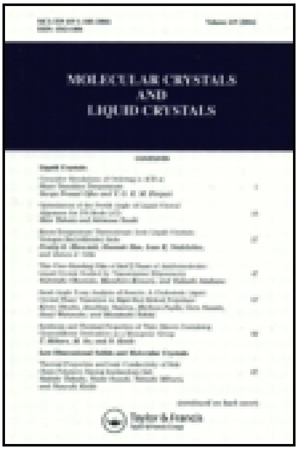

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Use of Atom-Atom Potentials in the Determination of Organic Crystal Structures

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Use of Atom-Atom Potentials in the Determination of Organic Crystal Structures

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The use of atom–atom potentials in the computation of crystal structures of organic molecular crystals has seen wider applications in recent years after the pioneering work of Kitaigorodsky and Williams. Our experience shows that with a prior knowledge of all or at least some of the lattice dimensions, space group and molecular structure, the packing calculations enable one to solve the crystal structure with reasonable accuracy. We report the successful solution of the crystal structures of the polymorphs of pyrene and 1,5 dichloro anthracene by this approach. The role of orientational point defects in the solid state photodimerization of the latter is also discussed.

PYRENE

Crystals of pyrene, upon cooling to below 120 K, generally shatter, probably due to a phase transition in which the $P2_1/a$ space group of the room temperature form[1] is retained. The luminescence[2] and Raman scattering[3] of the solid undergoes major changes during the phase transformation, the mechanism of which is obscure. Our understanding of the photophysical properties of pyrene is hindered by the fact that it has been hitherto impossible to determine the structure of the low temperature phase, though the unit cell dimensions have recently been obtained by x-ray methods[4] and electron diffraction.[5]

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The lattice energies were calculated using the intermolecular potential[6] function:

$$U = \tfrac{1}{2}\sum [B\exp(-Cr) - Ar^{-6}]$$

the lattice summation being carried out for $r \leqslant 8$ Å. For pyrene I the value obtained for U was -94.2 kJ mole^{-1}, in good agreement with the reported heat of sublimation,[7] -94.5 kJ mole^{-1}. The increase of 0.7 Å in b during the phase transition is accounted for by rotation of the molecules about the c-axis—the c-axis remaining unchanged during the transition. Rotation of the input co-ordinates of the pyrene molecule about the c-axis lead to a new low energy structure with no very short intermolecular contacts. Calculations, with initial co-ordinates describing angles of rotation between 15 and 30° for the pyrene molecule and different starting values for molecular centres were carried out and it was found that after successive steps of refinement, all such initial co-ordinates converged to the same structure with a lattice energy of approximately 98.3 kJ mole^{-1}. In both structures the molecules are in pairs (as predicted from excimer emission studies),[8] with the overlap increasing in the low temperature structure, the separation of the molecular pairs being 3.53 Å in pyrene I and 3.44 Å in pyrene II.

1,5 DICHLORO ANTHRACENE

In solution at room temperature 1,5 dichloro anthracene dimerizes[9] under u.v. irradiation to give a 40:60 mixture of the head-to-head (h–h) and head-to-tail (h–t) dimers. In the solid state, however, the nature of the product is dependent upon the polymorph within which photodimerization occurs. The monoclinic form ($A2/a$; $a = 19.00$, $b = 4.05$, $c = 14.4$ Å, $\beta = 95.11°$; $Z = 4$; grown from vapour) yields only the head-to-head dimer, not unexpectedly from the known crystal structure and the tenets of the topochemical preformation theory: neighbouring molecules are separated by a distance of $b = 4.05$ Å typical of the separations that are conducive for photoreactivity in the solid state. The triclinic form ($P\bar{1}$; $a = 7.20$, $b = 9.75$, $c = 4.00$ Å, $\alpha = 98°$, $\beta = 101°$, $\gamma = 84°$; $Z = 1$; grown from Xylene solutions), on the other hand generates, upon u.v. irradiation, 80% h–h and 20% h–t dimer and the question to be answered is how the h–t product is formed.

The crystal structure of the triclinic form has not yet been determined by diffraction methods. It may, however, be arrived at by computation using the procedure based on parameterized potentials.[10] To check the reliability of the calculated crystal structure, the monoclinic structure was also computed, using the same C . . . C[6], Cl . . . Cl[11] etc. parameters (in the expression for interatomic potentials) and was found to agree well with that determined experimentally.[12] The lattice energies computed for the polymorphic forms were −121 kJ/mole for the monoclinic and −130 kJ/mole for the triclinic phase. It transpires that neighbouring molecules in the triclinic phase are also partially overlapped (separation distance $c = 4.00$ Å) and arranged in stacks as in the monoclinic variant and one would, therefore, expect this polymorph to yield the h–h photodimer and not a mixture of the two possible products.

A reasonable suggestion, which certainly seems valid in other anthracenic systems,[13,14] is that linear or planar faults of an approximate kind may bring juxtaposed molecules into a state of mutual orientation that is not possible in the perfect structure. Closer examination of the triclinic crystal structure shows that, for intrinsic crystallographic reasons, it is impossible to formulate any slip system and displacement vector that would bring neighbouring molecules at planar, or linear faults into a potential h–t disposition. How therefore, is it possible for a h–t registry to be established?

Orientational point defects in which the defect molecule is rotated in plane, first discussed by Thomas and Williams[15] are of no consequence in this regard. But suppose that, during crystal growth, some molecules had been laid down anomalously such that a flip by an angle π, had occurred about an axis parallel to the length of the anthracene moiety and perpendicular to the stack axis, this operation would generate a potential h–t situation.

To test the reasonableness of this proposition we have estimated the extra energy endowed to the lattice by imposing such a point defect into both the triclinic and monoclinic forms. The calculations were carried out assuming a cluster of 26–30 molecules in the defect lattice. Eight to ten molecules including the defect were allowed rotational and translational degrees of freedom. The defect formation energy was found to be 4 kJ/mole in the triclinic structure and 100 kJ/mole in the monoclinic variant.

Significantly the energy of formation of the orientational point defect is very much less in the triclinic than in the monoclinic form. We conclude that this is the reason for the greater propensity of h–t dimer formation in the crystals of lower symmetry. If our interpretation is indeed correct it follows that the precise ratio of h–h to h–t dimers should be dependent upon crystal history.

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