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Order and Disorder in Molecular Crystals: *trans*-Stilbene

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Recent refinements of the structure of *trans*-stilbene suggested the presence of disorder at only one of the two crystallographically independent sites of the unit cell. Calculations based on atom–atom intermolecular potentials have shown that this disorder is adequately described by a model in which some of the molecules at that site are misoriented in a manner which results in large positional changes for only a few of the atoms in each molecule. A technique has been developed for including the degree of misorientation into the lattice energy calculations and the results are compatible both with the preference for disorder at one site and with the degree of misorientation at that site as estimated from difference maps. The system was analysed at two temperatures (113 and 298 K). The calculations confirm that the probability of orientational disordering at low temperature is smaller than at high temperature and show that it is limited to about 20% in the latter case.

1. Introduction

The improving accuracy of X-ray crystallographic structure determinations and the increasing number of these studies carried out at low temperature have led to the discovery of disorder in crystals where none had previously been observed and have aided in providing data suitable for use in proposing models by which the previously observed or suspected disorder can be understood. In *trans*-stilbene (Robertson & Woodward, 1937) it now seems clear that positional disorder of a fairly simple type is present.

The structure has recently been refined at room temperature by two different groups (Finder, Newton & Allinger, 1974; Bernstein, 1975), and a statistical comparison of the results has been carried out (Bernstein, 1975). A low-temperature (−160 °C) structure refinement was carried out by a third group (Hoekstra, Meertens & Vos, 1975).

The latter three investigations followed structural and theoretical studies on mixed crystals of stilbene and diphenylmercury (Frank, Myasnikova & Kitaigorodskii, 1971) and the closely related tolane–diphenylmercury system (Samarskaya, Myasnikova & Kitaigorodskii, 1969).

The points relevant to the present paper which emerged from these crystallographic studies are:

(1) *trans*-Stilbene crystallizes in the monoclinic system† with two independent half molecules comprising the asymmetric unit, each molecule lying on a crystallographic centre of inversion (Fig. 1).

(2) The two crystallographic sites are not equivalent with respect to the degree of substitution of diphenylmercury in the stilbene lattice (Frank *et al.*, 1971). One site A is virtually exclusively preferred over the other B

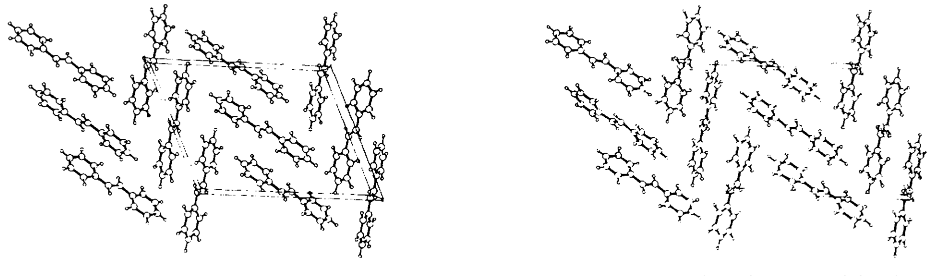

Fig. 1. Stereo view of the crystal structure of *trans*-stilbene along b; c is horizontal. Site A is at the origin, site B at $0,0,\frac{1}{2}$.

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† Various authors have chosen different unit cells, either in $P2_1/c$ or $P2_1/a$, which may lead to some confusion in comparing results. Our cell is that originally chosen by Robertson & Woodward (1937) and employed also by Frank *et al.* (1971) and Bernstein (1975). The results, of course, are independent of the choice of cell.

and lattice energy calculations based on 'fairly crude assumptions' (Frank *et al.*, 1971) indicate that the preferred site for substitution is lower in energy by *ca* 2·2 kcal/mole than the second.

(3) The room-temperature refinements yield a nearly normal —C=C— bond length for the molecule at site *A* [1·318 (3) Å, Finder *et al.*, 1974; 1·313 (4) Å, Bernstein, 1975]. At the second site the bond length is significantly shorter [1·295 (6) and 1·288 (6) Å, respectively]. Geometrical features of the phenyl rings are normal for both molecules in all refinements.

(4) At low temperature both the —C=C— bonds are longer [1·341 (2), 1·331 (3) Å] than at room temperature (Hoekstra *et al.*, 1975) and differ from each other by 3·5 standard deviations. Other features show no significant change on going to low temperature. Final difference maps in the region of the two molecules are different. For the molecule at the energetically preferred site, the map is featureless within the significance of the experiment, while at the second site there is evidence for a small degree of disorder. The mode of disorder suggested by the difference map is reminiscent of that first proposed by Brown (1966*a*) for *p*-azotoluene and noted as well in *trans*-azobenzene (Brown, 1966*b*) (which is isostructural with *trans*-stilbene) and in one of the polymorphs of *N*-(*p*-methylbenzylidene)-*p*-methylaniline (Bernstein, Bar & Christensen, 1976). This mode of orientational disorder at the second site could account for the shortening of the —C=C— length in the room-temperature studies.

Our aim in the work described in this paper was twofold:

(1) To test, with the aid of crystal lattice energy calculations, the validity of the above model for disordering exclusively at the *B* site.

(2) To test simultaneously the applicability of this type of calculation to physical situations governed by relatively small energy differences.

2. Calculation procedure

The probability of disorder in the stilbene crystal was estimated by comparison of the potential (lattice) energy of the ordered crystal structure with those of structures comprising various modes of orientational disorder suggested by the X-ray data. The case was analysed both for room- (Bernstein, 1975) and low- (Hoekstra *et al.*, 1975) temperature structures. The cell parameters (for $P2_1/a$) were used as given in the original papers: $a = 12{\cdot}382$, $b = 5{\cdot}720$, $c = 15{\cdot}936$ Å, $\beta = 114{\cdot}15°$ for room temperature (Bernstein, 1975) and $a = 12{\cdot}287$, $b = 5{\cdot}660$, $c = 15{\cdot}478$ Å, $\beta = 112{\cdot}03°$ for −160°C (Hoekstra *et al.*, 1975).*

In all calculations we used C—H lengths of 1·08 Å. Coordinates for the H atoms were generated assuming sp^2 hybridization of the C atoms. We considered the molecular dimensions obtained at the preferred site by Hoekstra *et al.* (1975) to be the best available to date and the coordinates of the C atoms in the molecular axial system were used to generate coordinates for the various disordered models. The details of this procedure are: The best plane for the fourteen C atoms of molecule at site *A* in the structure of Hoekstra *et al.* (the β molecule in their nomenclature) was calculated and coordinates were obtained in the inertial axial system shown in Fig. 2. The *L* axis is that with the smallest moment of inertia while the largest moment is about *N*. The signs of the *M* coordinates were reversed and the *L*, −*M*, *N* coordinates were transformed to fractional coordinates in the crystal structure in question with a transformation matrix obtained from a similar calculation on the crystal and molecular site in question. This procedure implies that a 'disordered' molecule is simply one which is misoriented at its crystal site. When we chose not to use a disordered molecule the *L*, *M*, *N* coordinates of the Hoekstra *et al.* molecule were simply transformed to fractional coordinates in the crystal structure in question.

In all calculations of the crystal potential energy the atom–atom potential method (Kitaigorodsky, 1973) was employed. The interatomic non-bonded interaction energy curves were expressed in the Buckingham form, $\varphi = -A/r^6 + B\exp(-\alpha r)$. Parameters for C···C, C···H and H···H potential functions were taken from Mirskaya, Kozlova & Bereznitskaya (1974) and are

Table 1. *Parameters of the potential energy curves used in the calculations*

Atom pairs	$A\left(\frac{\text{kcal}}{\text{mole}}\text{Å}^6\right)$	$B\left(\frac{\text{kcal}}{\text{mole}}\right)$	$\alpha\,(\text{Å}^{-1})$
C···C	421	$7{\cdot}16\times10^4$	3·68
C···H	118	$1{\cdot}86\times10^4$	3·94
H···H	29	$4{\cdot}90\times10^3$	4·29

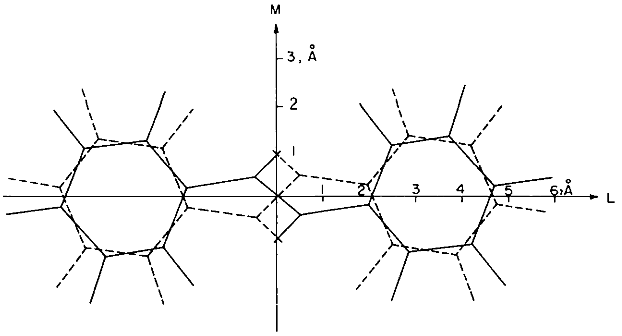

Fig. 2. Disordering model in the right-handed molecular inertial axial system. Normal molecule – solid lines, misoriented one – dashed lines.

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* Although the cells for the two temperatures are both in $P2_1/a$ the choice of the *c* axis is different: hence the differences in this axis and β between the two structures. Other differences are due to temperature effects.

given in Table 1 [see Mirsky (1976) for a discussion of transferability of these potential parameters]. Computations were carried out with *PCK*6 (Williams, 1972) and a locally written program for the interaction of a pair of crystallographically non-equivalent molecules.

The lattice energy of the stilbene crystal was calculated as half the sum of the lattice energy per two independent molecules in the unit cell, *i.e.*

$$U = \tfrac{1}{2}(U_A + U_B),$$

where U_A is the energy of interaction of the molecule at the A site with all its surroundings (including molecules at the B site) and *vice versa* for U_B.

For the structures at the two temperatures the lattice energies were first calculated at the experimental points, from experimental cell parameters and atomic coordinates. Then the lattice energy was minimized with respect to the molecular orientations at fixed cell geometry yielding the theoretical equilibrium structures.

Next the disordered molecules were placed exclusively first at site A and then at site B, and the same calculational procedure was repeated. The results thus obtained yield the crystal potential energy when all the molecules at the A site or all the molecules at the B site are in the wrong orientation (this case corresponds to a degree of misorientation of one). They yield as well a comparison of the energetic 'tolerance' of each site for the misorientation. The results of these calculations (next section) clearly suggest that misorientation at site B is significantly preferred over misorientation at site A.

For site B we then investigated the probability of partial disordering by calculating the dependence of the lattice energy on the fraction of misorientation (from 0 to 1). The partial disorder was introduced as follows:

(1) At the ordered site of the unit cell all the atoms of the first independent molecule occupied their experimental positions with a probability of 1.

(2) At the second site, two molecules (both the normal and the misoriented ones) were assigned probabilities for sharing the space available at the site, the probabilities being proportional to the fraction of misorientation. Thus, if n is the probability of occupying the normal position, $(1-n)$ is the corresponding value for the misoriented one. Accordingly, the energy terms for the interaction of the 'whole' atoms at the ordered site with those at the second site were reduced by factors of n and $(1-n)$ in all possible combinations.

Let us denote the C and H atoms of the molecule at the ordered site as C and H, as usual, and the atoms at the second site as nC and nH for the normal molecule and $(1-n)$C and $(1-n)$H for the misoriented one. Thus, it is as if we have six different kinds of atoms instead of two, which brings us to 21 potential-energy curves in place of the three basic ones, $\varphi_{\rm CC}$, $\varphi_{\rm CH}$ and $\varphi_{\rm HH}$:

$$\begin{array}{cccccc}
\varphi_{\rm CC} & \varphi_{\rm CH} & n\varphi_{\rm CC} & n\varphi_{\rm CH} & (1-n)\varphi_{\rm CC} & (1-n)\varphi_{\rm CH} \\
 & \varphi_{\rm HH} & n\varphi_{\rm CH} & n\varphi_{\rm HH} & (1-n)\varphi_{\rm CH} & (1-n)\varphi_{\rm HH} \\
 & & n^2\varphi_{\rm CC} & n^2\varphi_{\rm CH} & n(1-n)\varphi_{\rm CC} & n(1-n)\varphi_{\rm CH} \\
 & & & n^2\varphi_{\rm HH} & n(1-n)\varphi_{\rm HC} & n(1-n)\varphi_{\rm HH} \\
 & & & & (1-n)^2\varphi_{\rm CC} & (1-n)^2\varphi_{\rm CH} \\
 & & & & & (1-n)^2\varphi_{\rm HH}.
\end{array}$$

The use of this set of potentials is equivalent to the use of various combinations of the reducing factors n and $(1-n)$ in the corresponding lattice energy terms. In all other respects the calculation procedure for the partially disordered crystal was the same as for the ordered ones (degree of misorientation = 0,1). A similar approach of superimposing two molecules at one crystal site was employed (Mirsky, 1976) for consideration of orientational disordering in the cubic phase of adamantane, and served as one possible model of disorder in crystalline anthrone (Reynolds, 1975).

3. Results

For the purposes of the present study relative but not absolute values of the differences between the lattice energies of various packing patterns in the same unit cell are considered. Nevertheless, to check that the results of our calculations are reasonable not only qualitatively, but also quantitatively, we compare our calculated lattice energies to the heat of sublimation of *trans*-stilbene. The reported value for the latter is 23·7 ± $0{\cdot}1_9$ kcal/mole at 298 K (Morawetz, 1972). Our results for the theoretical equilibrium structures at 113 and 298 K are 23·6 and 23·0 kcal/mole, respectively, in good agreement with experiment.

The energy changes caused by the disordering at A and B sites of the crystal are shown in Fig. 3. The lowest energy levels correspond to the completely ordered structures at 113 and 298 K whereas the upper levels refer to the situations in which all the molecules at the sites A or B are disordered (misoriented).

Starting with the completely ordered structure and then introducing partial disorder in the B site, we find that the lattice energy increases gradually with increas-

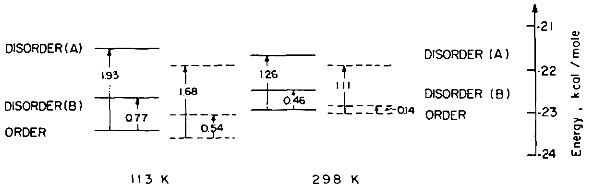

Fig. 3. Lattice energy levels corresponding to the complete order and two models of orientational disorder in the crystal structure. Differences in energy are in kcal/mole. Solid lines represent the energy levels for the experimental structures, the broken ones give the same after minimization (relaxation) with respect to molecular orientations.

ing fractional misorientation, as shown in Fig. 4 (solid line). When relaxation is allowed for every degree of disorder (that is the energy at every point is minimized with respect to molecular orientations) the 'energy *vs* fractional misorientation' curve changes its character (dashed line, Fig. 4). The minimization procedure yields changes in molecular orientations as well as in energy. The former are summarized in Fig. 5. Here θ_1 and θ_2 are, respectively, the angles of rotation of the molecule at the *A* site and of the joint molecule (ordered plus disordered) at the *B* site from the positions in the experimental structure to the equilibrium positions. These angles are calculated (*International Tables for X-ray Crystallography*, 1962) from the rotation matrices given by *PCK*6 (Williams, 1972).

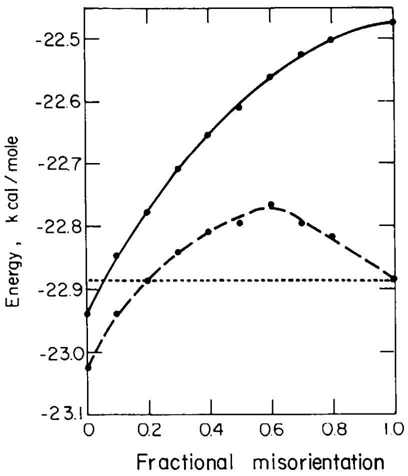

Fig. 4. Dependence of the lattice energy of *trans*-stilbene on the degree of the misorientation at the *B* site (at room temperature). Solid and dashed curves represent the energies before and after relaxation, respectively.

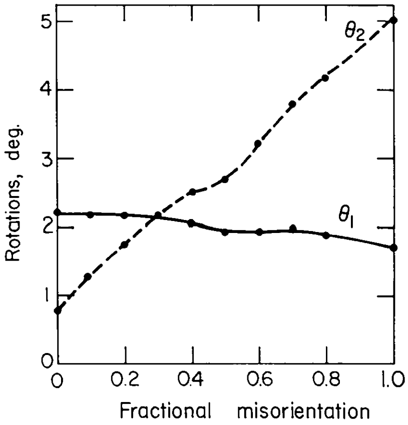

Fig. 5. Rotation of the molecules at the sites *A* (θ_1) and *B* (θ_2) from their experimentally determined positions to those resulting from the relaxation, as functions of the degree of the misorientation at the *B* site.

4. Discussion

The results of calculations for complete misorientation at either of the two independent crystal sites (Fig. 3) show that one of them, namely the *B* site [site 2 in the nomenclature of Bernstein (1975), the *α* site in that of Hoekstra *et al.*], is much less sensitive to the disordering than the other one. For example, at room temperature the increase in the lattice energy caused by disordering at this site is 0·46 kcal/mole before relaxation and 0·14 kcal/mole after relaxation (compare with $RT = 0{\cdot}6$ kcal/mole at 298 K), whereas disorder at the second site leads to the more significant increases in the lattice energy of 1·26 and 1·11 kcal/mole, respectively. This is in keeping with the conclusion of Finder *et al.* (1974) and of Hoekstra *et al.* (1975) that the extra maxima in the difference electron density map for the *B* molecule may be ascribed to disorder. The calculations confirm also that the disordering is less probable at low temperature since here the differences in energies for the ordered and disordered structures are more pronounced (in the best case the difference is 0·54 kcal/mole compared to the room-temperature value of 0·14 kcal/mole), and they are large in comparison with the thermal energy (at 113 K $RT = 0{\cdot}26$ kcal/mole).

Figs. 4 and 5 deal with the case of partial disordering at the *B* site at room temperature. Fig. 5 shows that with the increase of the degree of misorientation the molecule at the *A* site essentially does not change its orientation (*i.e.* it is more firmly bound at the lattice site) whereas the molecules at the *B* site adjust to the changing conditions more freely. However, the overall deviations from the initial orientations do not exceed 5°.

The dashed line in Fig. 4 provides an estimate of the possible limit of disorder at room temperature. The curve has a maximum showing that the greatest increase in the lattice energy occurs when about 60% of the molecules at the *B* site are misoriented. Such a degree of misorientation is hardly probable, however, as the same curve suggests that when the degree of misorientation reaches about 20%, the excess of the lattice energy over that for the ordered structure becomes the same as for complete misorientation at the *B* site (0·14 kcal/mole). The behaviour of this curve suggests that the degree of misorientation does not exceed 20%. This is consistent with the low-temperature crystallographic study (Hoekstra *et al.*, 1975) where the peak height at the position of the disordered C atom at the bridge on the final difference map is approximately 0·4 e Å^{-3} which is about 10% of the total electron density for the C atom.

5. Conclusions

The above calculations provide a quantitative test of the mechanism of disordering in stilbene which has been suggested by X-ray data. The results confirm that the proposed model of orientational disordering is quite plausible and may be responsible for the apparent shortening of the central —C=C— bond. All the atomic displacements due to the disorder, save those for the central C atoms, can apparently be accommodated by anisotropic temperature factors. As a result of the rectangular arrangement of the ordered and disordered central atoms, which places them all at least ~1 Å apart, the refinement tends to 'concentrate' the electron density towards the centre of the molecule, leading to an apparent shortening of the bond. It does not appear that other satisfactory models of orientational disordering in *trans*-stilbene can differ significantly from the one presented here.

The atom–atom potential method has been shown to be very convenient and useful for testing models for disordering in molecular crystals. The method is sensitive to small changes in crystal structure and yields results consistent with the crystallographic structural studies.

The calculation procedure, described here, appears to be quite general and should be applicable to any molecular crystal with orientational disorder.

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Analysis of Polytypic Structure with Stacking Faults on the Basis of X-ray Powder Patterns

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In this paper the possibility of applying powder diffraction patterns to determine polytypes and stacking sequences in disordered close-packed structures is discussed. It is shown that by using model structure analysis it is possible to establish some important features of the structure such as the presence of DS (Disordered Structure) and various simple polytypes.

Introduction

Polytypic structures with stacking faults are usually investigated on the basis of X-ray patterns obtained by the oscillating crystal method: Singer (1963), Ebina & Takahashi (1967), Farkas-Jahnke & Dornberger-Schiff (1970), Pałosz & Przedmojski (1976*a*,*b*). In earlier papers (Pałosz & Przedmojski, 1976*a*,*b*; Pałosz, B., 1977) an application of a structural-model method to the analysis of crystals with stacking faults was discussed. In that method the structure determination was based on the comparison of (1) experimental intensity curves, obtained by photometering of 10.*L* reflexions from oscillating crystal patterns, with (2) calculated theoretical curves. The theoretical curves were obtained on the basis of computed intensities for the 10.*L* re-