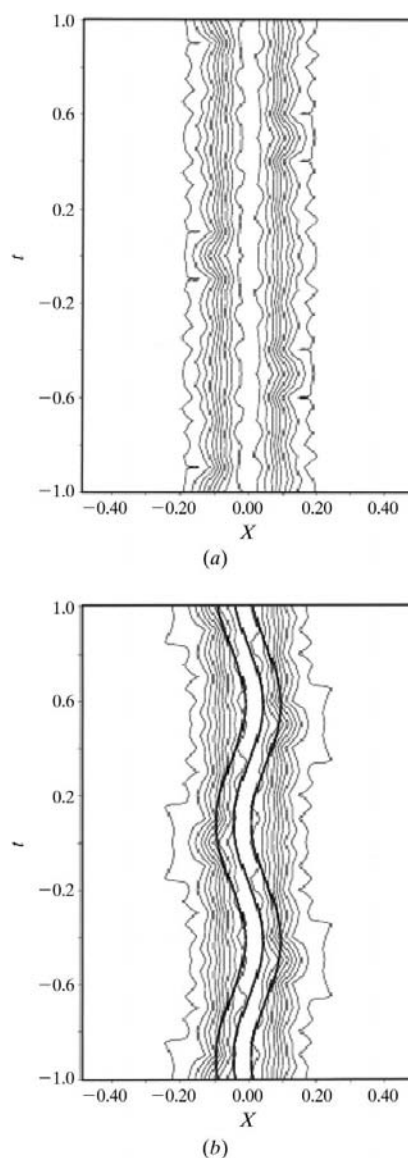
**Table 3**  
Final values of the amplitudes of the displacive modulation function for the rigid guest molecule.

The definition of the modulation function is given by

$$\mathbf{u} = \mathbf{u}^s \sin(2\pi\mathbf{q}\mathbf{r}) + \mathbf{u}^c \cos(2\pi\mathbf{q}\mathbf{r}),$$

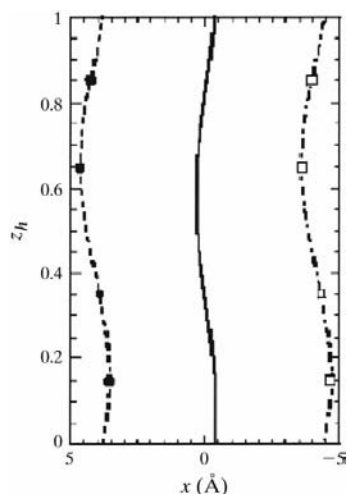
where  $\mathbf{r}$  is the position vector of the molecular centre and  $\mathbf{q}$  the modulation wavevector.

$\mathbf{u}^s$	$\mathbf{u}^c$
$[-0.0217(9), -0.0434(19), 0]$	$[-0.0376(16), 0, 0]$

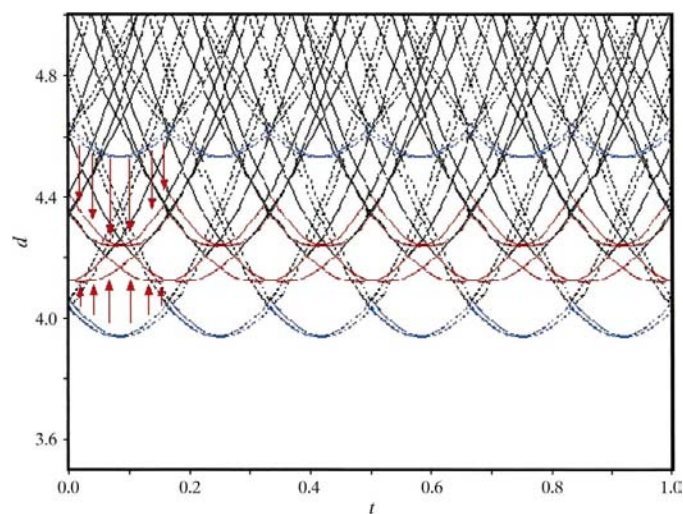


**Figure 5**  
 $x-t$  electron density maps of the guest substructure.  $t = \mathbf{q} \cdot \mathbf{l}$  refers to the guest subsystem and therefore  $\mathbf{l}$  is the cell index to which a given octane molecule belongs. (a) Calculated with all reflections; (b) omitting the  $(hk10)$  reflections. The lines represent the refined modulation function. The molecular centre and the two C atoms that determine the molecular size along  $\mathbf{a}$  are drawn.

tunnel wall (see Fig. 4). Their  $x$  coordinates when plotted as a function of the corresponding  $z_h$  show a distribution that can be fitted to a sinusoidal function similar to that used to describe the guest modulation (see Fig. 6). In this way the modulation of the octane molecules follows the tunnel modulation in such a way that the distances between their centres and the N atoms belonging to the walls perpendicular to the molecular plane are almost equal (see Fig. 7). Although in urea/heptadecane the modulation function is much more anharmonic, the global tendency of the heptadecane to be



**Figure 6**  
 $x$ - $z_h$  plot of the refined modulation function (solid line) together with the positions of the N atoms in two opposite tunnel walls perpendicular to the octane molecular plane. The dashed lines are the sinusoidal modulation functions fitted to the N positions.



**Figure 7**  
 Distances from the 12 N atoms within the urea unit cell to the centre of the octane molecule as a function of the internal coordinate  $t$ . Here  $t$  refers to the host subsystem (see the caption of Fig. 5). The blue and red lines represent the calculated distances without and with modulation, respectively.

closer to the farthest N atoms (and *vice versa*) is the same as in the present case (Weber *et al.*, 1997).

To check the correctness of the structural model,  $F_{\text{cal}}$  values for pure satellites and for the main reflections of the guest subsystem have been calculated. Only the reflections (0001), (0002), (0003), (1001) and (2101) have  $5e < F_{\text{cal}} < 10e$ , with  $5e$  being the maximum  $F_{\text{cal}}$  for the weakest reflections of the collected intensities. Given the weakness of the calculated (000 $\bar{1}$ ) reflection, the diffuse layer shown in Fig. 2 is probably a  $d$  band.

## 5. Conclusions

The superspace formalism has proved to be a useful tool to describe the structure of the composite urea/octane, even when the guest molecule presents a strong fluid-like character given its short length close to the lowest limit that makes inclusion phenomena possible. As a consequence, the intensity data set is very incomplete and does not contain reflections belonging to any guest other than those superimposed with the main reflections of the urea structure. Therefore, only the ( $x,y$ ) coordinates of the projected guest molecules have been refined. Nevertheless, the final model, although strongly constrained, is consistent with the diffraction pattern. Moreover, the use of the superspace approach allows a unified description of the whole urea/ $n$ -alkane family. In particular, a common origin for the modulation in the urea/octane and urea/heptadecane compounds can be envisaged.

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