procedure. The complex but compact volume for measurement is chosen to minimize the variation in the scattering-factor ratios. Nonetheless, errors do result, and because of the complex volume it is difficult to write expressions for the errors, or to generalize from other results. The recommended procedure to estimate errors is to synthesize data in a computer with information obtained by a preliminary analysis and then to analyze this by the procedures described here. It may result that neutron techniques are required for accuracy. Alternatively, Tibballs (1975) has suggested an extension of this procedure which essentially involves measurement of the intensity in a larger volume than described here, at points where the scattering factor is different but the rest of any term is the same. The volume is already large for these systems with multiple sublattices, so the feasibility of this new procedure is as yet unknown; it is currently being tested.

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Molecular Rearrangements in Organic Crystals.
I. Potential Energy Calculations for Some Cases of Reorientational Disorder

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The pairwise potential method was applied to the study of molecular reorientations in organic crystals. Several benzene and naphthalene derivatives were considered, along with some simple heterocycles and a few more complex compounds. The results of the calculations have been matched, where possible, with the results of X-ray analysis and other experimental data. The good performance of the method is considered encouraging in view of its application to the study of more complex solid-state processes.

The most interesting feature of molecular motions and rearrangements that occur in the solid state is that crystal packing can control the process to a very high degree. A theoretical study of such phenomena requires therefore a good insight into packing forces; and, *vice versa*, a knowledge of experimental facts can throw light on crystal force fields.

The most succesful theoretical approach to the problem of crystal forces for organic molecules involves the pairwise evaluation of non-bonded interactions between atoms by some kind of empirical potential (Kitaigorodskii, 1961; Kitaigorodskii & Mirskaya, 1962; for a recent review, see Kitaigorodskii, 1970); early calculations of this kind met considerable success

in the solution of the phase problem in X-ray crystallography (Williams, 1966a; Rabinovich & Schmidt, 1966; Damiani, Giglio, Liquori & Mazzarella, 1967; Giglio & Liquori, 1967). But as new techniques of direct determination of crystal structures became available, the simple and attractive pairwise potential model is being applied to such problems as thermal libration (Shmueli & Goldberg, 1973), molecular rotations in the crystal (Boyd, Fyfe & Wright, 1974), lattice dynamics (Pawley, 1967, 1972; Filippini, Gramaccioli, Suffritti & Simonetta, 1973), and even *a priori* calculation of crystal structures starting from symmetry information obtained from X-ray or infrared analysis (Ahmed, Kitaigorodskii & Mirskaya, 1971; Castellucci, Migliorini & Manzelli, 1972; Elliott & Leroi, 1973). The results obtained in this wide variety of applications make the model a well-established fact in the study of molecular organic crystals. A review of the work carried out in this field in our laboratory has appeared recently (Simonetta, 1974).

Outline of the crystal model

This paper is concerned with the application of the method to the study of some cases of reorientational disorder. In this first, simple approach, the crystal model is formed by a fundamental molecule, the only one allowed to move, and by a number of surrounding, ordered, motionless molecules obtained by space-group symmetry. The field experienced at any moment by the fundamental molecule is given by the pairwise addition of the non-bonded interactions between all its atoms and all the atoms of the surrounding molecules.

The motion of the fundamental molecule is, in general, a rigid-body rototranslation (see Appendix I for the geometric details); if, however, internal degrees of freedom are allowed to the molecule, the intra- adds to the inter-molecular potential.

Table 1 lists all the parameters needed for the non-bonded interactions; Table 2 contains the crystal data for the substances considered. The cases in which the crystallographic results had to be modified or supplemented in some details of molecular geometry are summarized in Appendix II.

A cut-off distance of 7 Å has been used in the calculation of packing energy (see, however, Appendix II). Comparison of the calculated lattice energies with the observed sublimation enthalpies (Table 3) shows that the limit is a fair one, and it was considered sufficient for the aims of the present work.

Scope of the calculations

In ordered, tightly packed crystals, far from the melting point, the molecules are allowed only small thermal librations. In terms of potential energy, this means that they lie in a narrow well with steep walls. As molecular freedom increases, parallel to the loosening of

Table 1. *Parameters for the non-bonded interactions*

For hydrocarbons and halogen-containing molecules[a]:

$$E = A \exp(-Br) - Cr^{-6}$$

Contact	A	B	C
C$\cdots$C[b]	83630	3·60	568
C$\cdots$H[b]	8766	3·67	125
H$\cdots$H[b]	2654	3·74	27·3
F$\cdots$F[c]	36990	4·26	129·5
Cl$\cdots$Cl[c, d]	243300	3·66	1468
Br$\cdots$Br[c]	270600	3·28	3628
I$\cdots$I[c]	372900	3·03	8373

For nitrogen- and oxygen-containing molecules[e, f]:

$$E = 30000 \exp\left(-\frac{13}{d_0}r\right) - 0·14 \, d_0^6 r^{-6}$$

$$d_0 = R_i + R_j$$

	$R_i^{(g)}$
C	1·7
H	1·5
O	1·5
N	1·6

(a) For crossed interactions, except for C$\cdots$H, the geometric mean was used for A and C, and the arithmetic mean for B. (b) Williams (1966b), set IVb. (c) The constants are those for the corresponding noble gas as obtained from Hill's (1948) data. (d) The same constants were used for sulphur. (e) Extension of the formula suggested by Kitaigorodskii (1961). (f) For pentachloropyridine and pentachloronitrobenzene, the parameters A, B and C for N$\cdots$N and O$\cdots$O were calculated in this way, and then the geometric and arithmetic means were calculated for the crossed interactions with the parameters for hydrocarbons and halogen-containing molecules. (g) Van der Waals radii.

Table 2. *Crystal data for the substances considered in the reorientational energy calculations*

	Space group	Z	$T°C^{(a)}$
Benzene	Pbca	4	−135
Benzene	Pbca	4	−55
Benzene II	$P2_1/c$	2	21 [b]
Hexachlorobenzene	$P2_1/n$	2	
1,2-Dichlorotetramethylbenzene	$P2_1/c$	2	
1,3,5-Trichlorobenzene	$P2_12_12_1$	4	−183
1,3,5-Tribromobenzene	$P2_12_12_1$	4	20
Pentachloronitrobenzene	$R3$	3	
Hexamethylbenzene	$P\bar{1}$	1	
Hexaiodobenzene	$P2_1/n$	2	
1,2,4,5-Tetrabromobenzene	$P2_1/a$	2	
Pentachloropyridine	$P4_12_12$	4	
	$P2_1$	2	
2-Fluoronaphthalene	$P2_1/a$	2	
2-Bromonaphthalene	$P2_1/c$	4	
1,5-Difluoronaphthalene	$P2_1/c$	2	
1,5-Dimethylnaphthalene	$P2_1/c$	4	
Pyrazine	Pmnn	2	20
Pyrimidine	$Pna2_1$	4	−2
Furan	Cmca	4	−121
	$P4_12_12$	4	−150
Thiophene	Cmca	4	−55
Cyclopentadiene	$P2_1/n$	4	−150
Hexachloroethane	Pnma	4	15
Hexabromoethane	Pnma	4	22
1,4-Diiodobicyclo[2,2,2]octane	$P4_12_12$	4	
Acepleiadylene	$P2_1/a$	4	

(a) Given only if the analysis was not carried out at room temperature. (b) High-pressure phase at 25 kilobars.

Table 3. *Observed sublimation enthalpies and calculated lattice energies*[(a)]

	ΔH_{obs}	E_{calc}	%calc/ obs
Benzene $-55\,°C$		9·6	90
Benzene $-135\,°C$	$10\cdot7^{(b)}$	9·7	91
Benzene II		9·7	91
Hexachlorobenzene	$21\cdot9^{(c)}$	19·5	89
1,2-Dichlorotetramethylbenzene		17·9	
1,3,5-Trichlorobenzene		14·1	
1,3,5-Tribromobenzene		16·1	
Pentachloronitrobenzene		16·6	
Hexamethylbenzene	$19\cdot2^{(d)}$	16·4	85
Hexaiodobenzene		23·4	
1,2,4,5-Tetrabromobenzene		17·2	
p-Dichlorobenzene $\alpha^{(e)}$ $15\cdot5^{(c)}$–$16\cdot3^{(d)}$		12·3	79–76
p-Dichlorobenzene $\beta^{(f)}$	$15\cdot5^{(c)}$	12·4	80
p-Dichlorobenzene $\gamma^{(g)}$		13·2	
Pentachloropyridine (tetragonal)		16·2	
Pentachloropyridine (monoclinic)		15·1	
2-Fluoronaphthalene		14·6	
2-Bromonaphthalene		16·5	
1,5-Difluoronaphthalene		15·5	
1,5-Dimethylnaphthalene		$17\cdot5^{(m)}$	
Pyrazine	$13\cdot5^{(h)}$	7·4	55
Pyrimidine		7·2	
Furan (tetragonal)		6·1	
Furan (orthorhombic)		5·7	
Thiophene		7·0	
Cyclopentadiene		8·1	
Hexachloroethane	$14\cdot1^{(i)}$	12·8	91
Hexabromoethane		16·3	
Carbon tetrachloride[(l)]	$9\cdot2^{(d)}$	9·5	102
1,4-Diiodobicyclo[2,2,2]octane		$13\cdot1^{(m)}$	
Acepleiadylene		$21\cdot9^{(m)}$	

(a) All values in kcal/mole. (b) Boyd, Fyfe & Wright, (1974). (c) Bonadeo & D'Alessio (1973). (d) *Handbook of Chemistry and Physics* (1967). (e) Crystal structure by Frasson, Garbuglio & Bezzi (1959). (f) Crystal structure by Housty & Clastre (1957). (g) Crystal structure by Fourme, Clec'h, Figuiere, Ghelfenstein & Szwarc (1974). (h) Poltev & Sukhorukov (1968). (i) Sasada & Atoji (1953). (l) Crystal structure of high-pressure phase by Piermarini & Braun (1973). (m) See Appendix II.

packing conditions, thermal motion becomes more and more important, and involves bigger displacements; one or more walls of the potential-energy well become flatter, and the X-ray view of the molecule becomes progressively blurred. In a statically disordered crystal, the molecules assume more or less randomly various orientations at the same molecular site. In terms of potential energy, this is a many-minima surface with high barriers between the various minima; the X-ray view is a population-weighted superimposition of the orientations. The dynamical disorder arises from jumps of the molecules through the potential energy barriers that separate those minima, the barriers being lower. If the frequency of the jumps is low enough, X-ray analysis still yields discrete atomic positions. Calculations of the potential energy in the crystal have been carried out for a number of structures, either ordered, disordered or affected by molecular motion, with the aim of establishing the applicability of the pairwise potential method to the study of dynamical effects involving large displacements.

Results

1. Benzene derivatives

Benzene itself was very early discovered to exhibit a reorientational motion in the crystal (Andrew, 1950). A neutron diffraction study is available at two temperatures, -55 and $-135\,°C$ (Bacon, Curry & Wilson, 1964). Calculations have already been performed on the reorientation of the benzene crystal (Boyd, Fyfe & Wright, 1974; Kitaigorodskii, 1966). Various methyl- and halogen-substituted benzenes were shown to have isomorphous crystal structures, and to be affected by easy reorientation in the molecular plane. The structure of hexachlorobenzene was determined (Tulinsky & White, 1958) and refined (Brown & Strydom, 1974), and packing calculations were done (Streltsova & Struchkov, 1961; Bonadeo & D'Alessio, 1973; Bates & Busing, 1974); its structure is isomorphous with that of 1,2-dichlorotetramethylbenzene (Tulinsky & White, 1958) and of hexamethylbenzene (Brockway & Robertson, 1939). For this last compound, a redetermination was carried out by neutron diffraction, and librational r.m.s. amplitudes determined (Hamilton, Edmonds, Tippe & Rush, 1969). The rotation of hexamethylbenzene in the crystal was reported early (Andrew, 1950) and confirmed by further studies, dealing also with methyl rotation (Rush & Taylor, 1966; Rush, 1967; Allen & Cowking, 1967). Rotation about an axis other than the hexad axis has been reported at high temperatures for benzene and hexamethylbenzene (Van Steenwinkel, 1969). For various other derivatives, dielectric measurements have yielded approximate activation energies for the in-plane rotations (Brot & Darmon, 1970). The in-plane rotation is reported also for hexafluorobenzene (Boden, Davis, Stam & Wesselink, 1973a,b) and 1,3,5-trifluorobenzene (Boden & Gibb, 1974). 1,2-Dichlorotetramethylbenzene and pentachloronitrobenzene are peculiar in that rotation in the molecular plane produces distinguishable orientations, so that their crystal structures are disordered. On the other hand, 1,3,5-trichlorobenzene and 1,3,5-tribromobenzene are ordered (Milledge & Pant, 1960); the same is true for the β phase of 1,2,4,5-tetrabromobenzene (Gafner & Herbstein, 1960). The crystal structure determination shows that hexaiodobenzene is not planar in the crystal (Steer, Watkins & Woodward, 1970); the implications of this fact with respect to molecular rotation are discussed below.

In view of the similarity of the bulk of the two substituents, the methyl groups have been treated in all calculations on benzene derivatives as Cl atoms centred on the C atom of the methyl group. This similarity is confirmed by the isomorphism of differently substituted compounds (Tulinsky & White, 1958), and by the similarity of the sublimation enthalpies of hexachloro- and hexamethyl-benzene (Table 2); moreover, in this way 85% of the experimental sublimation enthalpy is reproduced by the calculated lattice energy of hexamethylbenzene.

The curves in Fig. 1 show the variations of the barrier to rotation in benzene with temperature and pressure [the high-pressure phase II was reported by Fourme, André & Renaud (1971)]. All available values of experimental barriers in benzene derivatives are collected in Table 2, with our calculated values. The shapes of the energy profiles for the rotations in the molecular plane are shown in Fig. 2. Comparison of experimental and calculated activation energies show a rough correspondence of trends; in particular, hexachlorobenzene compares nicely with pentachlorotoluene, confirming the assumption of the similarity of chloro and methyl substituents. The method, however, gives the correct position of all the energy minima, and gives the correct order of magnitude of the barrier involved, thus allowing the separation of the molecules into (i) easily rotating, (ii) hindered but rotating, (iii) non-rotating. Compare (i) the low values for the planar, isomorphous 1,2-dichlorotetramethyl-, hexachloro- and hexamethyl-benzene, and for pentachloronitrobenzene, with (ii) the very high value for hexaiodobenzene, for which intermolecular cooperation or intramolecular rearrangement is probably to be invoked if rotation is to take place, and with (iii) the very high repulsive potentials for the ordered trichloro, tribromo and tetrabromo derivatives, whose packing arrangement is basically different from that of the rotating compounds, and for which rotation should be precluded.

The experimentally found disorder of 1,2-dichlorotetramethylbenzene is rationalized by the equivalence of all the minima obtained by 60° rotation (see Fig. 2); for pentachloronitrobenzene, in contrast with the sixfold shape of the potential energy profile (Fig. 2), the X-ray data were best fitted by a threefold disorder, obtained by 120° rotations, the difference being however as small as about 1% residual (Tanaka, Iwasaki & Aihara, 1974).

2. Naphthalene derivatives

Naphthalene appears to rotate in its molecular plane just below its melting point (Boyd et al., 1974). 2-Substituted naphthalenes are known to be isomorphous in the solid state and to give extensive solid solutions (Baumgarth, Chanh, Gay, Lascombe & Le Calvé, 1969; Chanh, Bouillaud & Lencrerot, 1970a). They are also known to exhibit polymorphism with a high-temperature, reorientationally disordered phase (phase I) and a low-temperature, ordered phase (phase II) (Chanh, Bouillaud & Lencrerot, 1970b). The crystal structures of some of these compounds are available; phase I of 2-fluoronaphthalene (Chanh & Haget-Bouillaud, 1972) and phase II of 2-bromonaphthalene (Chanh, Haget, Leroy & Hannoteaux, 1973) are suitable to test the validity of potential energy calculations. 1,5-Difluoronaphthalene is also known to exhibit reorientational motions in the crystal (Chanh, Housty & Leroy, 1973); finally, the structure of 1,5-dimethylnaphthalene was reported (Beintema, 1965),

but no information is available about molecular motion.

The results of potential energy calculations for the rotation in the molecular plane of naphthalene derivatives are given in Fig. 3. A rationalization of the different behaviour of phases I and II is found by comparing the relatively low barrier to reorientation in 2-fluoronaphthalene phase I (about 33 kcal/mole)
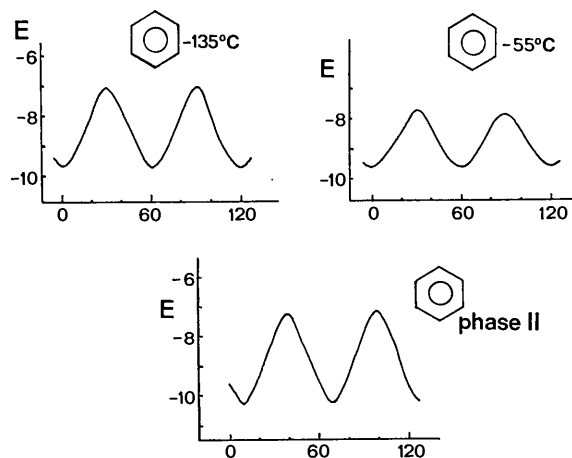

Fig. 1. Potential energy curves for in-plane rotation of benzene. Energy, E (kcal/mole) vs. angle of rotation (°). The centre of rotation is the centre of the ring.
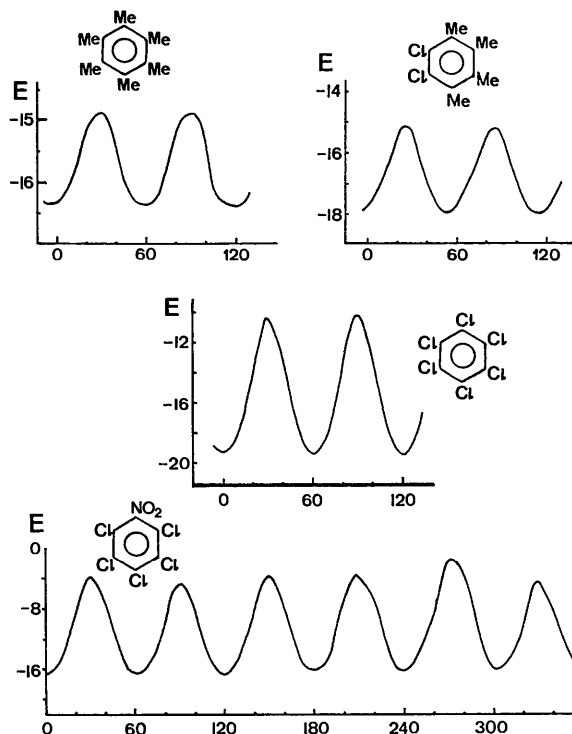

Fig. 2. Potential energy curves for in-plane rotation of benzene derivatives. Energy, E (kcal/mole) vs. angle of rotation (°). The centre of rotation is the centre of the ring.
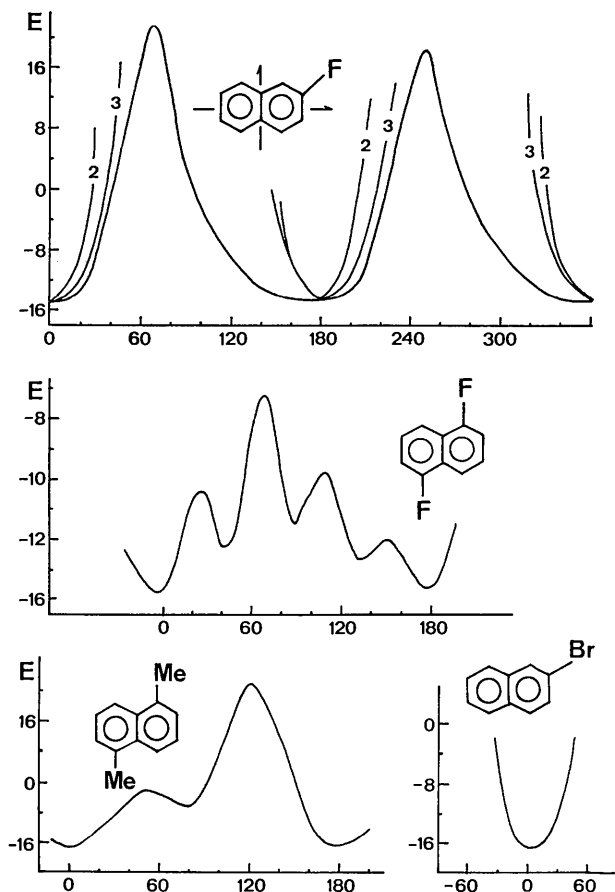
Fig. 3. Potential energy curves for molecular rotations in naphthalene derivatives. Energy, E (kcal/mole) vs. angle of rotation (°). For 2-fluoronaphthalene, the full curve refers to in-plane rotation, and curves 2 and 3 refer to rotations about the two axes in the molecular plane. For all other compounds, the curves refer to in-plane rotation. The centre of in-plane rotations is in the middle of the central C–C bond.
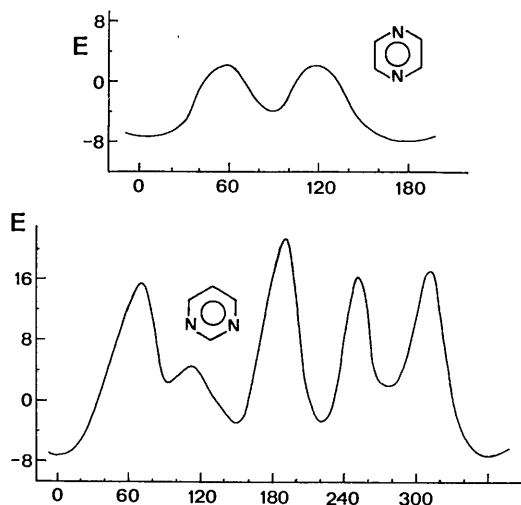
Fig. 4. Potential energy curves for in-plane rotation of pyrazine and pyrimidine. Energy, E (kcal/mole) vs. angle of rotation (°). The centre of rotation is the centre of mass.

with the enormous repulsive potential obtained for 2-bromonaphthalene phase II. The shapes of the energy minima (Fig. 3) have an immediate correspondence with the experimental thermal behaviour described for the two compounds; a marked anisotropy corresponding to motion in the molecular plane is observed in 2-fluoronaphthalene, whose potential well is very wide, while no such effect is present in 2-bromonaphthalene, whose potential well is accordingly much narrower. Besides, the perfect equivalence of the minima obtained for rotation about the three axes in 2-fluoronaphthalene is in accordance with the random distribution of the substituent among the four β sites found in the crystal.

For the disubstituted compounds, the molecular reorientation reported for the difluoro derivative is accounted for by the low calculated value of the activation energy (about 13 kcal/mole); a barrier of about 43 kcal/mole is calculated for the dimethyl compound, so that there is a reason for suspecting motion for this compound too (compare with the value for the 2-fluoro derivative, which is known to rotate). An interpretation of the various sub-minima that appear in the energy profiles for these last two molecules is not immediate. It has been pointed out (Boyd et al., 1974) that small uncertainties in the atomic positions can have consequences of this kind on the calculations. It is however possible that metastable positions in the crystal exist without affecting the X-ray analysis, being too scarcely populated.

3. Nitrogen-containing benzene analogues

The crystal structures of pyrazine (Wheatley, 1957) and of pyrimidine (Wheatley, 1960) have been chosen to explore the possible rotations in N heterocycles. Also, pentachloropyridine is polymorphous, and an X-ray investigation (Rossell & Scott, 1973) invokes a possible twofold rotational disorder to account for the observed data for the monoclinic phase.

The shape of the potential energy curve for pyrazine (Fig. 4) is easily rationalized by observing that 60° rotation produces a maximum variation of the bulk of the molecule, as two C–H groups take the place of the two N atoms, while 90° rotation produces a minimum variation of the bulk and hence a sub-minimum in the potential energy curve. The explanation of the shape of the curve for pyrimidine (Fig. 4) is less obvious. The maxima at 60, 180 and 300° rotation correspond to the replacement of both N atoms by C–H groups; those at 120 and 240° to only one N replaced by a C–H group. The minima correspond to minimum overall variation of the bulk of the molecule, in the same way as discussed for pyrazine.

The two structures are described as ordered, which implies that minima other than at 0° rotation are metastable ones. For pyrimidine, a barrier of 23–30 kcal/mole is calculated; for pyrazine, rotation should be easy, in view of the low value for the barrier (about 7 kcal/mole). Moreover, 180° rotation does not affect

the X-ray determination, the two positions being indistinguishable.

Calculations were done also for the two phases of pentachloropyridine. The ordered tetragonal phase has only one minimum of potential energy at 0° rotation; the same is true for the monoclinic phase, for which, on the contrary, a 30% occupancy of the orientation obtained by 180° rotation about the ring centre in the molecular plane was proposed to account for X-ray data (Rossell & Scott, 1973). Since for this last phase the hypothesis of twinning was also considered, our calculations, ruling out the possibility of reorientational disorder, are in favour of this alternative interpretation of the X-ray data.

4. Five-membered rings: furan, thiophene and cyclopentadiene

The crystal structures of thiophene at −55°C (Abrahams & Lipscomb, 1952) and of furan at −121°C (Fourme, 1972) are closely similar. Both belong to space group *Cmca* [for thiophene, confirmation of the space group came from Loisel, Pinan-Lucarre & Lorenzelli (1973)] with $Z=4$; in both cases, a reorientation in the molecular plane has been invoked to ensure a 25% occupancy of four equivalent positions, thus covering all the 16 equivalent positions of the space group.
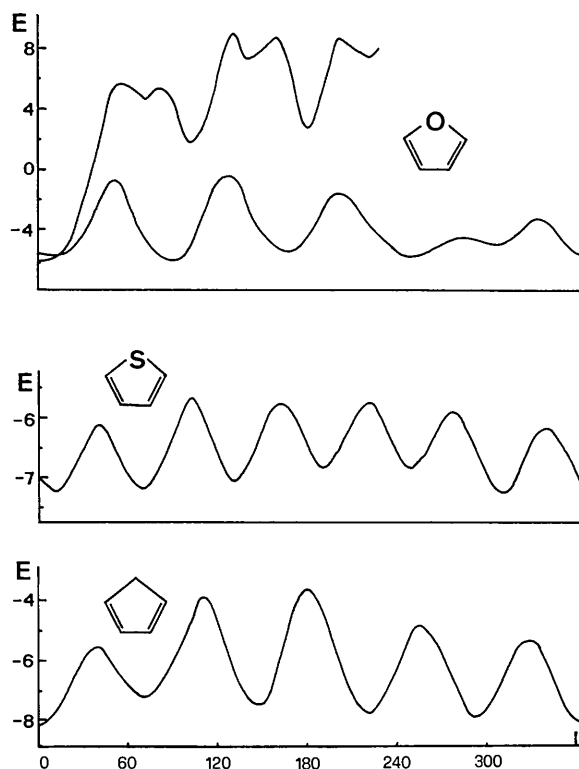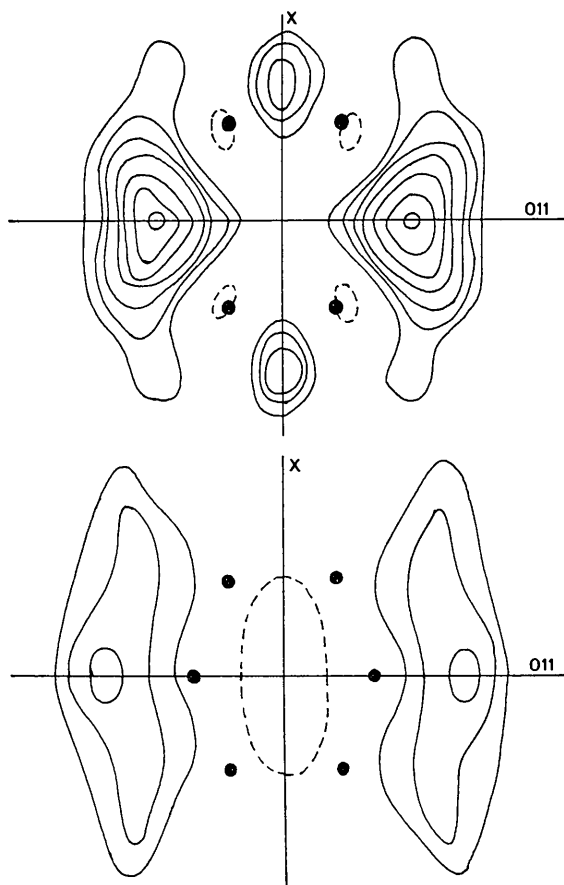
Fig. 5 shows the results of the potential energy

Fig. 6. Difference syntheses in the molecular plane for thiophene. Above, fourfold disorder; below, sixfold disorder. Contours drawn at intervals of 0·1 e Å^{-3} starting from 0·1. Dotted lines surround negative areas. Black spots show the positions of the fractional sulphur atoms.

calculations. A fourfold disorder model can be a good approximation for furan, but thiophene has six equally spaced minima. Furan refined smoothly, while thiophene, possibly due to the limited computing facilities of the time, was not refined. We checked the sixfold model against the X-ray data, and the best result was obtained by a slight rotation in the molecular plane of the published model, together with a 10% occupancy of the special position in the *yz* plane; this corresponds to an almost perfect sixfold symmetry at the molecular site. *R* drops from 32 to 26%, and the difference map takes on a smoother appearance (Fig. 6). Although this cannot be taken as a definite proof, since no anisotropic thermal analysis is possible owing to the paucity of the data, this result, together with the great resemblance of the cell parameters, might well provide a rationalization of the unusual stability of the benzene–thiophene solid solutions. NMR studies of such solutions (Anderson, 1970) confirm the rotational freedom of both benzene and thiophene over a wide range of solution composition.

A rotational barrier of 2 kcal/mole is reported for solid furan (Fourme, 1972). Our values are of the

Fig. 5. Potential energy curves for in-plane rotation of five-membered rings. Energy, *E* (kcal/mole) *vs.* angle of rotation (°). The centre of rotation is the centre of mass. For furan the upper curve refers to phase II.

order of some kcal/mole (Fig. 5). The resemblance of the values for thiophene to those for benzene has undoubtedly consequences on the ease of solid-solution formation. It is worth while to note that the six-minima shape of the energy curve for thiophene survived (though with small changes in the value of the barrier) changes in potential-energy functions and in cut-off distance, and small changes of rotation axis (both the [011] diagonal and the principal axis of inertia were considered). Finally, while thiophene retains its rotational freedom well below the lowest phase transition (Anderson, 1970), the low-temperature phase II of furan is ordered (Fourme, 1972). Accordingly, only one deep minimum is found in the potential energy curve (Fig. 5).

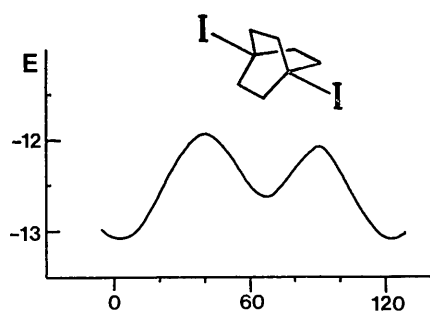The case of cyclopentadiene is a controversial one. The structure was solved and refined (Liebling &

Fig. 7. Potential energy curve for rotation of the bicyclooctane cage about the iodine–iodine axis in 1,4-diiodobicyclo-[2,2,2]octane. Energy, E (kcal/mole) vs. angle of rotation (°).
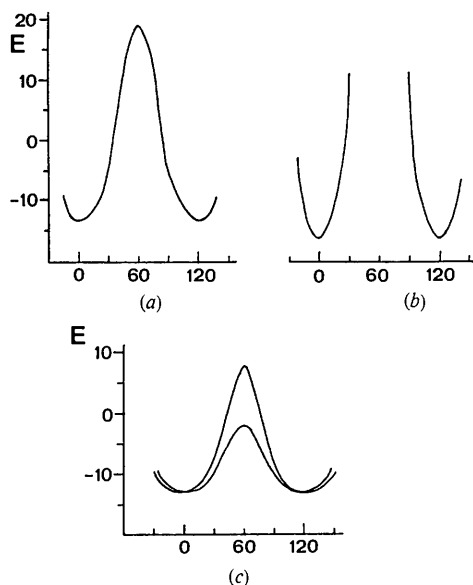

Fig. 8. Potential energy curves for rotation about the C–C axis in hexahalogenoethanes. (a) hexachloroethane, rotation of the molecule as a whole; (b) the same for hexabromoethane; (c) rotation of each one of the two CCl_3 groups with respect to the other in hexachloroethane. Energy, E (kcal/mole) vs. angle of rotation (°).

Marsh, 1965) on the hypothesis of an ordered crystal; because of experimental troubles, only 60 reflexions were observed. The refinement ended up with a clear distinction between bond lengths and angles at the double and single bonds. Potential-energy calculations (Fig. 5) are in favour of fivefold disorder around the axis perpendicular to the molecular plane. The only explanation that can match these two results is that at low temperature (the data were collected at -150 °C) the minima other than in the origin are little populated, and the effect of the different orientations is scarcely detectable.

5. 1,4-Diiodobicyclo[2,2,2]octane

The structure of this compound was determined by location of the heavy atoms, and then refined with some effort, until it was recognized that the bicyclooctane cage was disordered (Britton, 1974). Disorder by rotation about the axis defined by the two I atoms was inferred from a difference synthesis. A rigid model was then assumed for the bicyclooctane cage, and 50 % occupancy deduced of two orientations obtained by rotation of $\pm 20°$ away from the nearest ordered position.

This case is a good example of the use of potential-energy calculations in crystal structure analysis. A calculation based on the positions of the I atoms and the standard model for the bicyclooctane frame gave the result shown in Fig. 7, from which hints for the right kind of disorder are self-evident. Easy rotation about the $I \cdots I$ axis can be inferred from the low value of the potential energy barrier.

6. Hexachloroethane and hexabromoethane

As an example of combination of intra- and intermolecular potentials, the simple case of hexahalogenoethanes was considered. The structure of hexachloroethane (Sasada & Atoji, 1953; corrected in Sasada & Atoji, 1959) and of hexabromoethane (Mandel & Donohue, 1972) are known, although for the chloro compound the determination is not very accurate; our attempts to refine this structure from the published $R=0.21$ failed. Both isotropic and anisotropic refinements converge at $R=0.18$. A difference synthesis reveals a set of peaks (about 2 e Å^{-3}) that make up an image of the molecule rotated by 60°; attempts to refine this disordered model, however, lead to unacceptable thermal parameters.

In Fig. 8 are reported the curves of the intermolecular potential for rotation about the C–C axis for the two compounds; in accordance with the failure of the refinement, no minimum is found for the potential energy at 60° rotation of the whole molecule. Fig. 8 shows also the barriers to rotation of each to the two CCl_3 groups with respect to the other in hexachloroethane; the lower one is 10 kcal/mole, which, added to the about 11 kcal/mole of the intramolecular barrier (Karle, 1966) results in a total barrier of 21 kcal/mole for rotation in the crystal. This rotation should there-

fore be hindered but possible. The shape of the minima for this rotation show the high thermal motion that has possibly limited the goodness of the room-temperature X-ray data.

7. Azulene and acepleiadylene

The crystal structure of azulene has been the subject of various analyses, until the final result was obtained (Robertson, Shearer, Sim & Watson, 1962) that the structure is disordered by random distribution of the molecules between two orientations obtained by 180° rotation at a centrosymmetrical site of space group $P2_1/a$. The barrier to this rotation in the solid was determined to be 15·4 kcal/mole (Fyfe & Kupferschmidt, 1973). Calculations have been reported on the potential-energy variations during the rotation (Boyd et al., 1974). The disorder in the crystal of acepleiadylene is almost of the same kind, the space group being the same, although with $Z=4$ (Hanson, 1960). The results of potential energy calculations for acepleiadylene are reported in Fig. 9. The barrier is comparable with that of azulene, suggesting that the behaviour of the two compounds is similar, the disorder being dynamical for both.

Concluding remarks

The applicability of the atom-pair non-bonded interaction potential to the study of disorder and dynamical reorientation in crystals was tested for a number of molecules containing halogens, N and O, in relation to crystal structure analysis. The results obtained are considered qualitatively, and in some cases quantitatively, encouraging in view of the future development of methods of studying more complex processes in solids. In fact, reorientation as a rigid body can be considered the simplest case of rearrangement in the solid state; the crystal symmetry is unchanged, and no bonds are broken. An intermediate problem is the study of phase transitions, in which the crystal symmetry changes but still no bonds are broken. Although a considerable body of experimental evidence proves that in most cases extensive unpacking and repacking occurs at a phase transition, so that no relationship is to be found between the orientation of the unit cells of the two phases, recent evidence has been reported that this is not always so (see, for a discussion, Thomas, 1974). This offers a relatively easy field of application of the atom-pair model to the study of a phase transition. The most complex process that can take place in the solid is a reaction; the crystal symmetry of reactants and products are different, and bonds are broken and formed, so that an intramolecular energy must be evaluated by some empirical or quantum mechanical method. Interest in the experimental aspects of organic reactions in solids is rising (Paul & Curtin, 1973; Cohen & Green, 1973). An approach to this problem is in progress, with the ultimate goal of a full theoretical study of organic solid-state reactions.

APPENDIX I

The model crystal is made up of a fundamental molecule and of a number of symmetry-related molecules:

$$\mathbf{r}_{m, i} = \mathbf{M}_m \mathbf{r}_{0, i} + \mathbf{s}_m$$

where $\mathbf{r}_{m, i}$ are the vectors of the mth transformed molecule, and $\mathbf{r}_{0, i}$ the atomic vectors of the fundamental molecule. After orthogonalization, one gets the vectors $\mathbf{x}_{m, i}$ and $\mathbf{x}_{0, i}$ respectively. Defining now a local reference system for the fundamental molecule, one gets

$$\mathbf{w}_{0, i} = \mathbf{B}_0(\mathbf{x}_{0, i} + \mathbf{b}_0) ,$$

where $\mathbf{B}_0$ and $\mathbf{b}_0$ are the matrix and vector that represent the transformation from the orthogonalized-cell reference system to the local reference system (say, the inertial system or any other desired system). A rotation in this local system will be represented by a matrix $\mathbf{C}_0$:

$$\mathbf{w}'_{0, i} = \mathbf{C}_0 \mathbf{w}_{0, i}$$

where the prime denotes the rotated vectors. Transforming back into the orthogonalized cell reference system, in which the intermolecular distances are ultimately computed, and rearranging, one gets

$$\mathbf{x}'_{0, i} = \mathbf{S}_0 \mathbf{x}_{0, i} + \mathbf{S}_0 \mathbf{b}_0 - \mathbf{b}_0$$
$$\mathbf{S}_0 = \mathbf{B}_0^{-1} \mathbf{C}_0 \mathbf{B}_0 .$$

This simple treatment is quite suitable for computer application.

APPENDIX II

Where the X-ray determination of H atoms was thought unreliable for the purpose of the present calculations, they were placed in reasonable positions at a C–H distance of 1·08 Å. The dispersion centre of the H atoms was always placed at the nucleus. For 2-fluoronaphthalene, the position of the F atom (which was spread over the four β positions in the structure refinement) was recalculated on the basis of a trigonal geometry and a C–F distance of 1·354 Å (the same as in difluoronaphthalene).

In order to save computing time, the fundamental molecule is surrounded only by the molecules contained
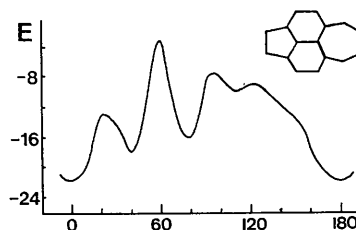

Fig. 9. Potential energy curve for rotation of acepleiadylene in the molecular plane. Energy, E (kcal/mole) vs. angle of rotation (°). The centre of rotation is the centre of mass.

in the 26 cells obtained by adding ± 1 to each component of the space-group translation vectors. In some cases, more cells might be needed to include all distances within 7 Å; it has been checked, however, that the missing contacts never contribute more than a few percent of the lattice energy. For dimethylnaphthalene and acepleiadylene, owing to the size of the molecules, the crystal was made up only of a reasonable choice of the nearest neighbouring molecules around the fundamental one; for the same reason, a cut-off distance of 6 Å was used for diiodobicyclooctane. In these cases too the differences from the true lattice energies at 7 Å were checked to be very small.

Table 4. *Energy barriers to in-plane rotation for benzene derivatives[a]*

	ΔE_{obs}	ΔE_{calc}
Benzene $-55\,°C$		1·80
Benzene $-135\,°C$	3·5–4·2[b]	2·65
Benzene II		3·14
1,2-Dichlorotetramethylbenzene	7·7[c]	2·47
Hexamethylbenzene	6·4–6·7[d]	1·48
Hexachlorobenzene		9·19
Pentachlorotoluene	12·1[c]	
1,2,3-Trichlorotrimethylbenzene	10·2[c]	
Pentachloronitrobenzene		12·98
Hexaiodobenzene		53·24
1,3,5-Trichlorobenzene		87·75
1,3,5-Tribromobenzene		very high
1,2,4,5-Tetrabromobenzene		very high
Hexafluorobenzene	3·02–7·45[e]	
1,3,5-Trifluorobenzene	10·2–11·0[f]	

(a) All values in kcal/mole. When there are different barriers for a compound, the average is reported. (b) Boyd, Fyfe & Wright (1974). (c) Brot & Darmon (1970). (d) Allen & Cowking (1967); Van Steenwinkel (1969). (e) Boden, Davis, Stam & Wesselink (1973b). (f) Boden & Gibb (1974).

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The Topotaxy of the Solid-State Crystal Growth of the Spinel MgGa₂O₄ from Its Constituent Oxides*

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The topotaxy of the reaction of single crystals of periclase, MgO, and β-Ga₂O₃ to form the spinel MgGa₂O₄ was investigated by optical and X-ray diffraction techniques after reaction at 1600°C. Three different reaction couples were studied, namely the (001) face of β-Ga₂O₃ contacting the (001), (110) and (111) surfaces of MgO. The three-dimensional coherency of the oxygen arrangement and packing between each constituent oxide and the spinel reaction product was demonstrated. In both cases the close-packed oxygen planes in the spinel product were aligned parallel to the close-packed oxygen planes in the respective reactant. The topotaxies between the spinel product and the parent crystals were: (*a*) $(111)_{sp} \| (013)_{gal}$, $[1\bar{1}0]_{sp} \| [100]_{gal}$; (*b*) $(111)_{sp} \| (111)_p$, $[1\bar{1}0]_{sp} \| [1\bar{1}0]_p$. The data for the topotaxy of the spinel reaction product with respect to β-Ga₂O₃ is fully consistent with an earlier study of the precipitation of β-Ga₂O₃ from a spinel crystalline solution. This study verified a Wagner-type reaction mechanism where the close-packed oxygen anion structure remains essentially unchanged while the reaction proceeds by a counter diffusion of Mg²⁺ and Ga³⁺ ions through the spinel layer formed at the interface. This method of solid-state crystal growth for binary oxide systems at a temperature far below the solidus temperature ($\simeq 2000$°C) can find application in the growth of crystals that decompose or melt incongruently or that have an undesirable polymorph when solidified directly from the melt.

1. Introduction

The feasibility of single-crystal growth by solid-state reaction below the solidus temperature has recently been demonstrated by the authors (Katz, 1965; Katz

& Roy, 1970). Those results were the outgrowth of an earlier study of topotaxy in the solid-state precipitation of the β-Ga₂O₃ structure from a spinel host crystal, a MgGa₂O₄–Ga₂O₃ crystalline solution (Katz, 1965; Katz, Nicol & Roy, 1969*a*,*b*). This was the first instance of the prepicitation of a structure, other than the corundum type, from a spinel crystalline solution. In particular, monoclinic β-Ga₂O₃ (Kohn, Katz & Broder, 1957) was exsolved topotactically from a