

# Average structure of the composite crystal urea/octanedioic acid at room temperature within the superspace formalism

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The average structure of the composite urea/octanedioic acid has been refined using the superspace formalism [superspace group  $H^3_121(00\gamma)001$ ]. Modulation effects seem to be almost negligible. The guest substructure appears to be largely disordered and has been modelled using rigid units occupying 12 equiprobable different orientations inside the urea tunnels. Guest molecules are slightly tilted with respect to the tunnel axis favouring a stronger guest–guest intratunnel interaction.

## 1. Introduction

Urea inclusion compounds are composite materials in which guest molecules fill a network of linear and parallel tunnels built up by urea molecules linked to each other by hydrogen bonds. The diameter of the tunnels ( $\sim 5.5$  Å) strongly restricts the type of guest molecule that can be accommodated inside them. Only large enough *n*-alkane chains (the lower limit seems to be *n*-hexane; Takemoto & Sonoda, 1984) and some simple derivatives stabilize urea inclusion compounds. Both the urea and the ideal (crystalline) guest substructure are periodic along the tunnel axis, but with different ( $c_h$  and  $c_g$ , respectively) periods. The  $c_h/c_g$  ratio determines the character as commensurate or (usually) incommensurate of the composite. In other directions the lattice relation between the host and the guest subsystems is commensurate. The packing of the guest molecules is described by  $c_g$  and the minimum offset,  $\Delta_g$ , between the positions of the molecules in any pair of adjacent tunnels. Given the tunnel distribution the projection of the guest substructure along  $\mathbf{c}_g$  is ordered. The host and guest substructures are modulated along the common  $\mathbf{c}$  direction with modulation wavevectors  $\mathbf{c}_g$  and  $\mathbf{c}_h$ , respectively.

The symmetry of the incommensurate members of the family is described by a one-dimensional superspace group, which determines the symmetry of each subsystem. The host structure is strongly pseudo-hexagonal. The space group of its average structure at room temperature is a subgroup of  $P6_122$ . The symmetry of the guest subsystem is determined by the packing of the molecules. Symmetry compatibility between the two substructures leads to configurational disorder of the guest and twinning. A list of the possible superspace groups

**Table 1**  
Experimental details.

Crystal data				
Chemical formula	C <sub>6</sub> O <sub>6</sub> N <sub>12</sub> H <sub>24</sub> ·0.893C <sub>8</sub> O <sub>4</sub> H <sub>14</sub>			
Chemical formula weight	515.4			
Crystal habit	Hexagonal prism			
Crystal colour	Colourless			
Superspace group	<i>H</i> <sup>3</sup> 21(00 $\gamma$ )00 $\bar{1}$			
Temperature (K)	293			
Lattice parameters	Refinement	Host	Guest	
<i>a</i> (Å)	14.185 (6)	14.185 (6)	14.185 (6)	
<i>c</i> (Å)	10.978 (1)	10.978 (1)	12.291 (6)	
<i>V</i> (Å <sup>3</sup> )	1913 (1)	1913 (1)	2142 (2)	
<i>Z</i> <sub>h</sub>	18			
Wavelength (Å)	0.71073			
2 $\theta$ range (°)	3.3–52.11			
<i>Z</i> <sub>g</sub>	1			
<i>D</i> <sub>x</sub> (Mg m <sup>-3</sup> )	1.34			
<i>D</i> <sub>m</sub> (Mg m <sup>-3</sup> )	1.33 (2)			
$\mu$ (mm <sup>-1</sup> )	0.10			
Data collection				
Diffractionmeter	Stoe IPDS			
Detector distance (mm)	70			
Number of exposures	100			
Phi movement mode	Oscillation			
Phi range (°)	0–200			
Phi increment (°)	2			
Profile function	Dynamic			
	( <i>a</i> )	( <i>b</i> )	( <i>c</i> )	( <i>d</i> )
Irradiation/exposure (min)	10	10	10	1
Smallest profile diameter (pixel)	15	19	19	13
Largest profile diameter (pixel)	25	29	29	15
Effective mosaic spread	0.014	0.010	0.010	0.010
Mean $F_o^2/\sigma(F_o^2)$	26.2	3.9	3.8	1.5
Range of <i>h</i> , <i>k</i> , <i>l</i> , <i>m</i>	–17 → <i>h</i> → 17 –17 → <i>k</i> → 17 –13 → <i>l</i> → 13 –2 → <i>m</i> → 2			
Refinement				
Refinement on	<i>F</i>			
<i>R</i> , <i>wR</i> , <i>S</i>	0.0591, 0.0601, 8.84			
No. of reflections and parameters used in refinement	2146, 62			
Weighting scheme	$w = 1/(\sigma^2(F) + 0.000004F^2)$			
Refined twin fraction	0.499 (2)			
( $\Delta/\sigma$ ) <sub>max</sub>	0.1756			
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.53, –1.1			
<i>R</i> factors	All	Dataset ( <i>a</i> )/( <i>d</i> )	Guest	Guest [ <i>I</i> > $\sigma(I)$ , <i>m</i> < 3]
<i>R</i> <sub>int,all</sub>	0.5867	0.0798/0.2220	0.6080	0.1247
<i>R</i> <sub>int,obs</sub>	0.5011	0.0786/0.0581	0.5210	0.1216
	<i>hkℓm</i>	<i>hk00</i>	<i>hkℓm</i> ( $\ell \neq 0$ )	<i>hk0m</i> ( $m \neq 0$ )
Unique reflections	2146	211	1566	369
Observed reflections [ <i>I</i> > 3 $\sigma(I)$ ]	1017	148	859	10
<i>R</i> <sub>obs</sub>	0.0591	0.0466	0.0698	0.0740
<i>R</i> <sub>all</sub>	0.2089	0.1037	0.1623	1.1104
<i>wR</i> <sub>all</sub>	0.0601	0.0301	0.0664	0.4530
<i>S</i> <sub>obs</sub>	6.05			
<i>S</i> <sub>all</sub>	8.84			

Computer programs used: Stoe IPDS (Stoe & Cie, 1998), JANA2000 (Petříček & Dušek, 2000), ORTEP3 (Farrugia, 1996), Xtal\_GX (Hall & du Boulay, 1997).

for the urea inclusion compounds at room temperature can be found in van Smaalen & Harris (1996).

Owing to the commensurate relation between the periodicities of the **c** projections of both subsystems there is always a common (**a\***, **b\***) reciprocal plane. The whole reciprocal lattice is spanned by four vectors. Although the usual choice is {**a\***<sub>h</sub>, **b\***<sub>h</sub>, **c\***<sub>h</sub>, **c\***<sub>g</sub>} any other is also valid. On this basis the reflections

(*hk00*) are common to both subsystems. The main reflections of the host and guest substructures are those with indices (*hkℓ0*) and (*hk0m*), respectively.<sup>1</sup> Satellites are, in general, indexed with four non-zero Miller indices.

Far from this ideal description of reciprocal space urea inclusion compounds exhibit only sharp (*hkℓ0*) reflections. The diffracted Bragg peaks belonging to the guest are always more diffuse and normally indistinguishable within diffuse planes perpendicular to **c\***. Moreover, satellites are rarely detected. This lack of information implies that the structural guest models have to be necessarily highly constrained. Perhaps due to the same reason the superspace approach has been systematically avoided for the description of this family of composites. Only recently has it been applied to the structural analysis of urea/*n*-octane (Peral *et al.*, 2001), urea/*n*-heptadecane (Weber *et al.*, 1997) and urea/*n*-nonadecane (Rabiller *et al.*, 2001). In these cases the displacive modulation of the guest molecules has been refined.

From the point of view of diffraction, substitution in *n*-alkane chains of some terminal H atoms by heavier groups or atoms could improve the structural resolution. Such substitution is accompanied by changes in the packing of guest molecules. For instance, unlike urea/*n*-alkane compounds for which  $\Delta_g = 0$ , for alkanedioic acid and  $\alpha$ ,  $\omega$ -dibromoalkane molecules (Yeo *et al.*, 1997; Harris *et al.*, 1991)  $\Delta_g = (1/3)c_g$ .

In this work we report the average structure of the compo-

site urea/octanedioic (suberic) acid. Despite the presence of the carboxylic groups the strong disorder of the guest molecules does not allow a full structure solution. Nevertheless, the

<sup>1</sup> Notice that in these reflections the main reflections of one subsystem and the satellites of the other superimpose. The most important contributions of satellites are expected to be on the (*hk01*) and (*hk10*) layers.

superspace formalism assigns correctly the symmetry to each subsystem and permits a more detailed description of the orientational disorder of the guest molecules.

## 2. Experimental

Crystals of urea/suberic acid were grown by the slow cooling method (Sarig, 1994) from a saturated solution of chemically pure urea and suberic acid compounds 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) suberic acid 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  $2\theta$ . Details about the experimental conditions are given in Table 1.<sup>2</sup>

## 3. Superspace-group assignment

Preliminary oscillation photographs at room temperature show that  $\mathbf{c}_g^*$  and  $\mathbf{c}_h^*$  are parallel and mutually incommensurate, with the misfit parameter  $\gamma = c_g^*/c_h^* = 0.89$  (1). Further precession photographs indicate that the symmetry of the host reciprocal space is hexagonal. The main reflections of the urea substructure were indexed with a hexagonal reciprocal lattice with periodicities  $a_h = b_h = 8.1$  (1) Å,  $c_h = 11.1$  (1) Å. The systematic absences point to the conventional average host space group ( $P6_122$ ) assigned to the whole family of urea inclusion compounds. A more detailed analysis of reciprocal space could only be achieved after processing the IPDS and powder measurements. Guest main reflections are only significant in the reciprocal planes  $(hk \pm 1)_g$ ,  $(hk \pm 2)_g$  and  $(hk \pm 3)_g$ . They are weak when compared with the urea main reflections and in the third layers  $[(hk \pm 3)_g]$  quite diffuse (see Figs. 1 and 2). They also show hexagonal symmetry and can be indexed with a lattice of parameters  $a_g = b_g = 14.1849$  (59) Å,  $c_g = 12.2909$  (63) Å. No satellites have been detected in single-crystal diffraction diagrams, although some extremely weak ones seem to be present in powder patterns (Fig. 3). The symmetry of the guest diffraction pattern and the systematic absences are compatible with an  $R$  lattice. Two individuals (corresponding to the obverse and reverse settings) can be easily detected. Their diffracted intensities indicate that each of them occupy an effective volume equal to 50% of the sample volume. The space group assigned to the guest subsystem is  $R32$ . Although the apparent global Laue symmetry is  $6/mmm$ , the guest symmetry precludes the exist-

<sup>2</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0117). Services for accessing these data are described at the back of the journal.

**Table 2**

Symmetry elements of the superspace group  $H'3_121(00\gamma)00\bar{1}$ .

Centring translations have been omitted.

{E 0000}	{ $C_3^+$   $00\frac{1}{3}0$ }	{ $C_3^-$   $00\frac{2}{3}0$ }	{ $C_{2x}$  0000}	{ $C_{2y}$   $00\frac{1}{2}0$ }	{ $C_{2[110]}$   $00\frac{1}{3}0$ }
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tence of a sixfold axis along the urea tunnels. Therefore, the superspace point group must be lowered. Given the  $R$  systematic absences the natural periodicities for the ( $\mathbf{a}$ ,  $\mathbf{b}$ ) plane are those of the guest subsystem. Choosing for the global reciprocal basis the set of four vectors  $\{\mathbf{a}_g^*, \mathbf{b}_g^*, \mathbf{c}_h^*, \mathbf{c}_g^*\}$  the superspace group is (van Smaalen & Harris, 1996)  $H'3_121(00\gamma)00\bar{1}$  (see Table 2).  $\{a = b = 14.185$  (6),  $c = 10.9779$  (12) Å;  $H'$  holds for the centring translations  $[(0,0,0), (2/3,1/3,0,1/3), (1/3,2/3,0,2/3)]$ ,  $\gamma = 0.8931$  (5).} Subsystem standard reciprocal lattices are obtained from the above by the  $W$  matrices (van Smaalen & Harris, 1996)

$$W_h = \begin{pmatrix} 2 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} W_g = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}. \quad (1)$$

With this choice the host and guest superspace groups are  $P3_12(1/3, 1/3, \gamma)00\bar{1}$  [ $a = b = 8.1778$  (9),  $c = 10.9779$  (12)] and  $R32(00\gamma^{-1})\bar{1}$  [ $a = b = 14.185$  (6),  $c = 12.291$  (6) Å], respectively. Notice that the host modulation wavevector is one of the primitive rhombohedral reciprocal lattices of the guest. In this work the election of the  $W_h$  matrix is different

$$W_h = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} W_g = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}. \quad (2)$$

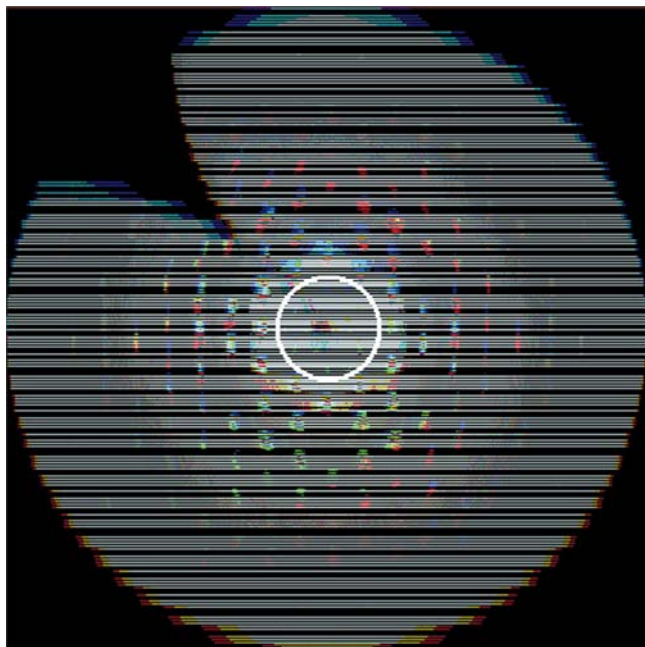
In this way the rational component of the host wavevector is removed with the host superspace group equal to the global superspace group  $H'3_121(00\gamma)00\bar{1}$  [ $a = b = 14.185$  (6),  $c = 10.9779$  (12) Å]. The host triple cell is centred by the translations  $(2/3,1/3,0)$  and  $(1/3,2/3,0)$ .

The existence of both obverse and reverse settings in the guest substructure provokes merohedral twinning in the host substructure. The twin law has been chosen to be a twofold axis parallel to the common  $\mathbf{c}$  axis.

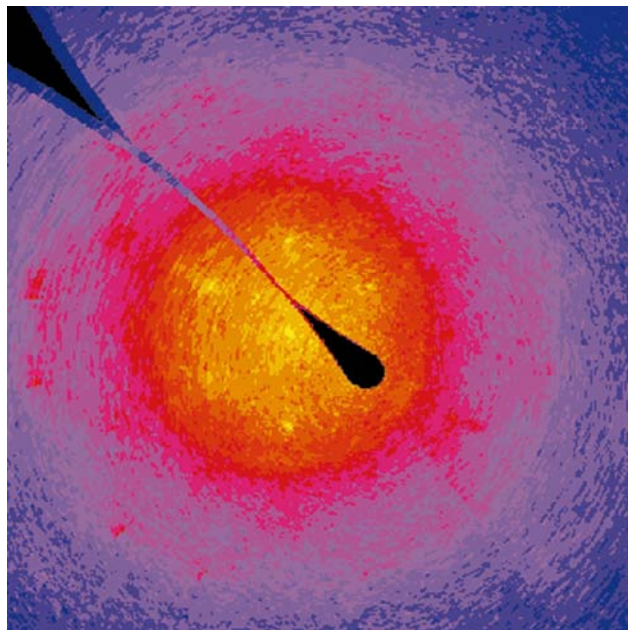
## 4. Intensity data collection

The information about the two-dimensional ordered structure of the guest molecules in the ( $\mathbf{ab}$ ) plane is contained mainly in the diffraction peaks of the lower indices of the  $hk00$  plane. One of the differences between the diffraction diagrams of the urea–suberic acid inclusion compound and urea– $n$ -alkane is the intensity distribution at very low Bragg angles. As an example the powder diagrams of urea/suberic acid and urea/nonadecane are compared in Fig. 4. Such an intensity distribution, also observed in urea/1,10-dibromodecane (Aliev *et al.*, 1996), increases the importance of higher-order structure factors to the electron density. In particular, the basal reflec-

tions (1100), (2000) and (0200) are the strongest ones. On the other hand, an accurate data collection of the weak ( $hk0m$ ) reflections requires exposure times long enough to overexpose (saturate) the above common reflections. Normally the loss of a few reflections does not hinder good structure solution and refinement. However, in this case the electron density map of



**Figure 1**  
( $hk01$ ) reciprocal plane showing some very weak main guest reflections (enclosed by a circle) at low Bragg angles. Given the closeness between this layer and the reciprocal plane ( $hk10$ ) the strongest peaks are the traces of the main host reflections.



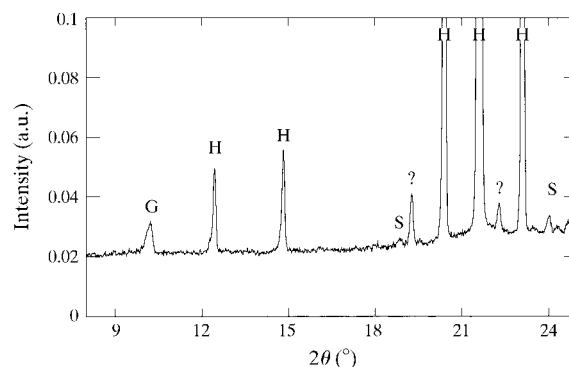
**Figure 2**  
( $hk03$ ) reciprocal plane showing the diffuse character of the guest diffraction peaks. As a consequence only the first and second guest reciprocal layers have been used during the structure refinement.

the guest substructure appears severely truncated (see Figs. 5 and 6). Therefore, using a different crystal a second data collection of the ( $hkl0$ ) reflections was performed. Intensity integration was achieved in four steps. First the common and main reflections of the urea substructure were integrated from the two datasets. Next the guest main reflections originating from both domains (obverse and reverse) were integrated using the first dataset. The latter integrations were performed with a narrower profile function (see Table 2 for details). As a consequence up to four scale factors were used during the refinement. Given the identical conditions used to obtain the two sets of guest integrated intensities, the corresponding scale factors are equal. It is important to notice that owing to the diffuse character (see Figs. 1 and 2) of the guest reflections and their increasing nearness to the main host reflections, only the first and second layer can be readily integrated. After blind integration the majority of the guest intensities are null or heavily contaminated by host reflections. Therefore, the values of  $R_{\text{int}}$  are extremely high. However,  $R_{\text{int}}$  is lowered to a reasonable limit when only the reflections with  $I > \sigma(I)$  and belonging to the reciprocal planes ( $hk0\pm 1$ ) and ( $hk0\pm 2$ ) are considered (see Table 1).

## 5. Structure refinement

### 5.1. Urea substructure

The host structure was refined using only the ( $hkl0$ ) reflections. The starting model was extrapolated from the literature. The space group of the average structure (extrapolating the notation used for the superspace group) is  $H'3_121$  ( $Z = 18$ ) when the structure is described in a centred cell spanned by ( $\mathbf{a}_g, \mathbf{b}_g, \mathbf{c}_h$ ). The centring ( $H'$ ) translations are  $(2/3, 1/3, 0)$  and  $(1/3, 2/3, 0)$ . The average symmetry  $P6_22$  common to many urea inclusion compounds is due to the

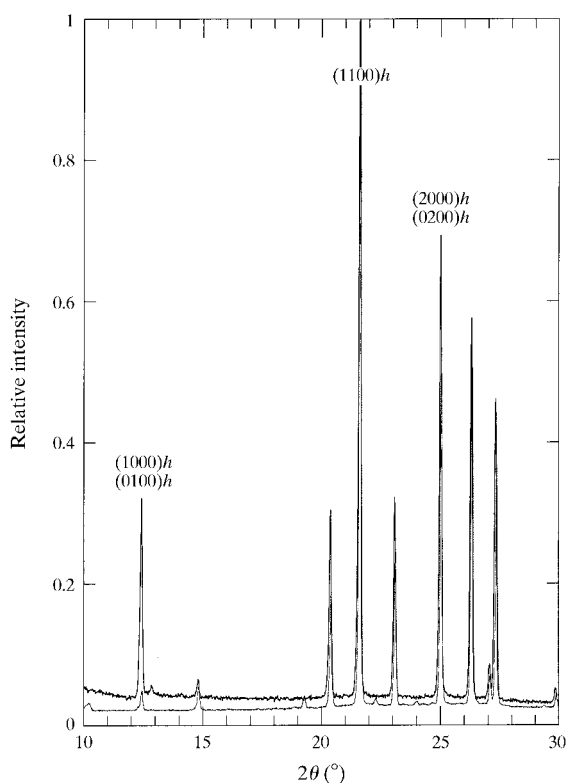


**Figure 3**  
Powder diffraction diagram at room temperature of the composite urea/suberic acid at room temperature. Peaks labelled with H, G and S are host main reflections, guest main reflections and satellites, respectively. The latter were identified by hand using the wavevector obtained from the single-crystal measurements. Reflections marked with '?' could not be identified since they do not appear in single-crystal diffraction patterns. The additional peaks could not be attributed either to impurities (single phases of urea or suberic acid) or to the distribution of the diffuse scattering. They can also be detected at low temperatures (even below a phase transition). However, these maxima are not present in powder diffraction patterns of the deuterated derivative.

twinning of the two individuals being related one to another by a twofold axis parallel to **c**. During the initial stages of the refinement twin fractions were fixed to 0.5. H atoms were excluded since their displacement parameters became negative. The refinement was rather unstable and C—O and N—O distances had to be constrained. During the last cycles twin fractions were allowed to vary. Their final values (0.5 within the standard deviation) are consistent with the strong pseudohexagonal symmetry of the structure. The agreement factors [ $R(hk00) = 0.42$  and  $R(hkl0) = 0.19$ ] clearly show the high contribution of the guest substructure to the diffracted intensities.

## 5.2. Guest substructure

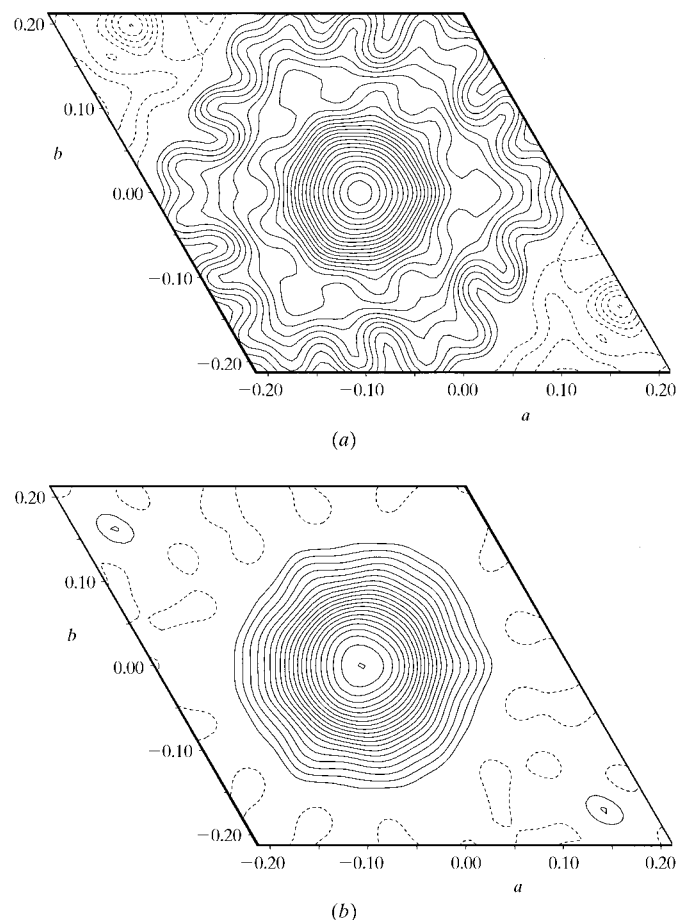
Guest molecules in urea composites are known to be largely disordered. Apart from the intrinsic lack of correlation along the **c** axis, the mismatch between the molecular point symmetry and the crystallographic symmetry of their packing introduces additional orientational disorder. Only the latter can be handled by an appropriate structural model. The number of configurational orientations can be estimated by projecting the whole structure (or substructure) onto the (**ab**) plane. A projection of the guest substructure can be obtained once the host substructure has been solved by a difference



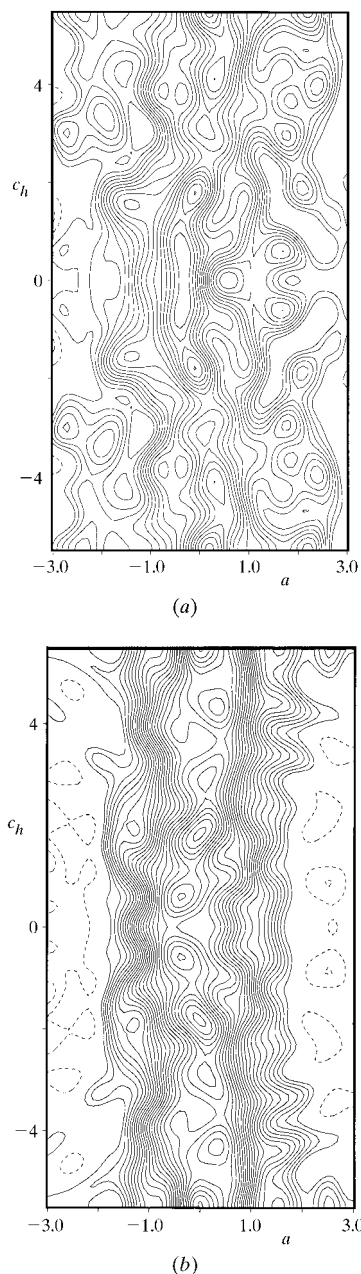
**Figure 4** Powder diffraction diagrams showing the different intensity distribution of the common ( $hk00$ ) reflections in the case of urea/nonadecane (upper line) and urea/suberic acid (lower line) inclusion compounds. Notice that these reflections contain almost all the information about the (**ab**) projection of the guest substructure. Therefore, the omission of the strongest one, (1100) in both cases, provokes very severe truncation effects in the electron density maps. Such effects are more pronounced in urea/suberic acid than in urea/nonadecane.

Fourier map. Alternatively, maximum entropy maps less biased and less sensitive to truncation effects seem to be the best choice. Although the latter show more structure (*cf.* Figs. 5*b* and 9*a*), both types of map show similar features: a practically isotropic maximum of electron density centred within the urea tunnels, which suggest a high degree of configurational disorder, showing only the effective size of the guest molecule.

Given the scarce number of reflections belonging to the guest substructure the suberic acid molecules have been refined as rigid units in the *trans* conformation. These plane molecules define basically a rectangular region of approximately  $c_g \times 0.5 \text{ \AA}^2$ . The atomic coordinates of the guest molecules have been taken from Gao *et al.* (1994). Basically guest molecules are supposed to be almost aligned with the tunnel axis. However, the orientation of the molecular plane (mostly defined by a rotation around the common **c** axis) has to be refined. In urea/*n*-alkane composites the symmetry-independent guest molecule can be oriented in such a way that its twofold axis is almost parallel to the twofold crystallographic axes of the guest superspace group. Depending on the direction of the crystallographic twofold axis the molecular plane is perpendicular to a tunnel wall (*wall model*) or



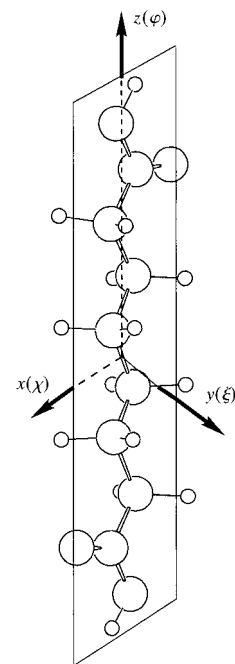
**Figure 5** (**ab**) difference Fourier map centred in one urea tunnel. In (*a*) a few overexposed reflections have been omitted (see text) giving rise to noticeable truncation effects. In (*b*) all reflections are included.



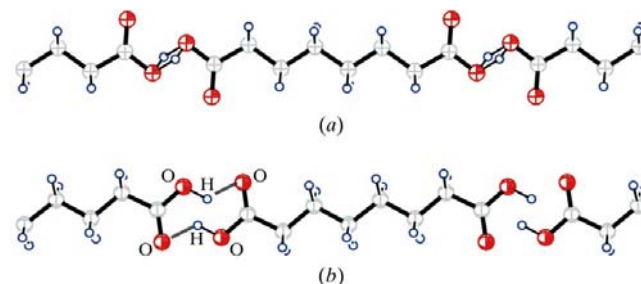
**Figure 6**  
 ( $ac_h$ ) difference Fourier map centred in one urea tunnel. The maps (a) and (b) have been calculated as in Fig. 5. The scale is in Å. In this case truncation produces a wavy shape [clearly reduced in (b)] of the electronic density along the tunnel axis, which could mask the true modulation of the guest electron density.

joins two opposite edges (in projection two corners of a hexagon) of the tunnel (*corner model*). In urea/*n*-heptadecane (Weber *et al.*, 1997) and urea/*n*-octane (Peral *et al.*, 2001) the alkane molecules were oriented in a *wall* configuration, although in the case of octane the refinement is not able to distinguish between both models. The molecular symmetry of the suberic acid is also approximately  $2/m$ ,<sup>3</sup> but only in the

<sup>3</sup> The guest molecule as refined by Gao *et al.* (1994) is not perfectly planar and its point group is  $\bar{1}$ . However, the deviation from  $2/m$  is very small.



**Figure 7**  
 Orthogonal axes used to describe the orientation of guest molecules.  $\chi$ ,  $\xi$  and  $\varphi$  are the rotation angles around each axis.



**Figure 8**  
 Chain of guest molecules along the common  $c$  axis. (a) Ideal configuration in which suberic acid molecules are parallel to  $c$ . (b) One of the refined configurations showing the tilt ( $\sim 5^\circ$ ) with respect to  $c$ . The molecular inclination favours the guest–guest bonding. Short (long) O–H distances are 1.0 (2) and 1.7 (1) Å, respectively.

*wall* configuration there is a possible coincidence between the molecular (approximate) symmetry axis and one crystallographic twofold axis. Since in any case the remaining symmetry elements introduce orientational disorder, the required rotation around the tunnel axis is always within a sector of  $30^\circ$  (the angle that separates two consecutive *wall* and *corner* orientations). The total number of configurations will depend on the position the molecular centre occupies within the guest unit cell. In the most general case the occupation of either the *wall* or *corner* orientations is  $1/6$ .

The refined molecular parameters were three rigid rotations, the position of its centre of mass and an isotropic thermal displacement parameter common to all the guest atoms. Subsequent difference Fourier maps show the positions of the urea H atoms that were refined, constraining the N–H

distances, with a common isotropic temperature parameter. Both *wall* and *corner* configurations were tested separately showing very similar (and highly improved with respect to those obtained only with the host substructure) agreement factors.<sup>4</sup> The position of the refined molecule with respect to the ideal *wall* or *corner* configurations<sup>5</sup> is given by three rotations  $\varphi \simeq 8^\circ$ ,  $\chi \simeq 5^\circ$  and  $\xi \simeq 5^\circ$  (see Fig. 7) and three translations parallel to  $\mathbf{a}_g$ ,  $\mathbf{b}_g$  and  $\mathbf{c}_g$  of  $\sim 0.2$  (0.3),  $-0.16$  (0.12) and  $-1.6$  Å (2.1 Å) for the *corner* (*wall*) model, respectively. The tilt of the molecular long axis with respect to the crystallographic  $\mathbf{c}_g$  axis favours the guest–guest intratunnel interaction through O–H...O bonds involving the carboxylic groups (see Fig. 8*b*).

The isotropic distribution of the electron density in the (**ab**) plane (Figs. 5*b* and 9*a*) suggests that the *corner* and *wall* models separately are not sufficient to handle the complete orientational disorder of the guest molecules. Therefore, a mixed model in which the orientations of the molecular planes were kept fixed was tested. Given the high correlation between both configurations and the reduced number of guest reflections neither the relative proportion of each of them nor the two molecular  $z$  coordinates could be refined. One of the molecules was fixed along  $\mathbf{c}_g$ , whereas the occupation of each model was varied by hand. The best result corresponds to a 50:50% mixture of the *wall* and *corner* configurations. The atomic coordinates of the final model have been deposited. This 12-fold orientational disorder of the guest molecules strongly reduces the  $R$  factor of the ( $hk0m$ ) ( $m \neq 0$ ) reflections.

The  $z$  offset between the two guest models could reflect the existence of fluctuations in the intermolecular distances within each tunnel. In urea/*n*-alkane inclusion compounds such an effect has been studied through the diffuse scattering distribution of the so-called ‘ $s$  layers’ (Weber *et al.*, 2000). However, the urea/suberic acid composite presents a different diffuse scattering scheme and therefore the results of Weber *et al.* (2000) cannot be directly extrapolated.

### 5.3. Modulation refinement

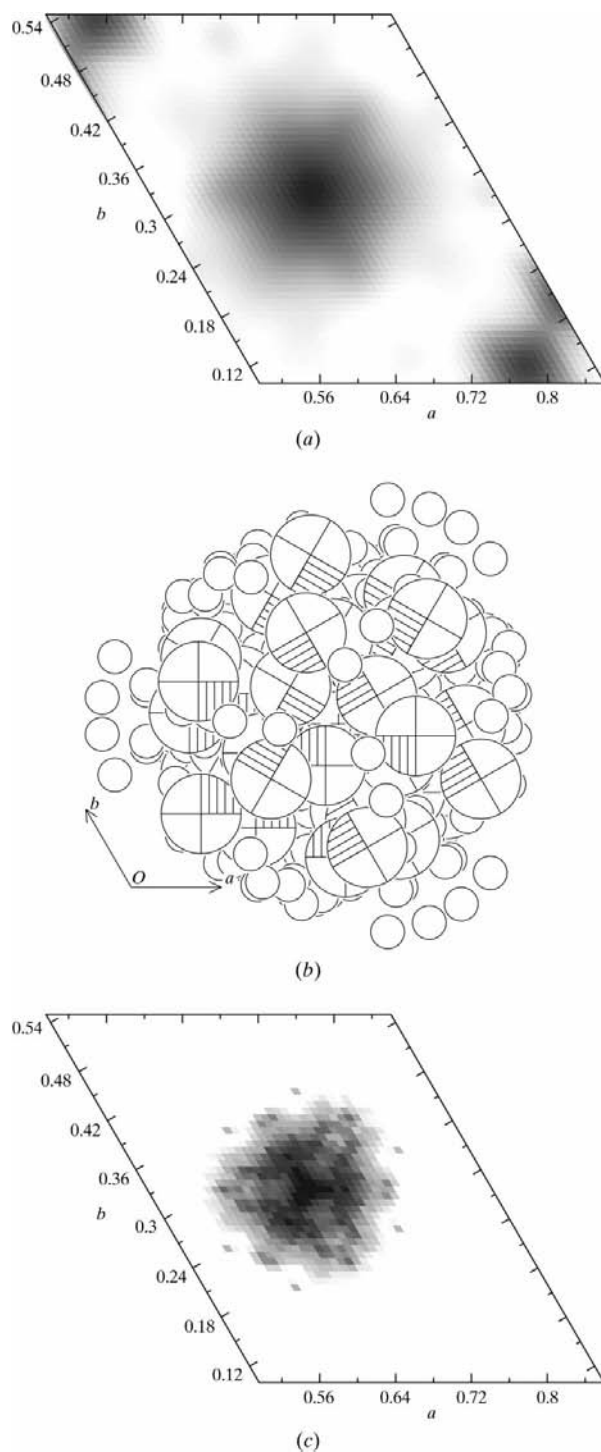
An analysis of the error distribution shows that the ( $hk \pm 1$ )<sub>*h*</sub> reflections are not so well reproduced as the rest of the host reflections. It would indicate that despite the lack of non-overlapping satellites, there is an appreciable contribution of first-order satellites to this group of reflections. Fourier maps in the (**ac**<sub>*h*</sub>) plane show an apparently wavy tube of electron density along the  $\mathbf{c}_h$  axis (see Fig. 6). However, any attempt to refine a transverse modulation using the ( $hk \pm 10$ ) reflections fails and implies a worse agreement for the guest main reflections. The guest modulation should be very small and perhaps the noticeable modulation present in Fig. 6(*b*) is due to truncation effects (*cf.* Figs. 6*a* and *b*).

<sup>4</sup> *Wall* model:  $R_{\text{all}} = 0.0606$ ,  $R_{\text{host}} = 0.0695$ ,  $R_{\text{guest}} = 0.22$  and  $R_{\text{common}} = 0.0493$ . *Corner* model:  $R_{\text{all}} = 0.0623$ ,  $R_{\text{host}} = 0.0694$ ,  $R_{\text{guest}} = 0.25$  and  $R_{\text{common}} = 0.0530$ .

<sup>5</sup> In the ideal *wall* configuration chosen as the starting model  $x \parallel [210]_g$ ,  $y \parallel \mathbf{b}_g$  and  $z \parallel \mathbf{c}_g$ . For the *corner* model  $x \parallel [110]_g$ ,  $y \parallel [\bar{1}10]_g$  and  $z \parallel \mathbf{c}_g$ .

## 6. Concluding remarks

The average structure of the urea/suberic acid composite has been analysed using the superspace approach. As usual in this



**Figure 9** (a) (**ab**) maximum entropy map calculated with the common ( $hk00$ ) structure factors phased with only the host substructure. (b) (**ab**) projection of the refined guest substructure including all the orientations generated by symmetry. H atoms do not reflect their isotropic temperature factor. (c) Calculated electron density using a Gaussian probability density function based on the atomic temperature factors (at a probability level of 50%).

type of compound guest molecules are highly disordered. Such disorder has been modelled locating (*trans*) guest molecules occupying 12 (equally weighted) different orientations inside the urea tunnels. They are generated by the symmetry operations of the guest subsystem acting on the *wall* and *corner* models in which the molecular planes are almost perpendicular to two opposite tunnel walls and two opposite tunnel corners, respectively. Using a Gaussian atomic probability density function based on the refined temperature factors (Fig. 9*b*) a projection of the electron density on the (**ab**) plane can be calculated. It agrees well (*cf.* Figs. 9*a* and *c*) with the maximum entropy maps based on the experimental structure factors phased with a model that only includes the host substructure. On the other hand, the refined structure predicts very weak intensities for the non-observed reflections. Both results support the reliability of the model. The modulation of the guest subsystem seems to be very weak and could not be refined.

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