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Molecular Rearrangements in Organic Crystals.
II. The Role of Intermolecular Cooperation and Dipole–Dipole Interactions

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A model to account for intermolecular cooperation during molecular rearrangements is described. A qualitative approach to electrostatic interactions is tested for some halogen-containing molecules.

As a first step towards a better understanding of solid-state rearrangements of organic molecules, some potential-energy barriers to rigid-body rotations have been calculated in paper I (Gavezzotti & Simonetta, 1975), by the pairwise potential method. The qualitative, and in some cases quantitative, success of these simple calculations was considered an encouraging start to the application of the same method to more complex problems.

The model that was built to perform these calculations (henceforth Model I) showed however some weak points. They are: (*a*) the crystal was built up of rigid, motionless molecules surrounding the one that undergoes a certain rearrangement, and (*b*) no electrostatic contribution was included in the calculations. The first point comes abruptly into play when large molecular displacements, such as those involved in phase transitions or solid-state reactions, are considered. The second, although very important in some cases, has presumably a smaller effect than the first. This paper is devoted to the description of a new model that can account for intermolecular cooperation, and, to a first approximation, for the electrostatic interactions in crystals of polar molecules.

The molecular cluster model (Model II)

If many molecules move at the same time in a crystal, it is no longer possible to evaluate the potential energy by summing the pairwise interactions of one molecule with the surrounding ones. The simplest way of accounting for energetic changes in this case is to consider a molecular cluster, made up of a finite number of molecules, and to calculate the pairwise interactions of each molecule with all other molecules in the cluster. Obviously, the 'energy' calculated in this way can never converge to a true lattice energy, and has no physical meaning in itself. However, differences in these cluster 'energies' reflect true energy changes in the crystal.

A given rearrangement is considered to have a driving force, or main reaction coordinate, visualized as the evolution of one or more internal coordinates of one fundamental molecule. Then one or more other molecules in the cluster are allowed appropriate motions, with respect to which the cluster 'energy' is minimized. In this way a minimum-energy pathway is described from reactant to product through the multidimensional energy surface. In doing this, care must be taken that (*a*) the cluster is large enough to allow the calculation of a substantial amount of the barrier, and (*b*) no undue freedom is allowed to the molecules nearest to the fundamental one, as a result of truncation of the cluster. The cluster is therefore to be modelled in two shells, the first including the cooperating molecules, and the second to ensure that they experience much the same field as the fundamental one. The size of the first shell can be established by subdivision of the total energy of the rearrangement, as calculated with Model I, into the contributions due to contacts between each of the surrounding molecules and the fundamental one. This allows us to pick out which of the surrounding molecules are chiefly involved in establishing the barrier to the rearrangement; these make up the first shell. In the cases considered of rigid-body reorientations, these are extremely few (see Table 1). As a final check, the potential energy for the movements of each molecule belonging to the first shell is calculated, to make sure that they are properly blocked by the molecules of the second shell.

Energy minimizations within the cluster were done by the steepest-descent method, and the first derivatives of the potential energy with respect to the motions of the molecules of the cluster were approximated by finite differences. The merits and limitations of this procedure are in its simplicity. Besides, steepest-descent is known to perform well in the first approach to the minimum, and to be much slower in the refinement of the minimum search. In a few cycles of our procedure a convergence well below 1 kcal/mole was reached, and we thought this satisfactory for our present purposes.

All the pairwise potential functions carry over from paper I, so that comparisons can be made in the cases in which the calculations were repeated with the new model.

Results for the reorientational motions of aromatic molecules

The reaction-driving coordinate in this case is the rotation of the molecule as a whole around an appropriate axis. The motions allowed to the cooperating molecules are three librational angles, $\theta_1, \theta_2, \theta_3$, around the inertial axes; we define the 'total libration' of a surrounding molecule as

$$\text{total libration} = \sqrt{\theta_1^2+\theta_2^2+\theta_3^2}\,.$$

General data for the compounds considered are given in Table 1.

1. *Naphthalene derivatives*

The reorientational freedom of substituted naphthalenes has already been discussed in paper I. Figs. 1 and 2 and Table 1 show the results obtained with Model I and Model II.

In 2-fluoronaphthalene, cooperation lowers the barrier from 33 to 16·5 kcal/mole, a value closer to the experimental one. For 1,5-dimethylnaphthalene, the barrier is lowered from 43 to 20 kcal/mole, so that rotation is predicted to be easy for this compound too (naphthalene itself is known to rotate with a barrier of 25 kcal/mole: Boyd, Fyfe & Wright, 1974). On the other hand, in the ordered structure of 2-bromonaphthalene, the barrier with cooperation remains as high as 95 kcal/mole.

The total librations of the cooperating molecules during the rearrangements (Figs. 1, 2) reflect the relative ease of the movements and are strongly dependent on the nature of the molecular packing. In 2-fluoronaphthalene one molecule shows a libration of about 25°, and still the contribution to the barrier due to contacts with the second shell is small. On the other hand, in 2-bromonaphthalene the cooperating molecule must undergo a 43° total libration to make way for the rotating molecule, and the contribution to the barrier due to its contacts with the second shell is substantial (35 kcal/mole).

For 1,5-difluoronaphthalene, the barrier calculated by Model I was already quite near the experimental value. The agreement was probably due to simultaneous neglect of cooperation and of electrostatic interactions. The monofluoro derivative gives better results, probably because of time-averaged vanishing of electrostatic interactions in the crystal, which is made

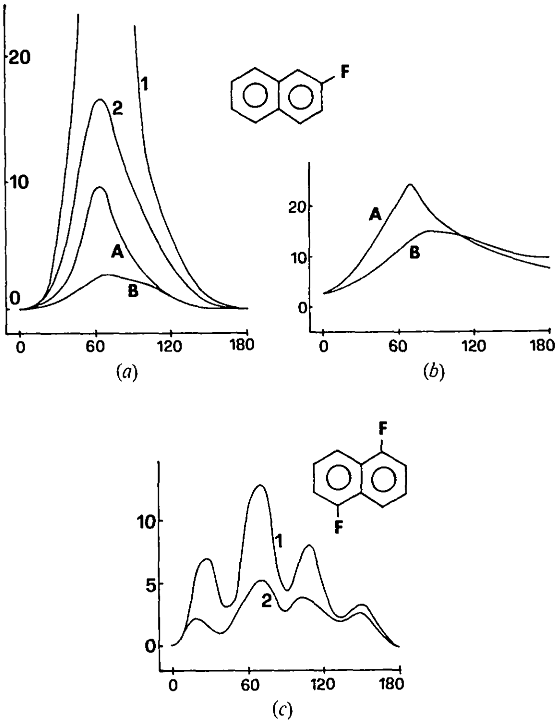


Fig. 1. (*a*) Potential energy (ordinate, kcal/mole) *vs* angle of in-plane rotation (abscissa, degrees) for 2-fluoronaphthalene. Curve 1: Model I. Curve 2: Model II. Curves *A*,*B* are the contributions due to contacts of the fundamental molecule with the two molecules of the first shell. (*b*) Total libration (ordinate, degrees) of the two molecules in the first shell during the rearrangement. (*c*) The same as (*a*) for 1,5-difluoronaphthalene, for which the total libration (not shown) never exceeded 10°.

Table 1. *General information about the compounds considered*

Compound	Space group	Number of molecules in the cluster	Number of first-shell molecules	Model I	Barrier Model II	Exptl.
2-Fluoronaphthalene[a]	$P2_1/a$	25	2	33	16·5	11[b]
1,5-Dimethylnaphthalene[a]	$P2_1/c$	29	2	43	20	–
2-Bromonaphthalene[a]	$P2_1/c$	23	1	very high	95	–
1,5-Difluoronaphthalene[a]	$P2_1/c$	23	4	13	5·5	13·3[c]
Biphenyl[d]	$P2_1/a$	23	2	200	22	23[e]
Decachlorobiphenyl[e]	$Pbcn$	–	–	very high	–	–
Hexaiodobenzene[a]	$P2_1/n$	21	2,4,6	53	38–46	–
1,3,5-Tribromobenzene[a]	$P2_12_12_1$	24	3	186	54	–

	Space group	Barrier without electrostatic interactions	Barrier with electrostatic interactions	Exptl.
1,8-Difluoronaphthalene[f]	$P2_1/c$	7·2–7·7	7·7–10·9	11·7[c]
1,2,3-Trichlorotrimethylbenzene[g]	$P2_1/c$	3·5	3·5–5·7	10·2[h]

(*a*) See paper I for the references to the crystal structures. (*b*) Chanh, Haget, Dufourcq & Lemanceau (1973). (*c*) Lauer, Stehlik & Hausser (1972). (*d*) Trotter (1961). (*e*) Pedersen (1975). (*f*) Meresse, Courseille, Leroy & Chanh (1975). (*g*) Fourme, Renaud & André (1972). (*h*) Brot & Darmon (1970). All energy values are in kcal/mole.

up of an average distribution of the F atom among the four β positions as a result of rotation.

2. *Biphenyl*

This molecule has been the object of experimental (Trotter, 1961; Hargreaves & Hasan Rizvi, 1962) and theoretical (Casalone, Mariani, Mugnoli & Simonetta, 1968) investigation in the solid state. A molecular motion in the crystal is present, although its nature is not completely understood (Lauer, Stehlik & Hausser, 1972); reorientation in the molecular plane, similar to that of the naphthalene derivatives, seemed likely, the molecule being planar in the crystal. Our calculations rule out this possibility, in view of the very high barrier implied; Fig. 3 shows instead that a highly cooperative tumbling motion around the axis of minimum inertia gives a barrier in close agreement with the experimental one (see also Table 1). Rotation of only one ring with respect to the other halves the value of the barrier, but the intramolecular contribution (a few kcal/mole) raises it again towards the experimental value. Both motion of the molecule as a whole and motion of only one ring are therefore possible in the biphenyl crystal.

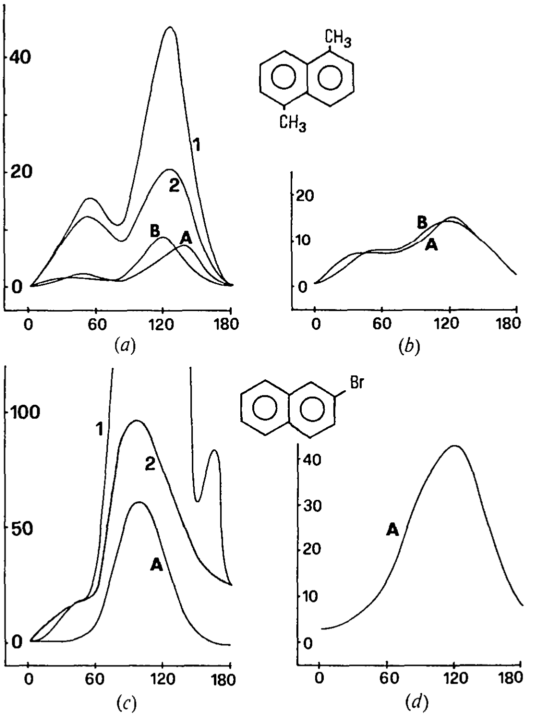


Fig. 2. (*a*) Potential energy and (*b*) total libration for the in-plane rotation of 1,5-dimethylnaphthalene. Curves 1,2,*A*,*B*: the same as in Fig. 1. (*c*) and (*d*) the same as (*a*) and (*b*) but for 2-bromonaphthalene.

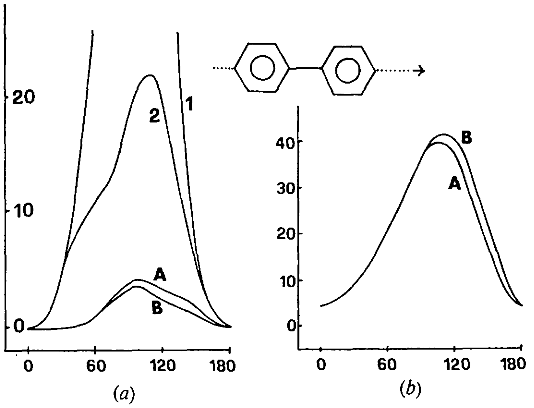


Fig. 3. (*a*) Potential energy and (*b*) total libration for rotation of biphenyl around the axis shown. Curves 1,2,*A*,*B*: the same as in Figs. 1 and 2.

The total librations for the cooperating molecules (Fig. 3) are themselves essentially rotations around the axis of minimum inertia; this suggests a gear-like nature of the movement. The energetic cost of these cooperating motions is 15 kcal/mole, *i.e.* a substantial part of the total barrier.

The effects of substitution on the mobility of biphenyl derivatives have been discussed (Lauer, Stehlik & Hausser, 1972). Fluorine substitution seems to decrease the mobility; this may be due to changes in molecular shape or packing conditions. Perfluorobiphenyl is known to have a 60° angle between the planes of the two rings (Mackenzie & Pawley, 1975), although the structure was not elucidated in detail. In perchlorobiphenyl, whose crystal structure is available (Pedersen, 1975), the planes of the two rings are almost orthogonal. The calculated reorientational barrier for this compound is very high.

3. *Some benzene derivatives*

A few benzene derivatives, which have already been studied by Model I calculations, have been chosen to study the cooperation in their solid-state rotations. In particular, hexaiodobenzene was used to check the influence of the size of the first shell surrounding the fundamental molecule, since the main contributions to its reorientational barrier come from contacts with six molecules (an unusually high number, see Table 1). Fig. 4 reports the results obtained with 0, 2, 4 and 6 cooperating molecules at increasing distance from the fundamental one, as well as with the hypothetical cooperation of all the molecules in the cluster. The differences of the barriers in curves 1 and 2, 2 and 3, 3 and 4 decrease from 7 to 5 to 3 kcal/mole. The value obtained from curve 5 sets the lower limit to the barrier, but it undoubtedly includes undue freedom of the boundary molecules in the cluster. The most reliable value should be the one from curve 4 (38 kcal/mole). For this compound, however, in view of its deviation from planarity and considerable strain due to overcrowding of the bulky substituents, intramolecular cooperation might also be invoked.

Fig. 4 reports also the results for 1,3,5-tribromobenzene. In deciding whether rotation can take place or not in these bromo and iodo derivatives, it should be kept in mind that the value of the barrier is also affected by the choice of the potential functions. For the halogens, they are approximated by the ones for the corresponding noble gas. The good performance of the functions for F has recently been tested (Filippini, Gramaccioli, Simonetta, Suffritti & Sala, 1976), and good lattice energies were calculated for chlorinated compounds in paper I, but much less evidence is available for the performance of the functions for the heavier halogens.

Dipole–dipole interaction energies

The problem of electrostatic forces has been mentioned in the explanation of some results of the calculations for the fluorinated naphthalenes. Various discussions of this problem have been given (Kitaigorodskii & Mirskaya, 1965; Kitaigorodskii, 1970; Hall & Williams, 1975). For hydrocarbons these forces are small, but they clearly increase when atoms of different electronegativities are present in the molecule. When the potential energies of molecular rearrangements involving large displacements in the crystal are calculated, electrostatic forces become important only in those cases when they are not overwhelmed by large intermolecular non-bonded interactions.

The simplest way in which a distribution of charges can be represented is as a dipole. The energy of interaction of two dipoles of charge q, with lengths equal to $\mathbf{r}_1$ and $\mathbf{r}_2$, and at a distance $\mathbf{r}$, is

$$E_{12}=q^2\left\{\frac{\mathbf{r}_1\cdot\mathbf{r}_2}{|\mathbf{r}|^3}-\frac{3(\mathbf{r}_1\cdot\mathbf{r})(\mathbf{r}_2\cdot\mathbf{r})}{|\mathbf{r}|^5}\right\}.$$

If each molecule in the crystal carries such a dipole, the electrostatic energy of the crystal can be written as

$$E=\tfrac{1}{2}K\sum_j E_{1j}\,.$$

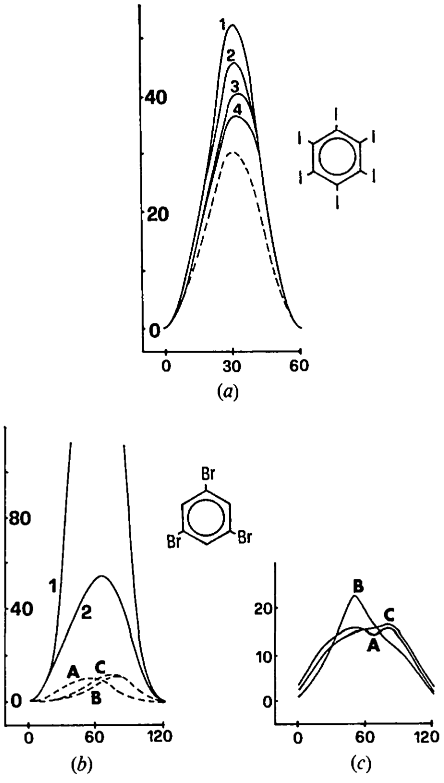
K is a parameter that can be adjusted to add flexibility to the model.

The problem of the slow convergence of such summations has been raised (Williams, 1971, and references therein). We therefore chose to perform Model I calculations of the potential energy for the reorientational motions of two halogen-containing molecules, and to increase progressively the cut-off distance for the calculation of the electrostatic contributions to test their convergence. The dipole–dipole energy involves only one simple term for each pair of molecules, so that a large number of terms can be included with little expense.

The first example is 1,8-difluoronaphthalene, whose crystal structure at room temperature is ordered, so that there is no appreciable population of the position obtained by 180° rotation in the molecular plane (Meresse, Courseille, Leroy & Chanh, 1975). The non-bonded interactions are effective in blocking the rotation around the axis coincident with the 9–10 bond of the naphthalene ring, the only rotation that produces an orientation indistinguishable from the original. Also rotation around the other axis in the molecular plane is impossible, since the calculated barrier is extremely high. The experimentally detected rotational motion (Lauer, Stehlik & Hausser, 1972) must therefore be in the molecular plane, but the population of a hypothetical 180° minimum must be so low as not to be detected by X-ray analysis.

Fig. 5 shows the results of the calculations. The electrostatic contribution is essential in raising the energy difference between the 0 and 180° minima; this is reasonable in view of the particular parallel arrangement of the directions of the molecular dipoles in the crystal. On the other hand, the agreement with the experimental barrier is not substantially improved by the inclusion of the electrostatic terms.

Another example is given by 1,2,3-trichlorotrimethylbenzene. This compound has two crystalline forms, a low-temperature ordered phase (Fourme & Renaud, 1972) and a high-temperature disordered one (Fourme, Renaud & André, 1972), in which the substituents are made indistinguishable by fast rotation about the pseudo-hexad axis. The electrostatic forces



(*a*)

(*b*) (*c*)

Fig. 4. (*a*) Potential energy (ordinate, kcal/mole) *vs* angle of in-plane rotation for hexaiodobenzene. Curves 1–4 correspond to cooperation of 0,2,4 and 6 molecules, the dotted line to cooperation of all the molecules in the cluster. Total libration (not shown) never exceeded 10°. (*b*) Potential energy and (*c*) total libration for in-plane rotation of 1,3,5-tribromobenzene. Labelling of the curves as in Figs. 1 to 3.

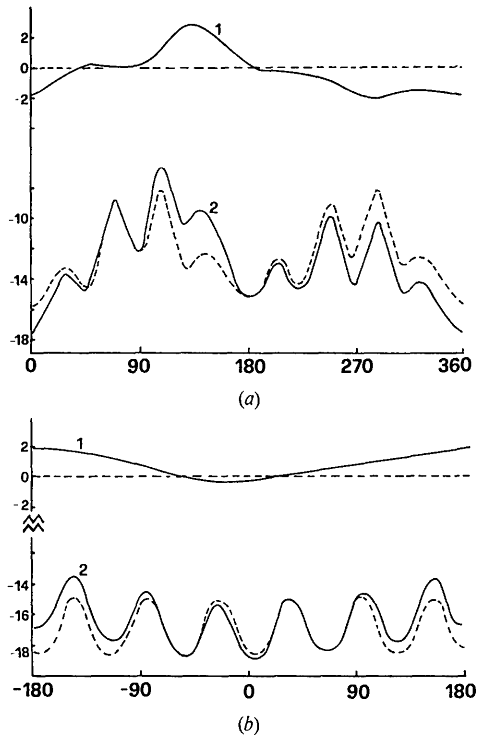


Fig. 5. (a) Potential energy (ordinate, kcal/mole) *vs* angle of in-plane rotation (abscissa, degrees) in 1,8-difluoronaphthalene. Curve 1: electrostatic contribution. Curve 2: total energy. Dotted curve: non-bonded energy. (b) The same as (a) but for 1,2,3-trichlorotrimethylbenzene.

are responsible for the setting in of order at low temperature (Brot & Darmon, 1970; Fourme & Renaud, 1972). The size of Cl being equal to that of the CH_3 groups, all the substituents have been treated as Cl atoms for non-bonded energy calculations, as discussed in paper I. Therefore, the non-bonded interaction part of the curve for the potential energy of the reorientational motion has an almost perfect sixfold symmetry (Fig. 5). This represents the energetics of the high-temperature phase, in which disorder averages out the electrostatic contributions to the reorientational barrier. Introduction of the electrostatic energy modulates this curve so that the six minima are no longer equivalent. Therefore, as cooling reduces the reorientational freedom by subtracting energy and by shrinking the cell edges, electrostatic interactions force the onset of order by removing the degeneracy of the six energy minima.

In both cases the dipole–dipole lattice sums were found to converge satisfactorily; for instance, in 1,8-difluoronaphthalene the electrostatic energy was practically constant when computed with 900, 2156 and 4212 terms. The results we have described were obtained with $q=-0{\cdot}2$ and $q=-0{\cdot}3$ electrons for Cl and F respectively, and $K=2$. These are of course all adjustable parameters, but their calibration is pointless at this stage, since this would require further tests. The inclusion of higher multipoles can also be considered for further developments.

Conclusions and perspectives

We have described a new, more flexible crystal model that accounts for intermolecular cooperation during a solid-state rearrangement, and a qualitatively reliable method for the calculation of electrostatic interactions. It is hoped that such approaches may lead the way to the study of solid-state reactivity. For instance, our concept of first and second shells in a cluster might develop into a quantification of the recently proposed concept of reaction cavity (Cohen, 1975). It is also hoped that experimental effort on solid-state reactivity will be enhanced in the near future.

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