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## LETTER TO THE EDITOR

# A study of the disordered structure of 9-chloro-10-methylanthracene using non-bonded interatomic potentials

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**Abstract.** Two molecular orientations, related to each other through inversion, are possible in crystalline 9-chloro-10-methylanthracene. Potential energy computations employing semi-empirical potentials and the atom–atom approach were carried out to justify the disorder crystal structure of 9-chloro-10-methylanthracene (CMA). The presence of two nearly equal potential wells separated by an angle  $180^\circ$  in the curve of energy versus rotation angle clearly confirms the two configurations and orientational disorder of the molecule in the lattice.

Measurement of the x-ray diffraction (Raymond *et al* 1981) from a crystal of 9-chloro-10-methylanthracene (CMA) shows that there is a substantial degree of crystalline disorder (during growth) at room temperature. The Bragg scattering indicated the space group to be monoclinic ( $P2_1/c$ ,  $Z = 4$ ). The structure determination reveals that the CMA molecule is able to take up either of two orientations statistically throughout the crystal lattice. The determination further reveals that the two alternative orientations are not equally probable but for the site labelled Cl in figure 1 (i.e. position 9) the average occupancy is Cl atom 68% and methyl group 32% while for the site labelled Me (i.e. position 10) the percentages are reversed. This molecular orientational disordering is possible only when the two species (here Cl atom and  $\text{CH}_3$  group) exchanging their positions are similar in size. This means that even in the presence of various intermolecular forces such types of mutual orientations of neighbouring molecules are thermally possible. This we have tried to show here by considering the potential energy curve of CMA (Mukhopadhyay *et al* 1989).

It is assumed that the intermolecular interactions are pairwise additive and that they can be described as non-bonded interactions between the constituent atoms; this is the characteristic feature of the atom–atom approach. The non-bonded interatomic potentials  $\varphi_{ij}$  are expressed in the generalised Buckingham (6-exp) form (Giglio 1969):

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

where  $r_{ij}$  is the non-bonded interatomic distance between atoms  $i$  and  $j$  of different

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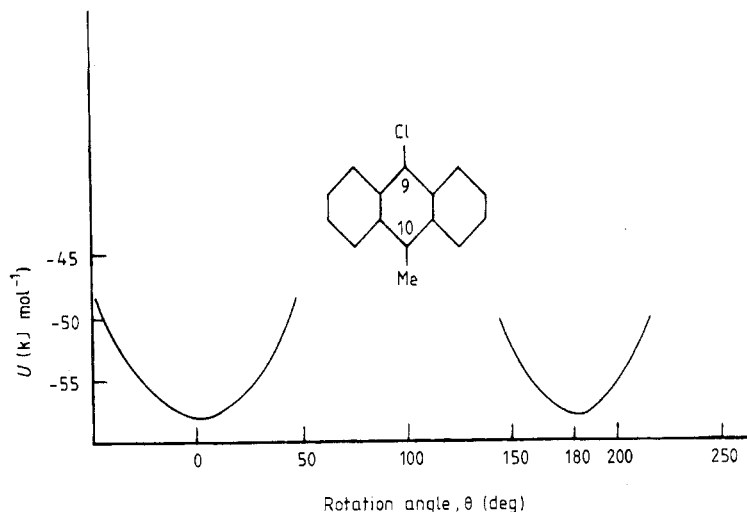


Figure 1. Potential curve calculated by rotating the CMA molecule about its plane normal.

molecules and  $A$ ,  $B$ ,  $C$  and  $D$  are parameters depending upon the atoms concerned. The crystal potential energy is expressed as

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

where the summation involves all distances between atoms of one molecule and all the atoms of surrounding molecules. We have not taken into account the small electrostatic energy contribution to the total lattice energy (Kitaigorodskii 1973). The parameters for atom–atom potential functions used in this work are those of Williams (1972) for the C.....C and those of Giglio (1969) for the CH<sub>3</sub>.....CH<sub>3</sub>, C.....CH<sub>3</sub> and Cl.....Cl interactions. These parameters are selected because their reliability has been assessed by a number of investigations (Williams 1972, Giglio and Liquori 1967, Shmueli and Goldberg 1973). The intermolecular energy  $U$  (kJ mol<sup>-1</sup>) of CMA was evaluated using our program of lattice energy calculation (Talapatra *et al* 1981). Assuming all other surrounding molecules are stationary, the CMA molecule (as given by x-ray data) is rotated by intervals of 10° 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 Å. A curve potential energy ( $U$ ) versus angle of rotation ( $\theta$ ) is drawn, as shown in figure 1. The curve reveals some interesting features.

The CMA molecule has no twofold 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°. Furthermore, Kitaigorodskii (1973) has deduced that the volume occupied by a Cl atom is 2.1 Å<sup>3</sup> and that occupied by CH<sub>3</sub> is 2.0 Å<sup>3</sup>. Thus from volume consideration we can also conclude that owing to their similar size the two species at the two ends of the molecule interchange their places at random in the lattice without appreciable energy difference. This energy, which is of thermal origin, can easily be obtained at room temperature.

Similar results have been obtained from studies of indole, 1:1 complex of indole with S-trinitrobenzene (Talapatra *et al* 1984) and p-indotoluene (Talapatra *et al* 1987) using the same program.

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