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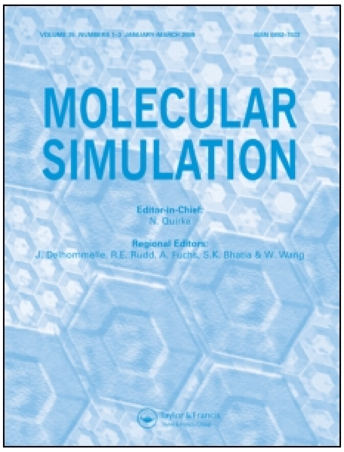

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Surface Structural Properties of Crystalline *s*-Triazine: A Computational Investigation

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SURFACE STRUCTURAL PROPERTIES OF CRYSTALLINE *s*-TRIAZINE: A COMPUTATIONAL INVESTIGATION

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This paper considers the surface structural properties and crystal morphology of crystalline *s*-triazine. A key feature of the computational approach adopted is the consideration of surface structural relaxation of the uppermost section of the crystal and the use of non-rigid molecules. Crystal morphologies calculated on the basis of surface energies and attachment energies are considered.

KEY WORDS: Surface structure, s-triazine, crystal morphology.

INTRODUCTION

A knowledge of the growth habits and morphological properties of molecular crystals is important with regard to understanding and exploiting many of their physico-chemical properties. Properties which relate to the surface structure (rather than the bulk structure) of a crystalline material clearly depend upon which crystal faces are well developed and upon the arrangement of the molecules at these surfaces. Computational approaches for determining the structural and energetic properties of the surfaces of crystalline solids have an important rôle to play in developing a fundamental understanding of these properties. Much of the reported computational work in this field has considered systems for which the morphology is known from experimental investigations [1, 2]. As reported here, this approach is now being applied to investigate materials for which the "bulk" crystal structure is known, but for which the surface properties are not known. It is important to emphasize, in this regard, that the structure at the surface of a crystalline material can differ substantially from the structure within the "bulk" of the crystal, and it is therefore important, in theoretical studies of surface properties, to take into consideration structural relaxation at the surface of the crystal.

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In view of the importance of considering surface structural relaxation in such studies, the work described in this paper employs methodology that has been developed to predict and rationalize the surface structural properties of a molecular crystal, and this methodology is applied here to crystalline *s*-triazine [3] (Figure 1). The bulk crystal structure of *s*-triazine has been investigated previously *via* computational techniques [4]. The lack of experimental data on the surface properties of *s*-triazine and, in particular, the absence of any experimental assignment of the predominant crystal faces, necessitates that the results reported here are of a predictive nature. Indeed, such work has exciting implications for the future modelling of crystal surfaces in cases for which experimental data on the surface and morphological properties are not available.

METHODOLOGY AND COMPUTATIONAL DETAILS

The potential energy of a molecular crystal can be represented by considering both intermolecular and intramolecular potential energy contributions. In this work, these potential energy functions were taken from the CVFF tabulated forcefield (1993), courtesy of BIOSYM Technologies [5]. Table 1 reports the potential energy functions and parameterizations used in this work. Atom-centred point charges were used to represent the Coulombic interactions, and intramolecular Coulombic terms were not considered. These charges were determined *via* Mulliken charge population analysis derived from periodic Hartree-Fock calculations (using a 6–21G basis set) on the experimental crystal structure [3] using the CRYSTAL program [6]. This approach does not necessarily provide the most accurate representation of the charge distribution for such a delocalized system, although such a simplified representation can nevertheless model successfully several properties of the crystal. The centre of mass to centre of mass cut-off distance for the consideration of short-range (non-Coulombic)

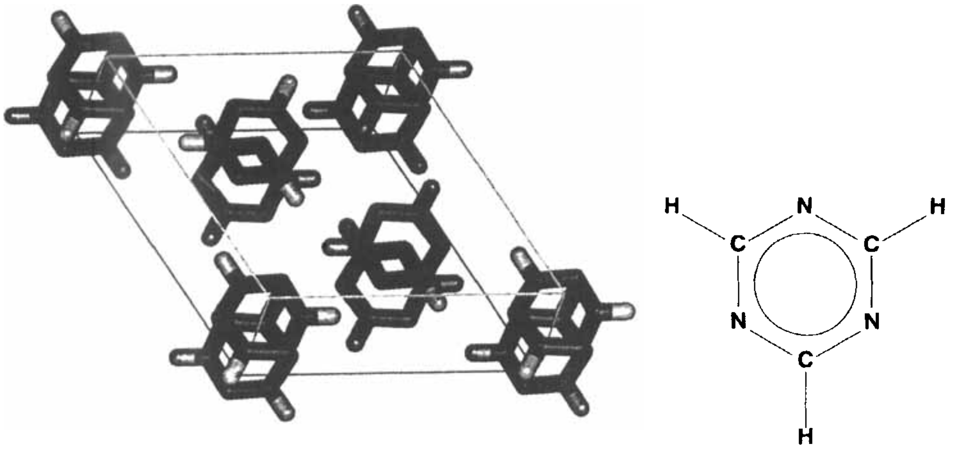

Figure 1 Crystal structure of *s*-triazine [3] [space group: $R\bar{3}c$; lattice parameters (hexagonal setting): $a = 9.647$ Å, $c = 7.281$ Å].

Table 1 Specification of the potential energy parameterization used in this work

Atomic charges			
Atom	Charge/$\lvert e\rvert$		
N	−0.6582		
C	0.3590		
H	0.2992		
Intramolecular potentials			
(a) *Morse*:	$V(r)=D_e(\{1-\exp[-b(r-r_0)]\}^2-1)$		
Interaction	D_e/eV	b/Å^{-1}	r_0/Å
C—H	5.0302	1.77	1.08
N—C	6.07096	2.00	1.26
(b) *Three body*:		$V(\theta)=\frac{1}{2}K_3(\theta-\theta_0)^2$	
Interaction	K_3/eV rad^{-2}	θ_0/°	
H—C—N	2.1682	120.0	
C—N—C	3.2566	114.0	
N—C—N	4.423	134.0	
(c) *Four-body*:		$V(\Phi)=\frac{1}{2}K_4[1+\cos(n\Phi-\tau)]$	
Interaction	K_4/eV	n	τ/°
H—C—N—N	0.01604	2	180.0
C—N—C—N	0.173546	2	180.0
H—C—N—C	0.173546	2	180.0
Intramolecular potentials			
	$V(r)=Ar^{-12}-Br^{-6}$		
Interaction	A/eV Å^{12}	B/eV Å^6	
C···C	128737.02	57.488	
C···N	112494.14	55.386	
C···H	6299.474	9.0522	
N···N	98300.6547	53.36187	
N···H	5504.664	8.721377	
H···H	308.2515	1.4254	

intermolecular interactions was 25 Å, and the longer range Coulombic interactions were summed according to the Ewald technique [7].

The crystal structure for *s*-triazine determined [3] from room temperature X-ray diffraction data was taken as the starting structure. The "bulk" structural properties were determined using constant pressure lattice energy minimization algorithms embodied within the program GULP [8] together with the potential energy parameterization discussed above. The bulk crystal structure determined in this calculation is in good agreement with the experimental crystal structure (Table 2).

Calculations using the MARVINs program [9] considered the following crystal faces (indexed on the basis of the hexagonal unit cell of the *rhombohedral system*):

Table 2 Comparison of the experimental lattice parameters determined for *s*-triazine at room temperature and the lattice parameters obtained from the lattice energy minimization calculation for the bulk crystal structure of *s*-triazine discussed in the text

	Calculated	*Experiment*	*Discrepancy*
a/Å	9.485	9.647	1.7%
b/Å	9.485	9.647	1.7%
c/Å	7.349	7.281	0.9%
α/°	90.0	90.0	
β/°	90.0	90.0	
γ/°	120.0	120.0	

$\{110\}, \{012\}, \{211\}, \{300\}, \{122\}, \{131\}, \{113\}, \{202\}, \{402\}, \{333\}, \{006\}$. These crystal faces were chosen on the basis that they represent lattice planes with large interplanar spacings. The $\{100\}$ surface is denoted $\{300\}$ because $\{300\}$ represents the irreducible growth slice corresponding to the $\{100\}$ surface (*vide infra*). The MARVINs program utilizes a two-region approach to model crystal surfaces, with planar two-dimensional periodic boundary conditions applied parallel to the surface. Region 1 contains the atoms closest to the surface and the structure of this region (taken initially to be the same as the bulk crystal structure) is relaxed explicitly until the force on each atom is negligible. The structure of Region 2 is taken as the bulk crystal structure and is not relaxed in the calculation. The surface energy (E_{surf}) is defined as:

$$E_{\mathrm{surf}} = \frac{E_{R1} - E_{\mathrm{bulk}}}{A}$$

where E_{R1} is the energy of the fully relaxed structure of Region 1, E_{bulk} is the energy of the bulk structure corresponding to the same number of unit cells as Region 1, and A is the surface area of Region 1. The depth of Region 1 is chosen to be sufficiently large to ensure that convergence in the surface energy is achieved (i.e. E_{surf} independent of increasing the depth of Region 1). The attachment energy (E_{att}) was also considered; this is defined here as the change in energy when a new layer of thickness d_{hkl} (the interplanar spacing) is attached to the $\{hkl\}$ surface of the crystal.

In all calculations reported here, the depth of Region 1 was 3 unit cells (in the hexagonal setting) and the depth of Region 2 was chosen to correspond to convergence of the Ewald summation (typically *ca.* 7–18 unit cells). In relaxing the structure of Region 1, *both* intermolecular and intramolecular geometries were allowed to vary. It is important to emphasize that this approach of relaxing the surface structure differs substantially from alternative approaches followed in previous studies of surface properties of organic molecular crystals (e.g. benzophenone [10], for which the intramolecular geometry was held fixed and the surface structure was not allowed to relax). A more detailed discussion of the importance of surface structural relaxation is given in ref. 1.

RESULTS AND DISCUSSION

In all diagrams of surface structures in this paper, the uppermost portion of Region 1 is shown, with the crystal surface horizontal (at the top of the figure) and viewed parallel to the surface. In each diagram, the fully relaxed structure is represented by black lines and is overlaid on the initial (unrelaxed) structure (taken as the bulk crystal structure) represented by light grey lines.

We consider first the results for the {110} surface (Figure 2). In the bulk crystal structure of *s*-triazine, the molecules stack in a direction perpendicular to the {110} surface, and the uppermost molecules at this surface are oriented with the molecular plane parallel to the surface. The precise orientation of the molecules at the surface has important implications with regard to solvation and other chemical properties of the crystal (*vide infra*). As shown in Figure 2, the molecules at the surface relax significantly from the corresponding positions in the bulk crystal structure. However, these structural changes occur only for molecules very close to the surface, and the third and fourth layers of molecules beneath the surface resemble very closely the bulk crystal structure.

The {300} plane is perpendicular to the *a* axis, and for alternate molecules hydrogen atoms and nitrogen atoms are exposed at the surface (Figure 3). The structure relaxes significantly at this surface, and the tilting of the uppermost molecules at the surface is particularly pronounced. The molecules also distort significantly from planarity (the H—C—N—N improper dihedral angle is 0° in the bulk crystal structure, but is 7.4° for the uppermost molecules in the relaxed {300} surface). However, for the third layer of molecules beneath the surface, and layers deeper than this, the structure is essentially indistinguishable from the bulk structure.

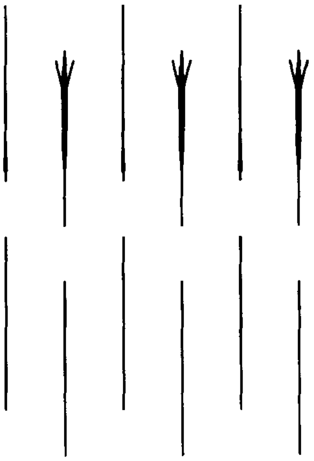

Figure 2 The initial (unrelaxed) and relaxed structures of the {110} surface of *s*-triazine. The initial structure is represented as light grey, whereas the fully relaxed structure is represented as black. The crystal surface is the horizontal plane at the top of the figure and is viewed parallel to the surface.

Figure 3 The initial and relaxed structures of the {300} surface.

Significant structural relaxations are also observed for the other surfaces considered, and are represented in Figures 4–12 for the {202}, {012}, {113}, {122}, {131}, {211}, {402}, {333} and {006} surfaces respectively. For all these surfaces, the structural relaxation is minimal from about the third layer of molecules beneath the surface, even though the molecules in this region were allowed explicitly to relax.

For the {113} surface, two distinguishable cleavage planes can be defined, differing in the orientations of the uppermost molecules at the surface. These different ways of cleaving the crystal to form the {113} surface have different initial and relaxed surface

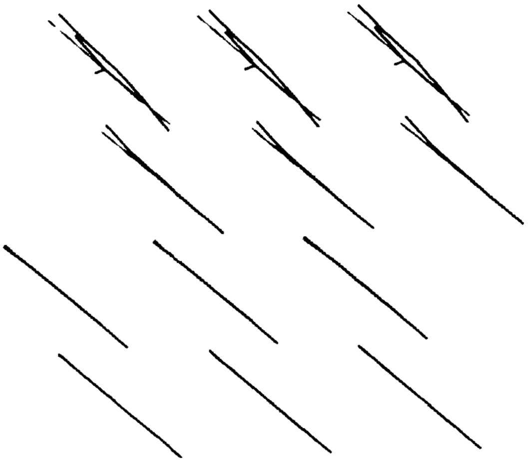

Figure 4 The initial and relaxed structures of the {202} surface.

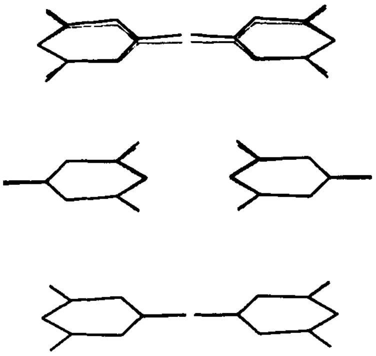

Figure 5 The initial and relaxed structures of the {012} surface.

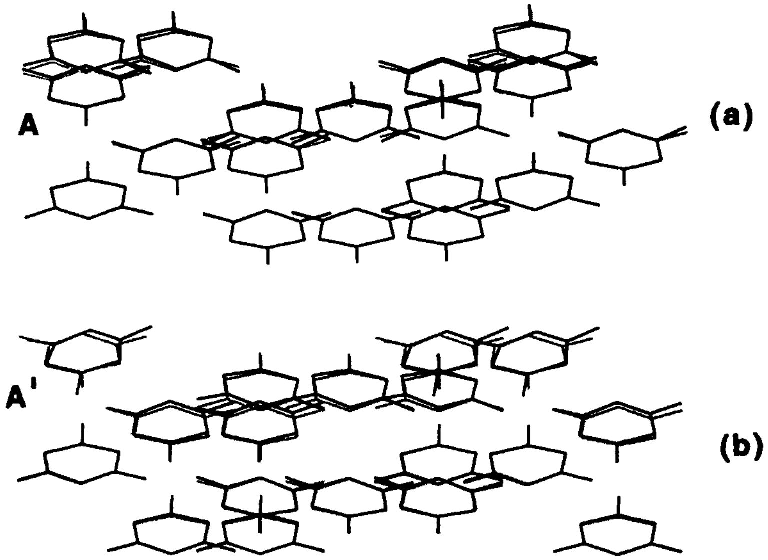

Figure 6 The initial and relaxed structures of the two different cleavage planes of the {113} surface: (a) Cut 1; (b) Cut 2.

Figure 7 The initial and relaxed structures of the {122} surface.

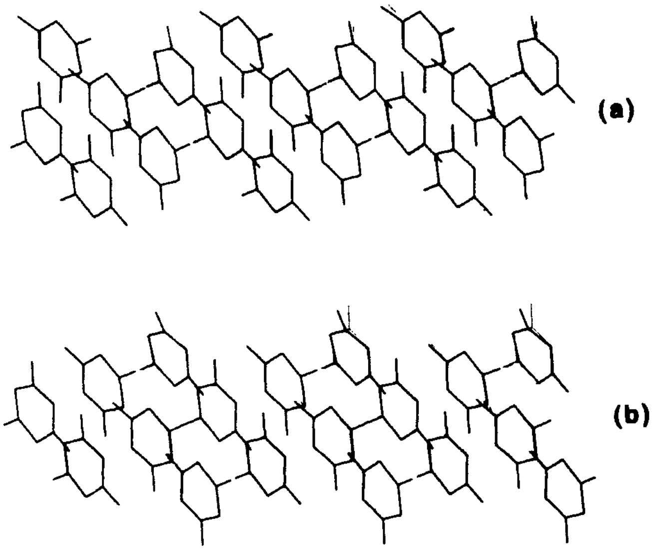

Figure 8 The initial and relaxed structures of the two different cleavage planes of the {131} surface: (a) Cut 1; (b) Cut 2.

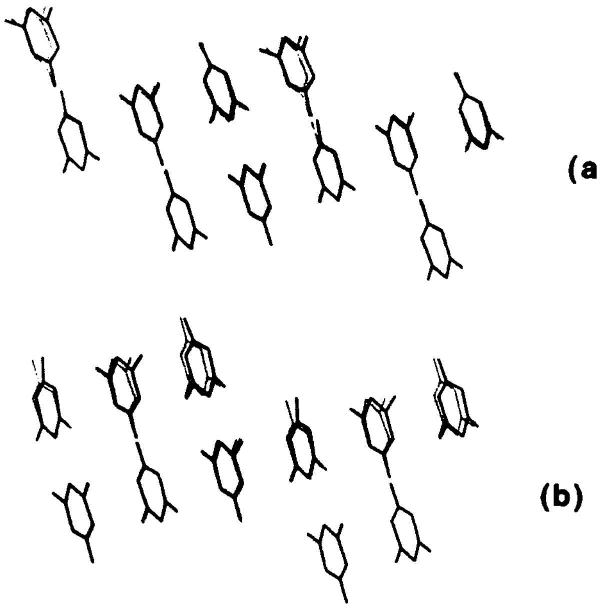

Figure 9 The initial and relaxed structures of the two different cleavage planes of the {211} surface: (a) Cut 1; (b) Cut 2.

energies (see Table 3). The relaxed structures of these cleavage planes are shown in Figure 6, demonstrating clearly that the surface structural relaxation is different in each case. For example, the way in which the molecule labelled A and A′ in Figure 6 relaxes depends upon its position with respect to the cleavage plane.

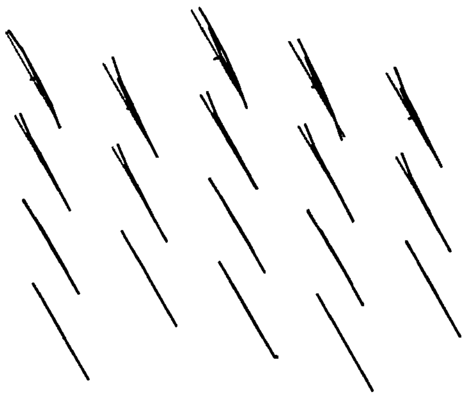

Figure 10 The initial and relaxed structures of the {402} surface.

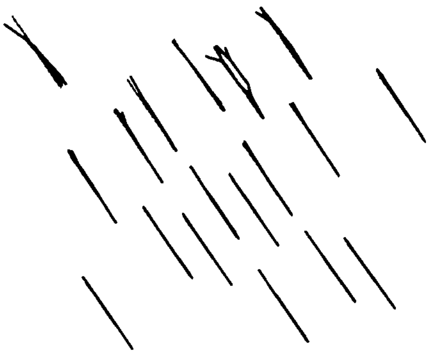

Figure 11 The initial and relaxed structures of the {333} surface.

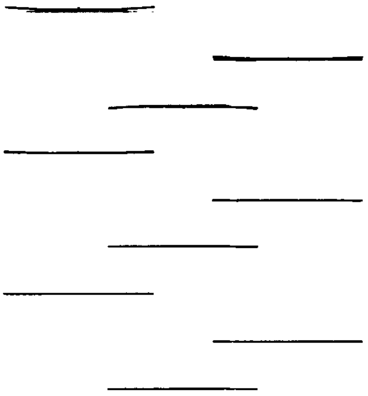

Figure 12 The initial and relaxed structures of the {006} surface.

The surface energy (E_{surf}) for each crystal surface considered is reported in Table 3 for the initial (unrelaxed) surface structure and for the fully relaxed surface structure. The order of increasing surface energy for the initial structures and the order of increasing surface energy for the relaxed structures are as follows (for surfaces for which more than one cleavage plane has been considered, the cleavage plane corresponding to the least positive surface energy is considered):

Initial Structures

$E_{surf}\{012\} < E_{surf}\{006\} < E_{surf}\{113\} < E_{surf}\{110\} < E_{surf}\{122\} < E_{surf}\{131\} < E_{surf}\{202\} < E_{surf}\{333\} < E_{surf}\{300\} < E_{surf}\{211\} < E_{surf}\{402\}$

Relaxed Structures

$E_{surf}\{012\} < E_{surf}\{006\} < E_{surf}\{113\} < E_{surf}\{122\} < E_{surf}\{110\} < E_{surf}\{202\} < E_{surf}\{131\} < E_{surf}\{333\} < E_{surf}\{211\} < E_{surf}\{300\} < E_{surf}\{402\}$

From Table 3, it is clear that, for all surfaces, the surface energy decreases following structural relaxation, emphasizing the importance of considering structural relaxation in computational investigations of surface properties. Importantly, the ranking of the crystal faces according to their surface energies changes upon consideration of surface structural relaxation, with important consequences in regard to the prediction of crystal morphology (*vide infra*). In particular, we recall that the relative morphological importance of a crystal face increases as its surface energy becomes less positive.

The attachment energies (E_{att}) for the crystal surfaces described above are reported in Table 4 for the initial (unrelaxed) structure and for the fully relaxed structure. The order of decreasing attachment energy for the initial structures and the order of decreasing attachment energy for the relaxed structures are as follows:

Table 3 Surface energies for the unrelaxed and fully relaxed surfaces of crystalline *s*-triazine

	E_{surf}/Jm^{-2}	
Surface	*Unrelaxed*	*Relaxed*
{110}	0.2759	0.2712
{012}	0.2301	0.2254
{211} Cut 1	0.3143	0.3018
Cut 2	0.3141	0.3007
{300}	0.3105	0.3023
{122}	0.2774	0.2680
{131} Cut 1	0.3010	0.2929
Cut 2	0.3008	0.2933
{113} Cut 1	0.2606	0.2515
Cut 2	0.2604	0.2491
{202}	0.3027	0.2924
{402}	0.3252	0.3140
{333}	0.3046	0.2938
{006}	0.2463	0.2435

Table 4 Attachment energies for the unrelaxed and fully relaxed surfaces of crystalline *s*-triazine

	$E_{att}/eV mol^{-1}$	
Surface	*Unrelaxed*	*Relaxed*
{110}	−0.6519	−0.6558
{012}	−0.7212	−0.7234
{211} Cut 1	−0.9247	−0.9321
Cut 2	−0.9245	−0.9338
{300}	−0.9346	−0.9580
{122}	−0.9635	−0.9963
{131} Cut 1	−0.9521	−0.9703
Cut 2	−0.9519	−0.9719
{113} Cut 1	−0.9567	−0.9601
Cut 2	−0.9552	−0.9702
{202}	−1.1207	−1.1189
{402}	−1.1734	−1.2065
{333}	−1.0978	−1.1467
{006}	−1.1926	−1.2114

Initial Structures

$$E_{\mathrm{att}}\{110\} > E_{\mathrm{att}}\{012\} > E_{\mathrm{att}}\{211\} > E_{\mathrm{att}}\{300\} > E_{\mathrm{att}}\{131\} > E_{\mathrm{att}}\{113\} > E_{\mathrm{att}}\{122\} > E_{\mathrm{att}}\{333\} > E_{\mathrm{att}}\{202\} > E_{\mathrm{att}}\{402\} > E_{\mathrm{att}}\{006\}$$

Relaxed Structures

$$E_{\mathrm{att}}\{110\} > E_{\mathrm{att}}\{012\} > E_{\mathrm{att}}\{211\} > E_{\mathrm{att}}\{300\} > E_{\mathrm{att}}\{113\} > E_{\mathrm{att}}\{131\} > E_{\mathrm{att}}\{122\} > E_{\mathrm{att}}\{202\} > E_{\mathrm{att}}\{333\} > E_{\mathrm{att}}\{402\} > E_{\mathrm{att}}\{006\}$$

The ranking of the crystal faces according to their attachment energies changes upon consideration of surface structural relaxation, again with important consequences in regard to the prediction of crystal morphology (*vide infra*). In particular, we recall that the relative morphological importance of a crystal face increases as its attachment energy becomes less negative.

Using the calculated surface energies, the crystal morphology can be predicted [11] on the basis of minimization of the total surface energy. Figure 13 represents the crystal morphologies predicted in this way using surface energies calculated for the initial structures of the crystal surfaces (i.e. with the surface structure identical to the bulk structure) and for the fully relaxed structures of the crystal surfaces. Figure 14 represents the crystal morphologies predicted, in a similar manner, considering the attachment energies of the crystal surfaces (again, for the initial structures of the crystal surfaces and for the fully relaxed structures of the crystal surfaces). It is clear from Figures 13 and 14 that the crystal morphologies predicted from both surface energies and attachment energies are approximately the same, with the {012} form dominant and the {110} form representing the long edges of the crystal. It has been suggested that crystal morphologies predicted on the basis of surface energies contain many more

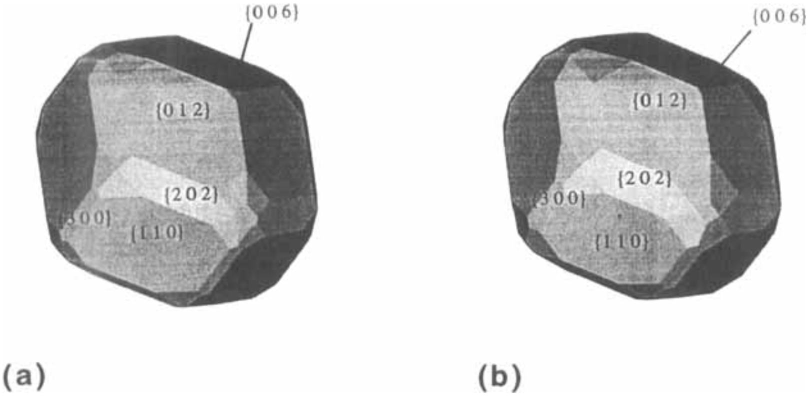

Figure 13 Predicted crystal morphologies, derived from the surface energies, for (a) the initial (unrelaxed) surface structures and (b) the relaxed surface structures of crystalline *s*-triazine.

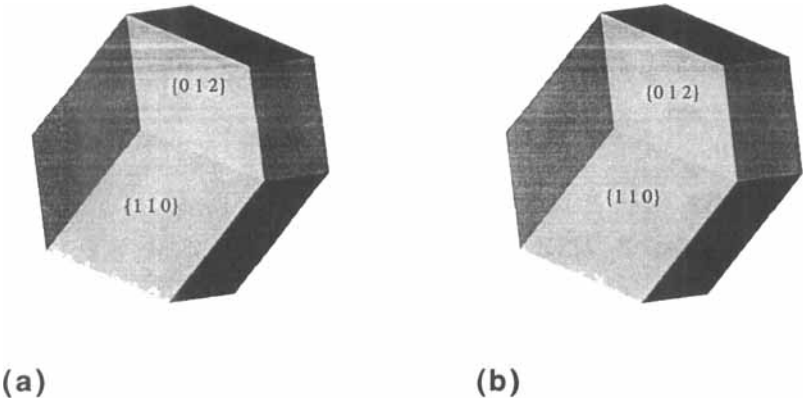

Figure 14 Predicted crystal morphologies, derived from the attachment energies, for (a) the initial (unrelaxed) surface structures and (b) the relaxed surface structures of crystalline *s*-triazine.

faces than usually observed experimentally[12], since the crystal morphology predicted on the basis of the surface energy is the equilibrium growth morphology, whereas, in practice, crystal growth is generally not an equilibrium process.

There are small, but important, differences between the crystal morphologies predicted on the basis of the unrelaxed and relaxed structures; for example, the {006} form is significant in the morphology predicted from the initial surface energies, whereas in the morphology predicted from the relaxed surface energies, the {006} form is substantially smaller, even though the {006} form has the second most favourable relaxed surface energy. The difference in the crystal morphologies predicted on the basis of relaxed surface energies and relaxed attachment energies mainly concerns the intersection of the prominent {012} and {110} forms. In the morphology predicted on the basis of attachment energies, there is a well-defined edge between the {012} and {110} faces. However, in the morphology predicted on the basis of surface energies, the edge between the {012} and {110} faces is more rounded, *via* the intervening {202} form and other forms. The intersection of the symmetry related {110} surfaces also appears somewhat rounded *via* the intervening {300} faces. The observation of these effects demonstrates the importance of taking surface structural relaxation into consideration in computational predictions of crystal morphology. Clearly, it would be of great interest if the experimental crystal morphology of *s*-triazine was known, and particularly to know how this morphology varies as a function of the crystallization conditions used.

CONCLUDING REMARKS

The work reported in this paper has demonstrated the application of computational techniques to develop an understanding of the surface structural properties of a molecular crystal. In view of the significant surface structural relaxations (both intramolecular and intermolecular) observed in this work, it is clear that any approach towards understanding surface structural properties that does not take structural relaxation into consideration must be viewed with caution. The structural relaxations observed here for the surfaces of *s*-triazine are generally larger than those observed in a previous study [1] of surface structural relaxation in crystalline urea. This predominantly reflects the stronger intermolecular forces (dominated by N—H···O hydrogen bonding) in crystalline urea. Nevertheless, the extent of atomic movements arising from the surface structural relaxation in *s*-triazine is relatively small in comparison with the atomic movements typically found upon relaxation of the surface structures of ionic materials.

The approach described in this paper essentially represents crystal surfaces exposed to vacuum. The methodology has now been developed further to allow investigations of the ways in which solvent molecules interacting with a crystal surface can modulate the structural properties of the surface. Our research on the surface structural properties of molecular crystals is now being extended to encompass studies of this type.

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