Molecular Configuration at the Solid−Solid Interface: Twinning in Saccharin Crystals

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Abstract: In a combined modeling and experimental study the twin interface in saccharin crystals has been used as the basis for energetic calculations and visualization of the solid−solid interface. A methodology has been developed that has wide applicability to a range of interfaces between crystalline materials.

Introduction

In recent years considerable effort has been expended on modeling and controlling structural and kinetic processes occurring at the solid−liquid interface during nucleation and crystallization of molecular[1] and inorganic[2] materials. The concepts and control strategies for molecular recognition and templating at such interfaces are now understood to the extent that strategies have been developed for the control of crystal structure, morphology, and nucleation by use of specifically designed additives.[3−5] Surprisingly, given its comparative and potential importance in the design and formulation of particulate materials the solid−solid interface has not been afforded equal effort and interest. Molecular design and engineering of even the simplest interface of this type has not been considered largely due to the inability of traditional crystallography to define the precise atomic positions, or juxtaposition of lattice planes in the interfacial region. While recent advances in the application grazing incidence X-ray diffraction[6,7] may ultimately give access to such information, this contribution considers the simplest solid−solid interface, a twin plane in a molecular crystal, and explores the combined application of crystallographic information and lattice energy calculation as a means of specifying the molecular-scale arrangement across the interfacial region.

A twinned crystal[8] comprises two (or more in the case of multiple twinning) individual single crystals joined as a single particle such that the component parts are related by a symmetry element that does not exist in the single crystal. Such elements are typically mirror planes, rotation axes, or centers of inversion, and much phenomenological work has been reported in which such systems have been characterized by appropriate crystallographic[9] and energetic relationships.[10−12] Saccharin has been chosen as a model system for this study and the work comprised three strategic elements: first the identification of the twin operation in saccharin crystals, second modification of the molecular mechanics based program HABIT[13] to enable the energy of a twin to be calculated as a function of the juxtaposition of molecules about the twin plane, and finally the transformation of these energetic considerations into a visualization of the most likely interfacial molecular configuration.

Saccharin−Identifying the Twin Plane

Twinned saccharin (ex Aldrich) crystals were easily grown from acetone solution. Briefly, a saturated solution was prepared at 50 °C and nucleated by cooling to 40 °C. After several hours the crystals were collected by Buchner filtration and examined by polarizing optical (Polyvar) and scanning electron (Hitachi S-520) microscopy. Saccharin ($C_6H_4SO_2$-NHCO) crystallizes in the monoclinic system as rhombic plates with four molecules in the unit cell, space group $P2_1/c$, a = 9.552 Å, b = 6.919 Å, c = 11.803 Å, β = 103.9°; molecules pack within the crystals as hydrogen-bonded dimers.[14] Typically between 30 and 50% of crystals grew as twins in unstirred solutions. Optical micrographs of single and twinned crystals are seen in Figure 1, parts a and b, respectively. The twins are of the simple contact type in which each half is approximately the same size and the interface between components is clearly visible. Optical goniometry enabled the angle between the normals of the major faces to be measured as 44° consistent with the “open book” morphology shown in the electron micrograph, Figure 1c.

The Weissenberg (Stoe) X-ray camera was used to correlate the physical and crystallographic geometry of these twins by analysis of the reciprocal lattice image collected from a single particle. An oscillation photograph (Cu Kα radiation) identified the b axis as the common axis of the twins (i.e. parallel to the twin plane) while a zero layer Weissenberg photograph of the

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(*h*0*l*) layer showed two reciprocal lattices arising from the two halves of the twin. The lattices are related by an angle of 44° between the a^* axes and 110° between the c^* axes, which is consistent with goniometry results and from which the twin plane was calculated to be $(10\bar{2})$. The Miller index of the twin plane determined in this way was confirmed by collecting an orientation matrix for each of the two halves of a twinned crystal, using a Rigaku 4-circle diffractometer. In the untwinned structure dimer pairs are related across $(10\bar{2})$ by inversion; this is replaced in the twin by a mirror. Crystallographic and trigonometric analysis relating to this work is available as Supporting Information.

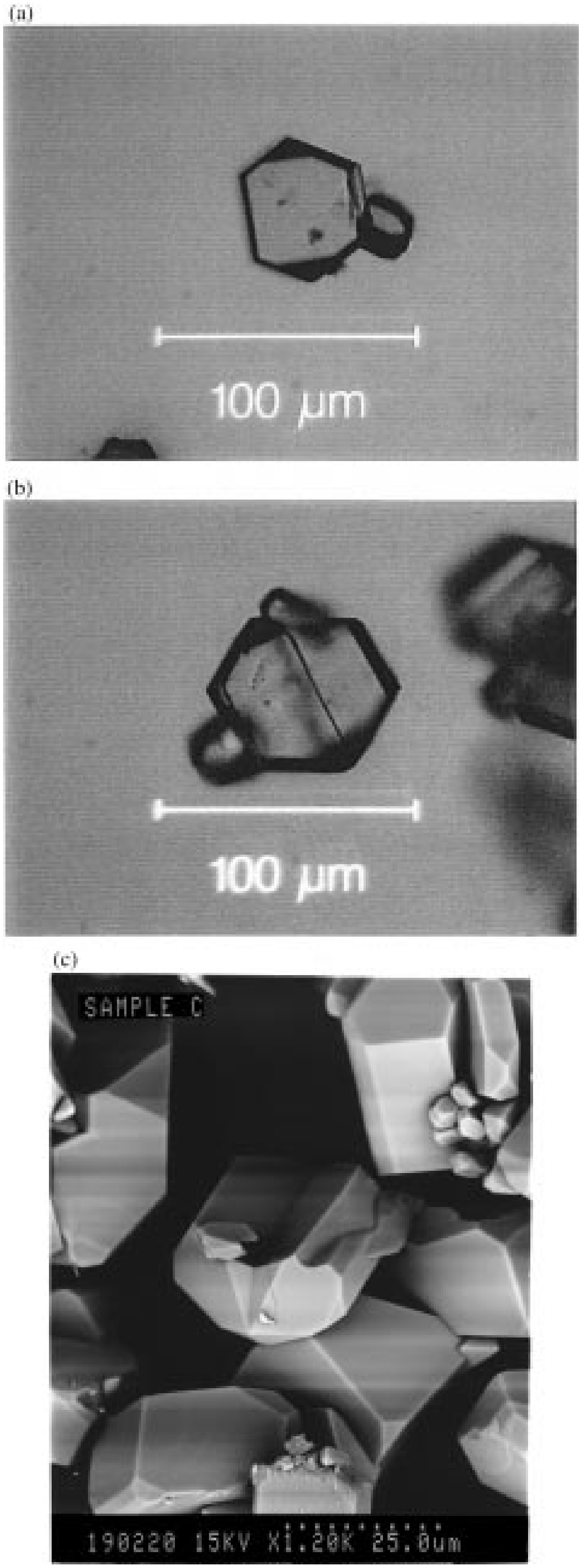

Figure 1. (a) Micrograph of a single saccharin crystal grown from acetone. (b) Micrograph of a twinned saccharin crystal grown from acetone. (c) SEM photograph of a twinned crystal showing "open book" morphology.

Calculating the Twin Energy

The calculations reported here have been carried out utilizing the lattice and attachment energy program, HABIT.[13] Energies are calculated by summing all interactions between nonbonded atom pairs using a potential function, V, which combines a Lennard-Jones term with a Coulombic electrostatic contribution. The Lennard-Jones 6−12 van der Waals potential may be replaced by a 10−12 hydrogen-bonded term, such that the potential between atoms i and j, separated by a distance r_{ij}, is given by

$$V_{ij} = -\left(\frac{A_{ij}}{r_{ij}^{6}} + \frac{D_{ij}}{r_{ij}^{10}}\right) + \frac{B_{ij}}{r_{ij}^{12}} + \frac{q_i q_j}{\epsilon r_{ij}}$$

where A_{ij} or D_{ij} is zero.

A three-dimensional model of a crystal is built up from the point group symmetry by adding cells along the crystallographic directions. For a twinned crystal, a new symmetry element is present that acts at the interface between the components of the twin and which may be included as the model crystal is being built. According to the attachment energy model the lattice energy of a crystal is given by

$$E_{\text{latt}} = E_{\text{slice}} + 2E_{\text{att}}$$

where E_{latt} is the lattice energy, E_{slice} is the slice energy, calculated by summing all the atom−atom interactions between a central molecule and all others within a slice of thickness d_{hkl}, and E_{att} is the attachment energy of slice (*hkl*). For a twinned crystal, this expression becomes

$$E_{\text{latt}}^{\text{twin}} = E_{\text{slice}} + E_{\text{att}} + E_{\text{att}}^{\text{twin}}$$

where E_{att} is the attachment energy of the untwinned half and $E_{\text{att}}^{\text{twin}}$ is the attachment energy of the twinned half. It is apparent from the above relationships that the difference in lattice energies (*twin energy*) between a twinned and an untwinned crystal, defined here as ΔE, is given by the difference in attachment energies ($E_{\text{att}}^{\text{twin}} - E_{\text{att}}$). The only experimental information obtained from crystallography on a twinned crystal is the common plane $(10\bar{2})$ in the case of saccharin) and the relationship between the two halves (reflection). No information is generated on the interplanar separation at the interface or any lateral shift within the common plane. To explore this precise geometrical juxtaposition it has been assumed that the process of twinning reduces the lattice energy compared to an untwinned crystal and that the actual interface configuration will be that for which the twin energy is lowest. Thus, the difference between the twinned and untwinned attachment energies, ΔE, has been calculated across all space for differing relative

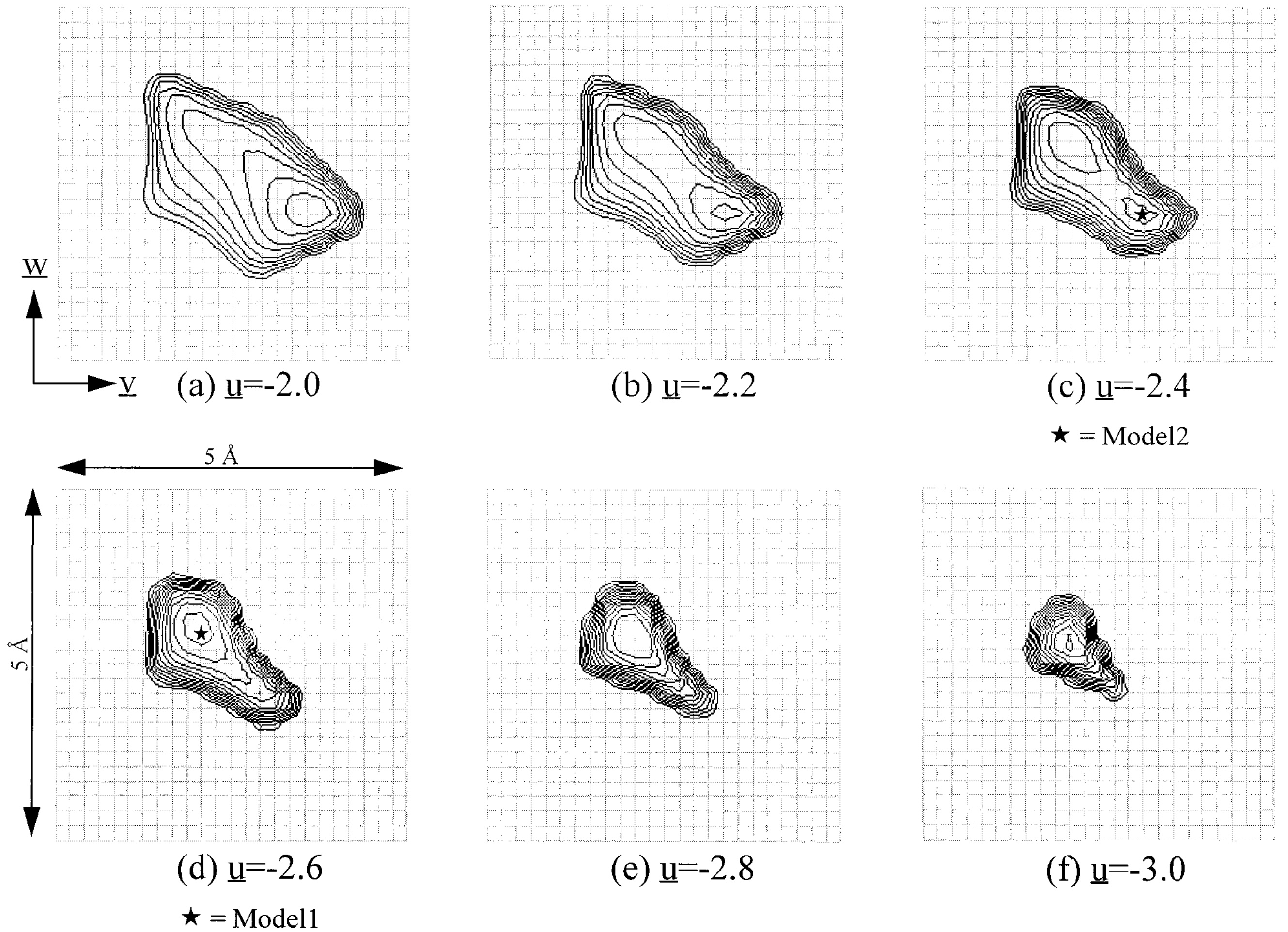

Figure 2. Contour maps of ΔE lattice interfaces between $u = -2.0$ and -3.0. Each point corresponds to a 0.2 Å shift in v and w. Contours range from 0.0 (outside) to -3.5 kcal mol^{-1} (inside).

positions of the interface. This was achieved by defining three unit vectors: $\hat{\mathbf{u}}$ which is perpendicular to the twin plane and $\hat{\mathbf{v}}$ and $\hat{\mathbf{w}}$, two mutually perpendicular vectors within the twin plane. The twinned half of the lattice may be moved along these vectors with respect to the rest of the crystal. Each value of (u,v,w) defines a unique lattice, although the translational symmetry present in crystals will create repeats. Implicit in this model is the assumption that no molecular relaxation occurs at the interface and that there is negligible strain in the interfacial region. This assumption has been shown to work well for the solid−liquid interface, and the apparent ease of twin formation in saccharin suggests that lattice strain is minimal.

A Molecular Model of the Interface

By using the above methodology, the parameters of Scheraga et al.,[15] and charges generated by using the AM1[16] method within MOPAC,[17] contour maps of ΔE versus vertical (u) and lateral (v,w) positions have been constructed. The initial position ($u = 0$, $v = 0$, $w = 0$) is taken as the molecular coordinates generated by applying the twin operation through the origin of the unit cell. As a check of the methodology and in particular the applicability of the Scheraga forcefield to saccharin, two independent calculations were carried out. First, by using the crystal packer with Cerius^2 (ref 18) and treating the molecules as rigid units, a minimization was performed within the bounds of a fixed unit cell. This reproduced the known crystal structure. Second, in an untwinned crystal, half of the lattice was moved about the normal to $(10\bar{2})$ as described above with use of steps of 0.2 Å. This located a single low-energy minimum, again corresponding to the crystal structure. To carry out the twin-energy calculation a range of ±3 Å in steps of 0.5 Å was used for u and ranges of 20 Å in steps of 0.5 Å were used for v and w. More positive values of u increase the distance between the twinned and untwinned halves, more negative brings the two halves closer together. The most negative values of ΔE (and hence most favorable lattices) were found with values of u of -2, -2.5, and -3 Å, so calculations were repeated at $u = -2.0, -2.2, -2.4, -2.6, -2.8$, and -3.0 Å with v and w intervals of 0.2 Å about a 5 Å × 5 Å range close to the only minima found on each level. Contour maps representing such plots may be seen in Figure 2. Each point on a map corresponds to a complete lattice and there are 625 such lattices calculated for each map (at v and w intervals of 0.2 Å), hence 625 configurations which obey the twin operation. The shallow contours at $u = -2.0$ and -2.2 indicate the ease of approach at the interface, higher values of u show the contours becoming tighter implying that the energy is steeper, and the relatively small area indicating that very few plausible models exist for the interaction across the twin interface.

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Two positions of local minima were found with use of a grid density of 0.2 Å, each indicating the possibility of 3-centered hydrogen-bond formation: model 1 at ($u = -2.6$, $v = 8.8$, $w = 11.8$), which is equivalent to shifts along the unit cell axes of $0.05a$, $0.71b$, and $0.50c$, and model 2 at ($u = -2.4$, $v = 9.8$, $w = 11.0$), which is equivalent to shifts along the unit cell axes of $0.05a$, $0.59b$, and $0.45c$. The two models lie 1.02 Å apart at each end of the low-energy channel seen in Figure 2, parts c and d, which corresponds to low-energy configurations of the 3-center hydrogen bond. The existence of this channel indicates the ease of distortion of this bond. Models 1 and 2, although differing in lattice space by 1 Å, essentially have the same geometry—their differences lying in a slight distortion of the distance and angle of the extra hydrogen bond. No other close contacts are observed, although it should be noted that the force field used does not explicitly include $-\mathrm{C-H \cdots O=}$ interactions.

Figure 3 provides a schematic view of the twin interface in which saccharin dimer pairs have been drawn as *bow-ties* in order to simplify the visualization. A projection of the single-crystal structure normal to the twin plane, $(10\bar{2})$, is seen in Figure 3a, while Figure 3b shows the superposition of layers on moving through the twinned interface. Thus if Layer 3 were in the plane of the paper then Layer 2 and Layer 1 would be stacked above it to form a single crystal. In creating the twin the next layers become Twin Layer 1 and Twin Layer 2, respectively, by application of the reflection operation and the (u,v,w) shifts as defined above.

Figure 4, parts a and b, shows detailed orthogonal molecular projections of twinned and untwinned interfaces and at this level of detail the three-center hydrogen bond linking two saccharin hydrogen-bonded dimers across the twin plane is clear. This intermolecular interaction does not exist in the crystal structure of saccharin and is revealed by this modeling procedure as a likely driving force for twin formation, which for this interface configuration yields an additional stabilization of 7% of the calculated lattice energy. Figure 4c shows in more detail the configuration of this hydrogen bond. For dimers in the bulk crystal structure the H-bond distances ($-\mathrm{C=O \cdots H-N}-$) are 2.034 Å and the $\mathrm{N-H \cdots O}$ angle is 166.8°, while along the low-energy channel (Figure 2c) the new H-bond has a distance that ranges between 1.897 and 2.216 Å and an $\mathrm{N-H \cdots O}$ angle between 118.7° and 136.8°. For the geometry corresponding to model 1, the most favorable value of ΔE, a distance of 2.123 Å, and an angle of 128.4° are found. A survey of the geometries of three-center H bonds in crystal structures published by Taylor et al.[19] indicates that $-\mathrm{H \cdots O}-$ distances typically lie in the range 2.00 ± 0.15 Å with $-\mathrm{N-H \cdots O}-$ angles of 113 ± 16°. Given the approximate nature of such experimentally derived limits it is clear that they support the geometry for the new hydrogen bond suggested here (Figure 4c). This geometry also satisfies Jeffrey's definition of an asymmetrical hydrogen bond: [20] $r_1 < r_2 < 3$ Å ($r_1 = 2.034$ Å, $r_2 = 2.123$ Å); $q_1 > q_2 > 90°$ ($q_1 = 166.8°$, $q_2 = 128.4°$); $350° < q_1 + q_2 + \alpha < 360°$ ($\alpha = 63.5°$).

Discussion

This work has demonstrated the use of lattice energy calculations in exploring and defining the molecular configuration of a twin interface and suggests the basis of a generalized approach for a range of structured solid−solid interfaces which would ultimately aid the design and control of their physical and chemical properties. In the case of saccharin, explored here, the existence of an additional interfacial hydrogen bond has been revealed which is a likely driving force for the twinning process and explains why saccharin twins so readily.

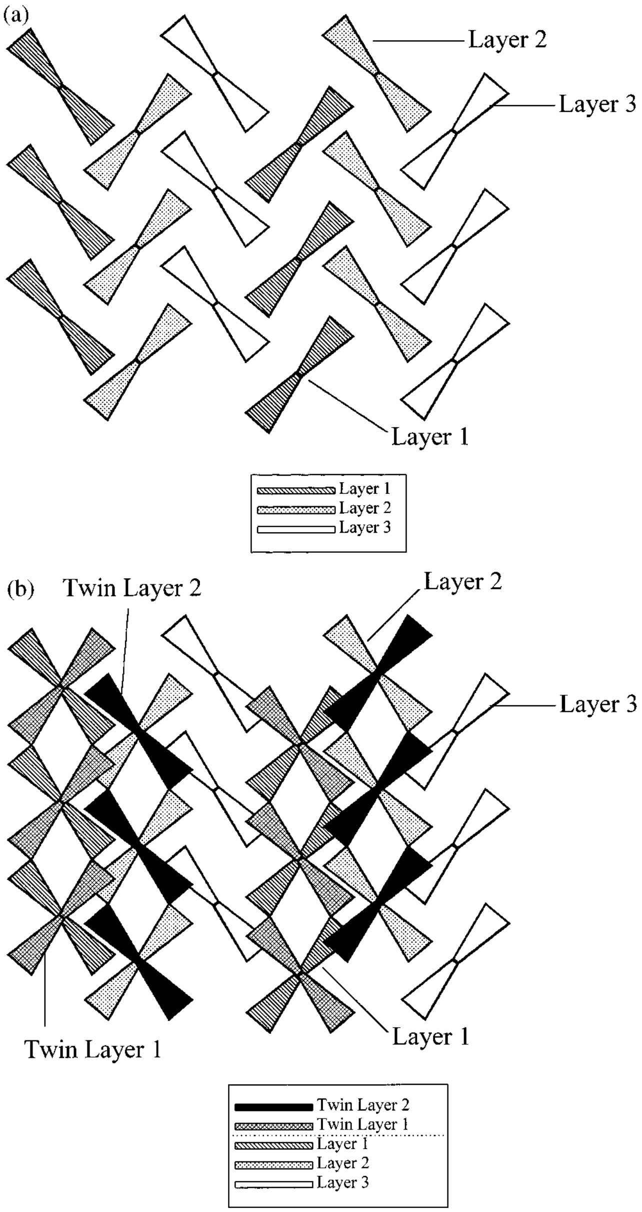

Figure 3. (a) Schematic "*bow-tie*" representation of the untwinned structure perpendicular to the $(10\bar{2})$ plane. The structure repeats after three layers. (b) Schematic "*bow-tie*" representation of the twinned structure perpendicular to the $(10\bar{2})$ plane. The twinned interface is in the plane of the paper with the untwinned layers behind and the twinned layers in front. Both twinned and untwinned structures repeat after three layers.

The additional experimental observations that in the case of saccharin the two halves of a twinned crystal are invariably of equal size and that lamellar twinning is absent allow some tentative comments to be made concerning molecular aggregation at the time of nucleation. Previous studies of impurity induced twinning have been interpreted to imply that the structure of the critical nucleus is identical with that of a mature crystal.[21] The data presented here appear to imply a more

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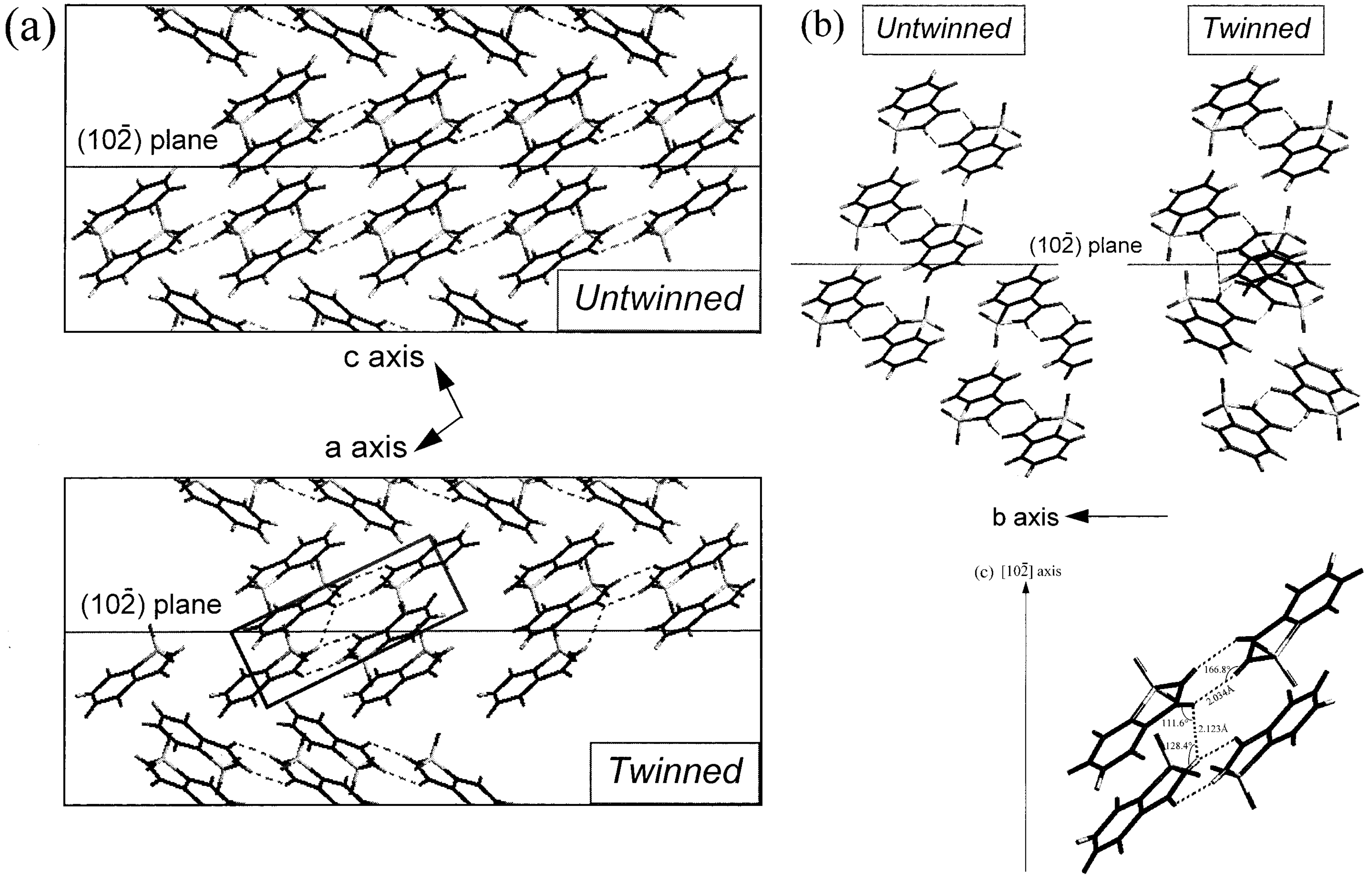

Figure 4. (a and b) Molecular visualization of the model 1 interface. (a) View perpendicular to the *ac* plane. [10$\bar{2}$] axis runs up the page. (b) View perpendicular to the (201) plane (perpendicular to part a). (c) Molecular configuration across the interface showing the three-centered hydrogen bond. Orientation is the same as in part a.

complex situation in the case of saccharin, since they suggest that the additional H bond found at the twin interface is only utilized at the time of nucleation. Subsequent twinning during growth would be unfavorable since in order to adopt the required molecular configuration (Figure 4) across the growing interface an incoming dimer pair would have to adopt a tilt angle of 49° to the $(10\bar{2})$ surface. This would be impossible due to significant steric repulsion with the sulfoxide groups of neighboring molecules in the surface. Thus these results suggest that in some systems the balance between symmetry, packing forces, and surface tension may mean that molecular aggregates present at the point of nucleation do not adopt the structure of a mature crystal.

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Supporting Information Available: A listing of the calculation of the twin plane by Weissenberg and 4-circle diffractometer (4 pages). See any current masthead page for ordering and Internet access instructions.

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