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Calculated Potential Barrier Heights and Dynamic Reorientation Process in Molecular Crystals: Dichlorodurene

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Barrier heights of reorientation are calculated from semiempirical potential functions between non-bonded atoms. Different dynamic processes are shown to be possible and values of the calculated barrier heights are in fair agreement with those given by N.M.R. Results of the X-ray analysis are also explained.

INTRODUCTION

Some successful attempts to find molecular conformation[1] and molecular packing in crystals have been made by means of semi-empirical potential functions describing Van der Waals interactions between non bonded atoms, and in a recent work Sanquer and Messager[2] have shown that intermolecular potential calculations could explain various physical properties of molecular crystals, namely benzene and hexamethylbenzene. Some attempts were made also to study disordered structures, like Chlorodurene[3] but phenomenon is complicated by the presence of four molecules in the unit cell. In this article are presented some results about dichlorodurene, which structure presents the advantage of having two molecules only in the unit cell, and the same space group $P\,2_1/a$. Molecular reorientation in crystalline solids has long been a subject of intrinsic interest because it manifests the subtle nature of the intermolecular interactions and little is yet known about its mechanism. It has been argued[4,5,6] that the reorientation of neighbouring molecules are correlated, as cog-wheels, but po-

tential energy calculations in benzene[2] show that motions may be independent. In fact, it seems that these reorientations are both possible with a probability which depends on the concerned energy. One can imagine other reorientation processes: if molecules are close-packed along a direction in the crystal, this is the case for instance in dichlorodurene, it is reasonable to think there are correlations along this axis[7] and we must calculate barrier heights to say if reorientations are possible or not. The Dichlorodurene X-ray structure analysis[8] shows that disorder is a function of temperature and some disorder remains below the ordering temperature at 163°K[9]. Furthermore, conventional refinement of the structure at room temperature leads to a solution physically unreasonable and we know elsewere (by NMR technique[10]) that disorder is dynamic. Then, to explain these two phenomena some potential energy calculations were carried out.

STRUCTURE

The crystal structure of Dichlorodurene, or D.C.D., was previously determined[8] and we recall briefly some important results: D.C.D. cristallizes in space group P $2_1/a$ with two molecules on point group symmetry 1 in unit cell. Very high thermal motion parameters and equivalent substituants observed at room temperature led to propose a model with a statistical distribution of two carbon methyl and one chlorine atoms, on the basis of orientationally dynamic disorder in the structure. Molecular reorientation takes place most probably about the normal to the central ring.

To improve X-ray structure of D.C.D. we introduced anisotropic temperature factors and a weighting scheme taking acount of counting statistics, but conventional least squares refinement led to a solution physically unreasonable in both atomic positions and thermal parameters with R index of 0.11. Thus, on the assumption of rigid body approximation, according to Cruickshank[11], further constrained refinement was carried out. Librational and translational tensors were directly refined and reported here (Table 1).

In fact, it seems that thermal motion ellipsoïds obtained from conventional or constrained refinement do not represent solely thermal motion but also delocalisation of atoms in the structure, disorder making representation of electronic cloud very difficult. Then, to explain dynamic properties of D.C.D. we have performed some calculations using interaction potential functions between nonbonded atoms.

TABLE 1

Rigid body thermal parameters with their standard deviation, as determined from the constrained refinement.

$$T_{(A^{\circ 2})} = \begin{bmatrix} 0.0378 & -0.0046 & 0.0019 \\ 60 & 25 & 27 \\ & 0.0573 & 0.0012 \\ & 30 & 22 \\ & & 0.0622 \\ & & 36 \end{bmatrix}$$

$$L_{(deg^2)} = \begin{bmatrix} 23.0 & & \\ 1.7 & & \\ & 24.3 & \\ & 3.1 & \\ & & 15.2 \\ & & 2.9 \end{bmatrix}$$

– Axes are inertial molecular axes with y parallel to the $S_3-S'_3$ (8) vector in the ring and x perpendicular to the plane of the ring.

MODEL

For potential energy calculations, it is very important to choose a good geometrical model and, if bond lengths are well known in benzene ring, it is impossible to get informations about hydrogen atoms of methyl groups from X-ray analysis because of disorder. So, in first approximation we make use of a molecular model with an average methyl-methyl interaction as determined by analogy with the potential energy between two methane molecules.[12] All atoms or groups are assumed to lie in the plane of benzene ring with the following bond distances:

$C_{ar}-C_{ar} = 1.39$, $C_{ar}-Cl = 1.77$, $C_{ar}-CH_3 = 1.54$ Å (angles = 120°).

Then, the model is placed in the unit cell near the position given by X-rays, chlorine atoms in positions corresponding to stable structure at low temperature, and neighbouring molecules are obtained by symmetry elements. First of all, we should be sure that observed structure is very near equilibrium position and corresponds to a minimum potential energy: we can verify this is true for the three angles fixing the molecule in crystal (there are no translations) within the limits of experimental errors. Parameters used in intermolecular potential functions are those of references.[12,13] After this calculation we notice that we really find a minimum potential energy which corresponds to the structure, but heat of sublimation thus obtained is too high (∿ 30 kcal/mole) compared to those of similar compounds. An other point is, we find a second minimum nearly equal to the first one, by molecule rotation around the normal to its plane of twenty degrees. A conventional least-squares refinement of X-ray data with molecule in this second position diverges. It does not correspond to a real structure and our conclusion is that parameters used to describe methyl-methyl interactions do not answer our purpose.

Then, we decide to change our model and place hydrogen atoms by means of intramolecular potential calculations based on Van der Waals interactions. The carbon-hydrogen bond length is 1.00 Å and the C-C-H angle is the tetrahedral angle 109.5°. Methyl groups are then introduced by allowing internal rotation about C-C bonds. Results are reported therin (Figure 1) and can be compared with durene configuration[14,15,16] (chlorine atoms being far from methyl groups relatively). Calculations carried out with this new model, considered as rigid

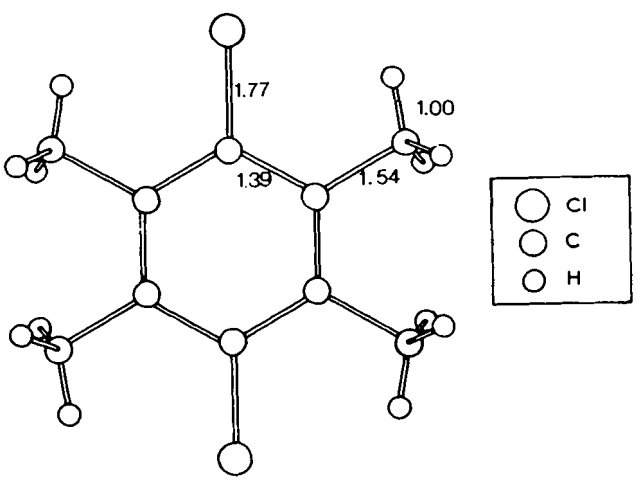

FIGURE 1 Molecular configuration of dichlorodurene.

now, reach to satisfactory results i.e.d. sublimation heat about 20 kcal/mole, and only one minimum very near the position given by X-rays.

REORIENTATION BARRIER AND DYNAMIC PROCESS

From X-ray analysis at room temperature we know that molecule of D.C.D. occupies three equivalent sites and from N.M.R. there are possibilities of jump from one site to another since disorder is dynamic. If we suppose that chlorine atoms and methyl groups have the same overcrowding, the molecular model can be compared to hindered single axis rotator, rotation axis being a pseudo sixfold axis perpendicular to the plane of the molecule while other motions are difficult to imagine because of the molecular packing.

To calculate barrier heights, several motions have been considered:

a) first ones correspond to normal modes: all molecules move together with respect to crystal symmetry.

b) second correspond to motions of the molecule which is at the origin and is solely allowed to move.

c) b axis is very short, so that molecules are close packed along this axis while alignements are impossible in perpendicular directions. Correlations may appear along b axis only and structure can be described now as juxtaposition of "cigarillos", as Canut and Hoseman[17] called them, "cigarillos" which have perhaps possibility to turn. This is our third set of calculations.

In each case, we study potential variations on the molecule situated at the origin and we keep unit cell parameters constant, (room temperature) so that we calculate activation energy at constant volume. We can see results on Figure 2.

If molecules are moving in phase by rotation of π around the normal to their plane (Figure 2A) we notice that potential energy minima thus obtained differ sensibly from expected equilibrium positions inferred from X-ray analysis at 0, $\pi/3$ and $2\pi/3$, hereafter also called positions 1, 2, 3. Then, other calculations with rotation around the normal by steps of 10 degrees and research of potential energy minimum by rotation about the two other axes give the curve in broken lines. We remark that there is a departure of about twenty degrees between expected and real rotation axis. Minima thus obtained, at $\pi/3$ and $2\pi/3$ notably are very flat and not centered on previous positions. It can be deduced that phonons vibrations are of great amplitude and anharmonic. The three positions are not equivalent, those at 0 and $\pi/3$ being more probable with a barrier of 2.0 kcal/mole.

Figure 2B shows potential energy variations when one molecule is moving solely and, as previously, broken line represents the "way of minimum energy". We can consider in first approximation, that motion of this type occurs around

the normal to the plane of the molecule. Minima are well defined, but there is a departure of about 7 degrees with position 3. The three positions have approximately the same energy level (within the limit of 0.2 kcal/mole for position 2) but barrier heights are quite different, the smallest one being equal to 1.4 kcal/mole between positions 1 and 3.

In our third set of calculations, we have previously thought that "cigarillos" turn around axis parallel to $\vec{b}$ but we have not obtain equilibrium positions and barriers are too high for dynamic reorientation process. Then, we have turned in phase each molecule in the cigarillo, around the normal to its plane and results are presented in Figure 2C. We can see that position 3 is very probable while

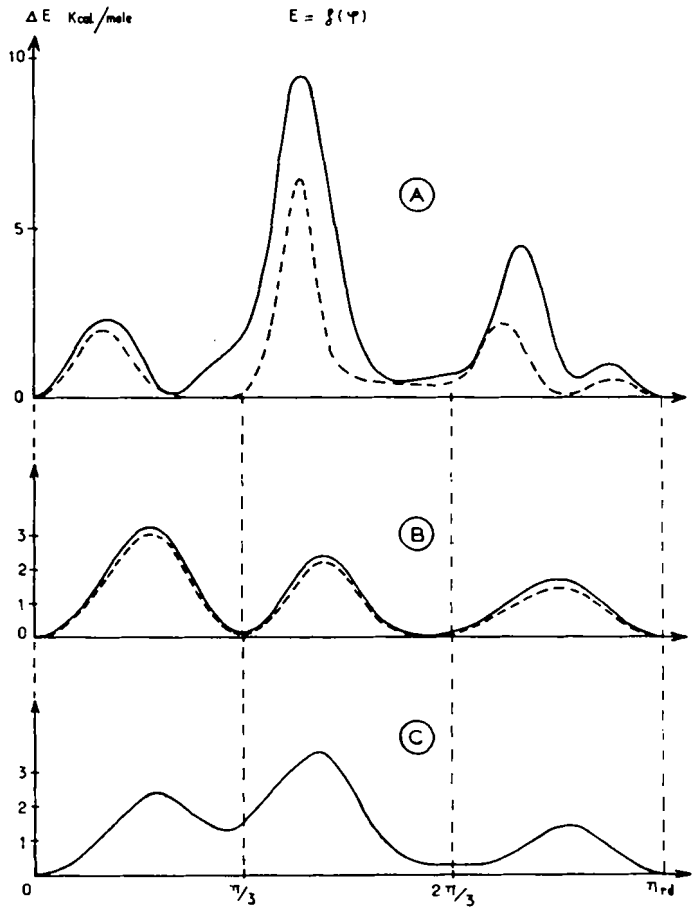

FIGURE 2 Potential energy variations versus rotation angle (A-B-C see the text).

position 2 is not and barrier height between positions 1 and 3 is similar to that found previously: 1.4 kcal/mole.

DISCUSSION

Barrier heights are small enough to think that dynamic reorientation is possible in the three cases mentionned above and the values obtained in this paper are comparable to that obtained with NMR technique for dibromodurene: [18] 1.7 kcal/mole. Furthermore, we can explain now why it is so difficult to refine X-ray structure. From X-ray analysis we obtain an average structure: in fact, it is seen that positions 1, 2, 3 are not equivalent and molecules are not superposed by themselves in dynamic reorientation. There is delocalisation of the atoms in the structure. It must be mentionned also that position 1 is found here to be the most stable and this is well verified at low temperature, where we have a greater percentage of chlorine in this position.

A rigorous estimate of the possible error involved in the calculations is difficult to make because the model is highly simplified and we have neglected some effects. For example, a remainder of the barrier height could be attributed to the electrostatic interactions between the charge distributions in the molecule, but from experience we know that multipole interactions fall of less rapidly with distance than do Van der Waals repulsions, so that Van der Waals interactions are much more important at small internuclear distance. Furthermore, multipole interactions in molecular crystals like D.C.D. or benzene for instance, enter in a very few percentage in the bonding energy of the crystal inasmuch as in Chlorodurene,[3] which is polar, contribution is still negligible. Although numerical results concerning the electrostatic term are identical to those calculated by C. Brot[19] our conclusions are quite different: the effect of electrostatic interaction may be neglected. The same result was previously obtained by Kitaigorodsky.[20,21] Moreover, constants used in potential calculations are semi-empirically determined so that they include certainly the electrostatic part at least partially in molecular crystals. An other effect which may be important is the deformation of bond angles and variation of bond lengths. It is seen that molecular model built from average methyl interaction is not in fair agreement with our purpose but the new model can be certainly improved because, in fact, methyl groups are not rigid. Nevertheless, our model seems capable of giving quantitative results. The ultimate justification of the procedure we have used must come empirically from comparing model calculations with experimental results as we attempt to do in the present paper.

CONCLUSION

In our second set of calculations, where one molecule is moving solely, potential energy so calculated can be decomposed in two parts: one part coming from the other molecules in the cigarillo and the other part coming from the juxtaposed cigarillos. When all the cigarillo is turned (Figure 2C) this second part is calculated only.

By difference of these two potential energies we obtain variations for one molecule when it turns in the cigarillo considered solely. We see at this time that the stable configurations are at $\pi/3$ and $2\pi/3$.

It can be deduced that correlations in directions perpendicular to b axis are relatively important, to impose position 1.

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