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LETTER TO THE EDITOR

POTENTIAL ENERGY STUDY OF THE DISORDERED STRUCTURE OF 2,3-DICHLORO-6,7-DIMETHYL ANTHRACENE USING NON-BONDED INTERATOMIC POTENTIALS

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In crystalline 2,3-dichloro-6,7-dimethyl anthracene there are two molecular orientations, related to each other through inversion. Potential energy computations employing semiempirical potentials and the atom-atom approach were carried out to justify both the disordered crystal structures (I) Sublimation grown and (II) Solution grown of 2,3-dichloro-6,7-dimethyl anthracene (DC DMA). The two nearly equal potential wells separated by an angle of 180° in both the potential energy vs. angle of rotation curves clearly explain the two configurations and orientational disorder of the molecules in the lattice.

Welberry et al.[1] solved the crystal structures of the two species of DCDMA obtained from sublimation and from solution. The two types of crystals were obtained by slow evaporation of $CHCl_3$ mixture of the compound. Both the crystals are monoclinic ($P\,2_1/C$; $Z = 4$) having slight variations in the crystal data. The molecules are nearly planar. A detailed study of the diffuse scattering of X-rays and structure solution by X-ray method reveal that the 2, 3, 6, 7 substituents (as labelled in figure) show disorder of Cl-atoms and CH_3-groups having different

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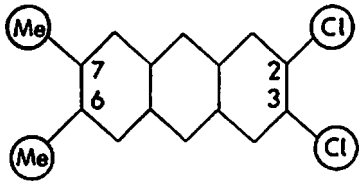

2,3 - Dichloro - 6,7 - Dimethyl Anthracene ($C_{16}H_{12}Cl_2$)
(Solution grown)

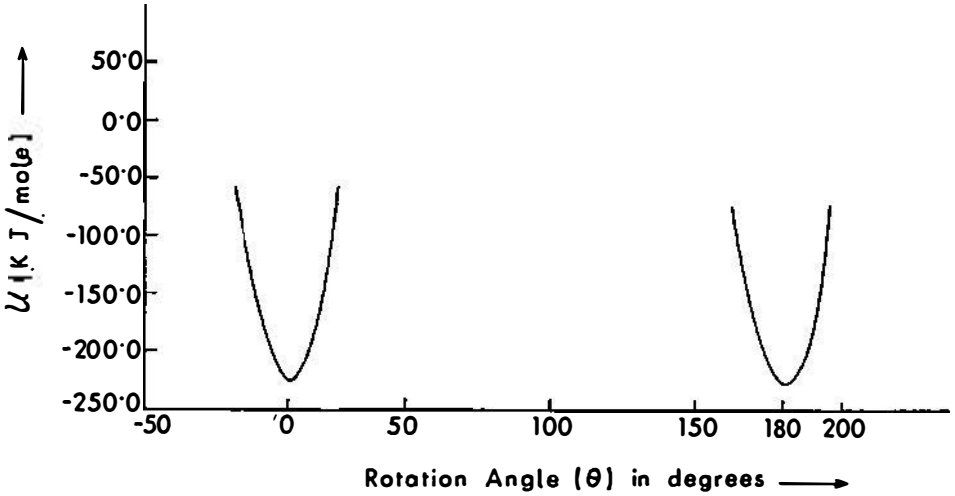

Fig. 1. Potential curve calculated by rotating the DCDMA molecule (type I) about its plane normal

sites occupancy. For (I) the 2,3 sites are occupied on average by 60% Cl and 40% methyl and vice versa for 6,7, while for (II) the values are 80% Cl and 20% methyl. This type of disorder is known as orientational disorder and is possible only when the two species exchanging their positions are similar in size. This means that even in the presence of various intermolecular forces such types of molecular rearrangements are thermally possible. This we have tried to show here by considering the potential energy curve of DCDMA.

It is assumed that the intermolecular interactions are pair-wise additive and that they can be described as nonbounded interactions between the constituent atoms; this is the characteristic feature of the atom-atom approach. The non-bounded inter-atomic potentials Φ_{ij} were expressed in the modified Buckingham or (6-exp) form (Williams 1969)[2)]

$$\Phi_{ij} = -A/r_{ij}^6 + B \exp(-Cr_{ij})$$

where r_{ij} is the non-bounded interatomic distance between atoms i and j of different molecules and A, B, C are parameters depending upon the atoms concerned.

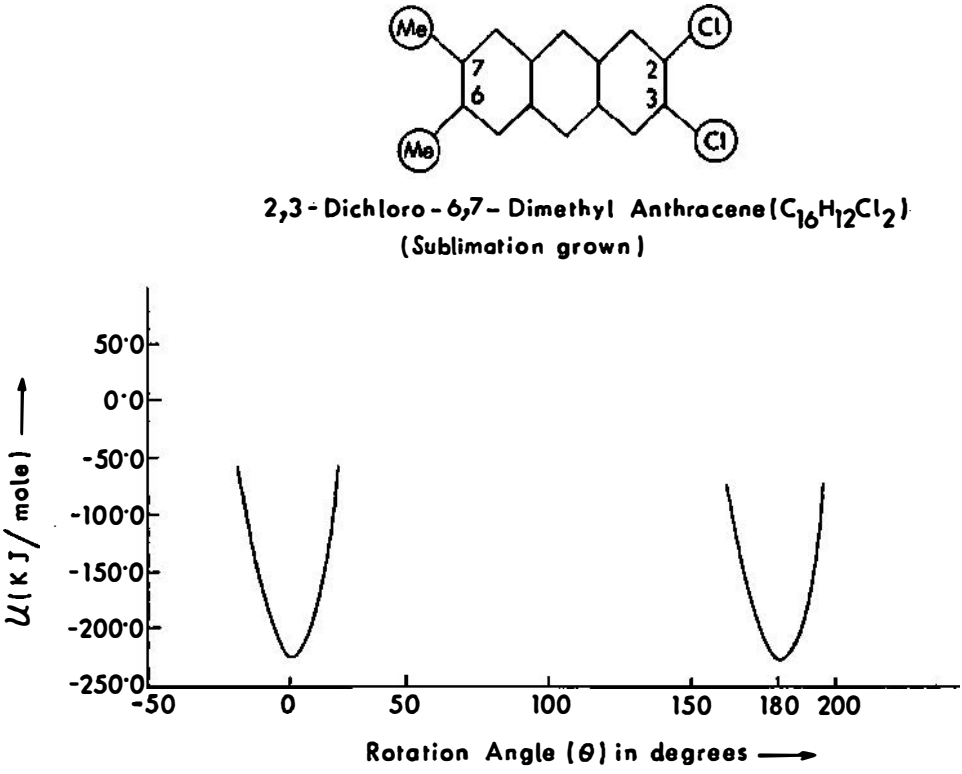

Fig. 2. Potential curve calculated by rotating the DCDMA molecule (type II) about its plane normal.

The crystal potential energy is expressed as

$$U = \frac{1}{2} \sum_i \sum_j \Phi_{ij}$$

where the summation involves all distances between atoms of one molecule and all the atoms of surrounding molecules. At 0 K and neglecting zero-point energy, this quantity must be a minimum for the equilibrium structure of a perfect crystal. We have not taken into account the small electrostatic energy contribution to the total lattice energy (Kitaigorodskii 1973)[3]. The parameters for atom-atom potential function used in this work are those of Williams et al. 1977[4] for the C.....C, C.....H and H.....H interactions. These parameters are selected because they are reliable and transferable to any molecular system containing carbon and hydrogen (a conclusion drawn by Criado et al. 1988[5] from lattice dynamical comparison). Cl.....Cl and Cl.....C interactions from L. Y. Hsu et al. 1980[6]. These parameters are also reliable and transferable Williams 1985[7]. Additional heteronuclear interactions are parametrized by taking the geometrical mean of the relevant homonuclear interaction parameters.

The intermolecular energy U (KJ/mole) of DCDMA was evaluated using our program of lattice energy calculation (Talapatra et al. 1981)[8]. Assuming all other surrounding molecules are stationary, the DCDMA molecule (as given by X-ray data) is rotated at an interval of 10 degrees about its best plane normal passing through the centre of the molecule (i. e. the centre of the anthracene ring). The summation radius is kept fixed at 10^{-9} m. The potential energy (U) vs. angle of rotation (Θ) curve is drawn, as shown in figures. The curve reveals some interesting features.

The DCDMA molecule has no two hold axis of symmetry about its plane normal. But the appearance of two nearly identical potential wells separated by an angle of 180° clearly indicates the presence of two configurations of the molecule in the lattice. The higher occupancy molecule corresponds to the potential well at 0° while the lower occupancy molecule i. e. the reversed molecule corresponds to the well at 180°. The discontinuities in the curves are due to short contacts (and hence high positive value of energy) between atoms. Otherwise the two P. E. curves are identical in all respects.

In crystal lattice the size and shape of individual atom are strictly governed by the intermolecular forces. In case of electronegative elements polar flattening occurs (Nyberg et al. 1985)[9]. But in the present structural study by Welberry et al.[1] the authors were not able to resolve the Cl and C (methyl) at the disordered sites so that an average atomic positions had been refined. Since energy calculation requires an exact atomic position in the lattice, we refrain from commenting anything from energy standpoint regarding the non-sphericity of Cl-atom and its possible influence on packing. But (as a first approximation) Kitaigorodskii 1973[3] has deduced that the volume occupied by Cl-atom $\approx 2.1 \times 10^{-10}$ m and that occupied by CH_3-group $\approx 2.0 \times 10^{-10}$ m. Thus from volume consideration also we can conclude that owing to their similar size the two species at the two ends of the molecule interchanged their places at random in the lattice without appreciable energy difference (as shown in figures). This energy which is of thermal origin can easily be obtained from the room temperature. The internal rotation of methyl H-atoms plays a dominant part in packing. For (I) at 2,3-positions the methyl groups orient themselves in such a fashion that Cl/Me occupancy becomes 60% and 40% and vice versa for 6,7, while for (II) the orientation of methyl groups is such that the values are 80% Cl and 20% methyl (as found from difference map), respectively.

Similar results were obtained from the study of indole, 1 : 1 complex of indole with S-trinitobenzene (Talapatra et al. 1984)[10] and p-iodotolune (Talapatra et al. 1987)[11] and 9-chloro 10-methyl anthracene[12] using the same program.

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IZUČAVANJE ENERGIJE REŠETKE U NEUREĐENOJ STRUKTURI 2,3-DIKLORO-6,7-DIMETIL ANTRACENA POMOĆU ATOM-ATOM MEĐUMOLEKULARNOG POTENCIJALA

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U kristalu 2,3-dikloro-6,7-dimetil antracena postoje dvije molekularne orijentacije povezane međusobno centrom inverzije. Račun energije rešetke uz upotrebu atom-atom potencijala proveden je da pokaže da su dvije neuređene strukture (I i II) energetski vrlo bliske.