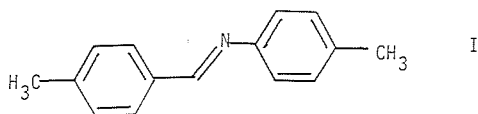


**17.6-04** CONFORMATIONAL POLYMORPHISM. CRYSTAL ENERGETICS OF A TRIMORPHIC SYSTEM INCLUDING DISORDER. By I. Bar, and J. Bernstein, Department of Chemistry, Ben-Gurion University of The Negev, Beersheva, Israel.

Lattice energy minimization techniques have been applied to study the influence of crystal forces on molecular conformation. With the inclusion of orientational and positional disorder we have extended the methodology developed previously (Bernstein & Hagler, J. Am. Chem. Soc. (1978) 100, 673; *ibid.*, 6349), which takes advantage of the phenomenon of conformational polymorphism - the existence of multiple crystal forms of a molecule exhibiting significantly different conformations. The compound chosen for this study is the trimorphic I.



Form I exhibits positional disorder with an energetically unfavorable planar conformation. A similar conformation is found in Form III with orientational as well as positional disorder. Form II is ordered with a minimum energy molecular conformation.

Lattice energy calculations were carried out employing three different potential functions; all yield lowest energies (most stable) for Form I, highest for Form II and intermediate for Form III. Minimized lattice energies were analyzed in terms of partial atomic energy contributions to the total energy. The relative energetic contributions of various groups of atoms to the total energy is the same for the three polymorphs, indicating that the energetic environments of these groups is similar in the three forms. The stability of Form I with respect to Form II is due to the relatively favorable environment of the aniline group and the bridge, while the stability of Form III relative to Form II is due to favorable contributions of the atoms on the bridge and those in the benzylidene group. The energetic role of disorder is obtained explicitly from the calculations.

**17.6-05** CALCULATING ATOMIC DENSITY MAPS WITHOUT X-RAYS OR NEUTRONS. I.D. Brown, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada, L8S 4M1.

It is possible to use a knowledge of crystal chemistry to find the positions of the cations in a crystal when only the anion positions are known. K. Waltersson (*Acta Cryst.* A34, 901 (1978)) has shown that this can conveniently be done using valence maps,  $V$ , where

$$V(xyz) = \prod_i S_i(xyz)$$

$S_i$  is the valence (or strength) of a bond between the cation placed hypothetically at  $(xyz)$  and the  $i^{\text{th}}$  anion neighbour.  $S_i$  can be calculated from the bond distance,  $R_i$ , using  $S_i = (R_i/R_0)^{-N}$  where  $R_0$  and  $N$  are tabulated constants (Brown, I.D. and Wu, K.K., *Acta Cryst.* B32, 1957 (1976)). The correct positions for the cations are ones in which  $V$  has a value equal to the valence of the cation. In many cases this position is at a minimum in the  $V$  map which therefore resembles a potential energy diagram for the cation. An alternative is to plot the map

$$A(xyz) = [V(xyz)]^{-M}$$

in which the atomic positions are now at maxima. With  $M = 16$  the  $A$  map resembles an atomic or electron density difference map. Like difference maps,  $A$  maps can be used to locate atoms, and to predict thermal anisotropy and disorder.  $V$  and  $A$  maps can also be used to explore the crystal chemical implications of models of disordered systems, in particular the local relaxation that occurs in such systems. In the illustrations below the  $A$  maps (left hand side) show the density of Ag atoms in  $\text{Ag}_{16}\text{I}_{12}\text{P}_2\text{O}_7$  (top) and  $\alpha\text{-AgI}$  (bottom). For comparison the right hand side shows the corresponding difference synthesis. (The neutron difference map for  $\alpha\text{-AgI}$  is taken from Cava, R.J., Reidinger, F. and Wueesch, B.J., *Solid State Comm.*, 24, 411 (1977).)

