

Structure and Packing Arrangement of Molecular Compounds. IV.* On Packing, Librational Motion and Orientational Disorder

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Problems of molecular libration and orientational disorder in several π -molecular compounds are attacked with the aid of semi-empirical non-bonded potential functions. A satisfactory correlation was found between the root-mean-squared amplitudes of libration and the results of potential calculations in ordered crystal structures. It is shown for several examples that indications of orientational disorder obtained by the present approach complement in a useful manner other methods of dealing with such disorder.

Introduction

Analysis of anisotropic atomic vibration tensors in terms of rigid-body motion parameters is by now an almost inseparable part of an adequate description of a structure composed of approximately rigid molecules. It is sometimes easy to give a qualitative interpretation of these parameters by considering the molecular shape and environment as related to the principal axes and eigenvalues of the rigid-body tensors. This has been done in a great number of cases and in our opinion, it must precede (wherever possible) any attempt at a detailed interpretation. However, if one wishes to go beyond stating that 'the largest amplitude of libration is associated with the direction of smallest inertia', which is often but not always the case, the situation frequently becomes complicated. During investigations of molecular compounds carried out in this laboratory the problem of interpreting the results of thermal motion analysis received some attention, and it is the purpose of this communication to describe the approach employed and to present some examples of its application.

The questions we posed ourselves, and which have arisen in many other crystallographic studies, can be summarized as follows.

- (a) Consideration of molecular shape and close approaches shows that the results of thermal motion analysis are consistent with the packing. Can this agreement be expressed quantitatively?
- (b) Is the observed thermal motion genuine or does it conceal orientational disorder?

Any attempt at providing answers involves mainly considerations of intermolecular forces although the question of disorder can also sometimes be settled with the aid of constrained refinement techniques (*e.g.* Bailey & Dahl, 1965).

In the present context we wish to consider the application of semi-empirical potentials of the Buckingham

and Lennard-Jones types to the above problems. The increasing number of successful crystallographic (*e.g.* Williams, 1972, 1973; Coiro, Giacomello & Giglio, 1971) and other applications of these potential functions makes their application to the above problems worth while before a more rigorous study, employing lattice dynamics (Pawley, 1967; Scheringer, 1972), is attempted.

Description of the calculation

The present application consists of simulating a postulated type of motion in the computer and evaluating the intermolecular interaction along the path of the motion. Thus, *e.g.*, in the important case of librational motion the pairwise interactions given by the expression

$$V(r) = a \exp(-br)/r^d - c/r^6 \quad (1)$$

which combines both types of potential (Giglio, 1969), are summed for each orientation of the molecule in question and a curve referred to below as a libration potential is constructed, assuming that the neighbouring molecules are stationary. This approach was employed by others (*e.g.* Craig, Mason, Pauling & Santry, 1965; Rietveld, Maslen & Clews, 1970) and will be discussed in some detail in the Appendix. Translation potentials can be constructed in an analogous manner.

For the calculation, atomic parameters and space-group operations are transformed to the inertial system of the molecule with the origin at the centre of mass and components of the unit vector about which rotation takes place are input along with range and intervals of rotation. Eigenvectors of the libration tensor and coordinate axes of the inertial system are usually the interesting rotation vectors. The rotation itself is performed with the aid of the relation

$$C_{\mathbf{k}}(\alpha)\mathbf{r} = \mathbf{k}(\mathbf{k} \cdot \mathbf{r})(1 - \cos \alpha) + \mathbf{r} \cos \alpha + (\mathbf{k} \times \mathbf{r}) \sin \alpha \quad (2)$$

(Lyubarskii, 1960), where \mathbf{k} is a unit vector along the rotation axis, \mathbf{r} is referred to an origin on the axis and α is an angle of clockwise rotation, looking along \mathbf{k} . The

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operator $C_k(\alpha)$ is much better suited to the problem than are Eulerian matrices. The parameters used with equation (1) for the various pairwise interactions were taken from Williams (1972) for C...C, C...H and H...H, from Giglio (1969) for O...O and from Kuan, Warshel & Schnepf (1970) for N...N non-bonded interactions. Additional heteronuclear interactions were parametrized by taking the geometrical mean of the relevant homonuclear interaction parameters. All parameters used here are summarized in Table 1.

Table 1. *The parameters for the potential functions*

The resulting potentials are expressed in kcal mol⁻¹.

Interaction	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
H...H	2171	3.74	24.39	0
C...C	71782	3.60	512.69	0
C...H	8503	3.67	111.82	0
O...O	259000	0	358.5	12
N...N	64155	3.64	402.7	0
O...H	23707	1.87	93.5	6
O...C	136350	1.80	428.7	6
O...N	128900	1.82	380.0	6
N...H	11802	3.69	99.1	0
N...C	67863	3.62	454.4	0

The examples which follow were chosen to illustrate the method as applied to results of usual thermal motion analyses and to cases of certain and suspected orientational disorder. The atomic coordinates were taken in most cases from published room-temperature structures. In the anthracene-7,7,8,8-tetracyanoquinodimethane (TCNQ) and naphthalene-tetracyanoethylene (TCNE) complexes the coordinates of the donors were evaluated from the published structures of anthracene (Mason, 1964) and naphthalene (Abrahams, Robertson & White, 1949). This had to be done since the reported dimensions of these molecules in their complexes were obviously and admittedly (Williams & Wallwork, 1967, 1968) distorted.

All interatomic intermolecular distances shorter than 8.0 Å were included in the calculations. The horizontal lines crossing all the potential curves are drawn at the height of 0.6 kcal/mole above the minima.

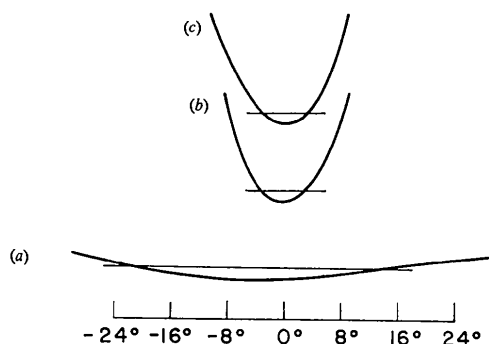


Fig. 1. Libration potentials of muconodinitrile. The corresponding libration r.m.s. amplitudes are: (a) 17.0, (b) 2.6 and (c) 2.2°.

Examples

Muconodinitrile

The librational motion observed in this structure (Filippakis, Leiserowitz & Schmidt, 1967) is among the largest reported, amounting to an amplitude of 17.0° about the long molecular axis. This behaviour is not unexpected in the case of this elongated dicyanobutadiene derivative but the magnitude of the libration is rather unusual. Fig. 1 shows the libration potentials obtained by rotating the molecule about the three eigenvectors of the published libration tensor. The correlation between the half-widths of the potential wells at a height of kT (0.6 kcal/mole) above the minima and the r.m.s. amplitudes of libration, shown in the figure, is indeed encouraging. It is however difficult to decide whether or not there is any appreciable internal libration about the central butadiene bond because this bond is nearly parallel to the long molecular axis. In any case, there is no indication of disorder. The thermal motion in this compound was also considered by Trueblood (1969) in his discussion of molecular dynamics in crystals.

TCNE-paracyclophane

In the investigation of this structure Bernstein & Trueblood (1971) found that the TCNE molecule exists in two perpendicular orientations about the normal to its plane. The relative occupancies of these orientations were found to be 0.75 and 0.25 by least-squares unconstrained refinements; Fig. 2(b) was constructed from their data by rotating the TCNE molecule about the best-plane normal. It shows, as expected, two minima 90° apart but the depth of the minima is nearly equal, whereby the deeper one (by 0.3 kcal/mole) corresponds to the 0.25 orientation, contrary to what was expected. Such a discrepancy may stem from neglect of interactions other than those accounted for by equation (1) as well as from the approximate nature of the calculation.

It appears from this and even more clearly from the following example of TCNE that neglect of interactions other than those on which the potential functions applied are based, probably precluded the correlation of the minima with their actual population.

Naphthalene complexes with TCNB and TCNE

The investigation of the molecular complex of naphthalene with 1,2,4,5-tetracyanobenzene (TCNB) (Kumakura, Iwasaki & Saito, 1967) showed that the structure is disordered in that the naphthalene molecules can occupy, with equal probabilities, two orientations relative to the acceptor. The centres of donor and acceptor overlap almost completely but the long axes of the two disordered donors deviate by ~18°, in opposite directions, from the long axis of the acceptor.

The results of potential-energy calculations as a function of the angle of rotation of naphthalene about its plane normal are shown in Fig. 3(a). There are in-

deed two minima at $+18^\circ$ and -18° , in good agreement with the results of the partially constrained refinement of Kumakura *et al.* (1967). The energy barrier separating the minima is about 3 kcal/mole high, which is consistent with the preference of the disordered structure at room temperature.

A very similar in-plane disorder follows from the energy calculations for naphthalene in the naphthalene-TCNE complex [Fig. 3(b)]. Two minima separated by about 34° are obtained, indicating the existence of two preferred orientations of naphthalene in the structure solved by Williams & Wallwork (1967). These authors concluded, on the basis of difference maps, that a slight disorder of this kind most probably exists in the structure. This point was taken up again by Herbstein (1971) who from an examination of isotropic temperature factors and recalculation of difference maps arrives at the same conclusion. It must also be pointed out that the separation of the minima, as can be judged from the difference maps, is only 15° .

In this complex we were also interested in the behaviour of the rotation potential of TCNE with respect to rotation about its plane normal. The reasons are (a) comparison with the disordered TCNE-paracyclophane (see above) and (b) the proximity of the in-plane moments of inertia of TCNE, *i.e.* the nearly square shape of the molecule. Fig. 2(a) shows that similar minima, 90° apart, are also obtained in this complex. However, Williams & Wallwork (1967) found no such indication, and only one minimum, apparently satisfying the geometrical requirements of the Diels-Alder reaction, is populated.

Anthracene complexes with TCNB and TCNQ

The in-plane vibrational behaviour of anthracene in its crystalline complexes with TCNB (Tsuchiya, Marumo & Saito, 1972) and with TCNQ (Williams & Wallwork, 1968) is very similar, the libration amplitudes about the molecular plane normal being 8.6° and 8.7° respectively.

Tsuchiya *et al.* (1972) tend to suspect the rather large libration amplitude of anthracene in the TCNB complex of camouflaging an orientational disorder. However, no definite conclusion was reached on this issue.

As far as the anthracene-TCNQ complex is concerned, there is no mention in the original paper (Williams & Wallwork, 1968) of possible disorder. However, such a possibility is suggested rather strongly by Herbstein (1971).

We have therefore tried to apply the present method to anthracene in these two complexes in order to see to what extent this quantitative packing consideration can help in clarifying problems of suspected disorder.

The results presented in Fig. 4 show two similar flat and broad potential wells corresponding to rotation of anthracene about its plane normal. The half-widths of the wells, at height of 0.6 kcal/mole, are $\sim 10^\circ$ and $\sim 12^\circ$ for the TCNB and TCNQ anthracene complexes respectively.

It appears that these results do not permit one to reach any definite conclusions as to the presence of disorder, but taken at their face value suggest an anharmonic behaviour and a loose packing of the donor.

In contrast to the relatively poorly resolved electron density map of anthracene (Tsuchiya *et al.*, 1972), the corresponding map of TCNB yielded accurately defined atomic positions. The thermal behaviour of TCNB, as reflected in the atomic anisotropic vibration parameters, does not reveal any exceptional features. The libration potentials and amplitudes of TCNB shown in Fig. 5 support the above impression.

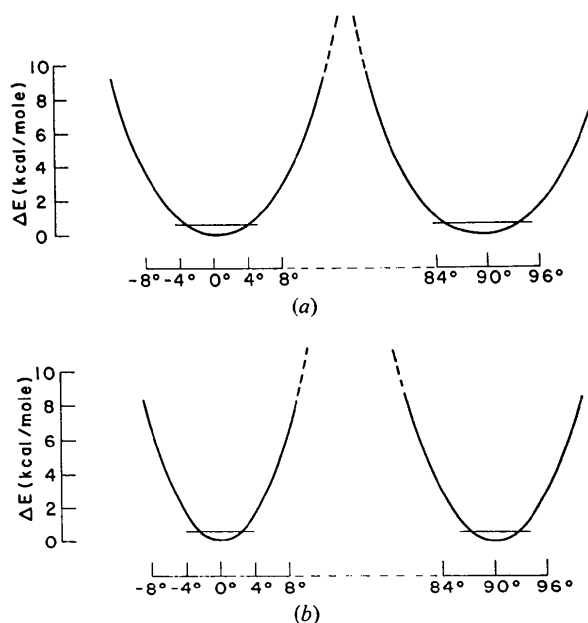


Fig. 2. Potential curves calculated by rotating the TCNE molecule about its plane normal (a) in TCNE-naphthalene complex (b) in TCNE-paracyclophane complex.

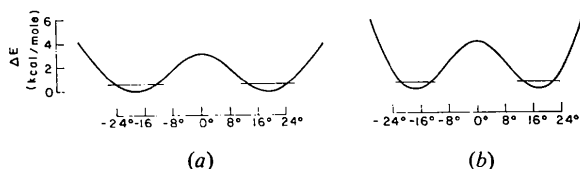


Fig. 3. Potential curves calculated by rotating the naphthalene molecule about its plane normal (a) in TCNB-naphthalene complex (b) in TCNE-naphthalene complex.

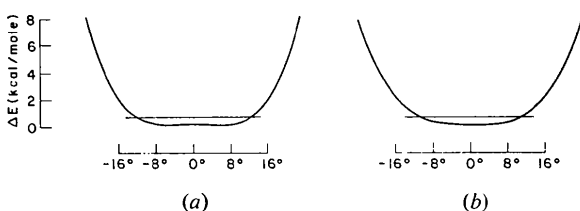


Fig. 4. Potential curves calculated by rotating the anthracene molecule about its plane normal (a) in TCNQ-anthracene complex (b) in TCNB-anthracene complex.

TCNQ in its π -molecular compounds

Rigid-body motion analyses of TCNQ in its complexes with anthracene (Williams & Wallwork, 1968), *N,N'*-dimethyldihydrophenazine, dibenzo-*p*-dioxin, phenazine and 1,10-phenanthroline (Goldberg & Shmueli, 1973*a, b, c, d* respectively) indicate that the librational behaviour of TCNQ is rather similar in all these complexes. The libration is anisotropic and the highest amplitude of libration is associated with a direction deviating by 0–7° from the long molecular axis of TCNQ. The libration about the other two molecular axes is much more restricted. Such a behaviour may

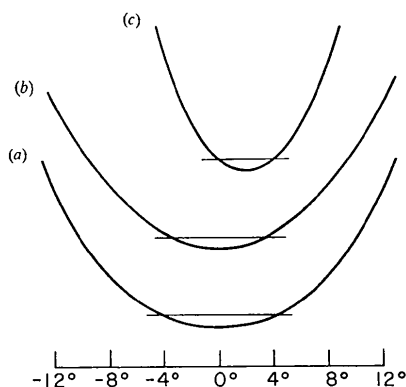


Fig. 5. Libration potentials of TCNB (in its complex with anthracene). The corresponding libration r.m.s. amplitudes are: (a) 5.4, (b) 2.6 and (c) 2.4°.

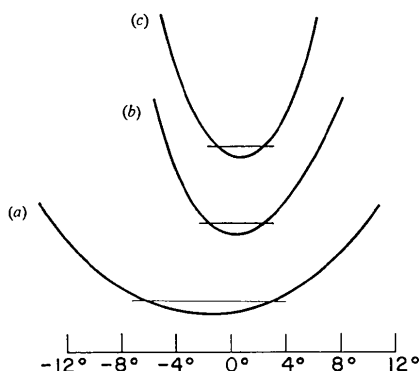


Fig. 6. Libration potentials of TCNQ (in its complex with phenazine). The corresponding libration r.m.s. amplitudes are: (a) 6.0, (b) 1.9 and (c) 0.0°.

stem from the elongated shape of the molecule and from the fact that in most cases the cyano groups are involved in short contacts which probably inhibit the motion about these directions. It is further noted that all these complexes form stacks and it can *a priori* be expected that rotations of the large acceptor (TCNQ) about the short axis and about the plane normal should be the more restricted ones.

We calculated the libration potentials corresponding to rotation of TCNQ about the three eigenvectors of the tensor of libration in each of these compounds. The results, given in terms of the widths of the corresponding potential wells ($\Delta\phi$) at the height of 0.6 kcal/mole above the minimum, are compared with the relevant libration amplitudes in Table 2.

The correlation between the quantities shown in Table 2 is encouraging with the exception of the phenazine complex. Although the results of thermal-motion analysis in this compound appear to be very inaccurate since a zero libration amplitude is meaningless, the present calculations show (Fig. 6) that this libration (about the direction close to the short molecular axis) corresponds to a very narrow potential well, *i.e.* to a strongly inhibited type of motion. The variations within the series of results shown in Table 2 may, on the other hand, be attributed in part to the different detailed environments of the TCNQ molecule in these complexes.

Libration potentials of an ordered donor

As a last example it is desirable to present the results for a donor in a structure in which there is no indication of disorder. Among TCNQ complexes mentioned in the last paragraph the complex with *N,N'*-dimethyldihydrophenazine is almost certainly ordered and the vibrational behaviours of the donor and the acceptor are similar (Goldberg & Shmueli, 1973*a*). The dependence of the libration potentials on the rotation about the principal axes of **L** is shown in Fig. 7 along with the r.m.s. amplitudes of libration.

This example, as well as those illustrated by Figs. 1, 5 and 6, was chosen in order to illustrate the correlation of potential calculations and results of rigid-body motion analysis.

Discussion

The examples presented above show that semi-empirical potential functions are a valuable tool in packing

Table 2. Libration amplitudes and widths of libration potentials for TCNQ

Compound Space group	Anthracene -TCNQ <i>C</i> 2/ <i>m</i>			DMPH-TCNQ <i>C</i> <i>m</i>			PHT-TCNQ <i>P</i> 2 ₁ / <i>n</i>			DPDO-TCNQ <i>P</i> 2 ₁ / <i>c</i>			Phenazine-TCNQ <i>P</i> $\bar{1}$		
	$\sqrt{\omega_i^2}$	$\Delta\phi$	<i>D</i>	$\sqrt{\omega_i^2}$	$\Delta\phi$	<i>D</i>	$\sqrt{\omega_i^2}$	$\Delta\phi$	<i>D</i>	$\sqrt{\omega_i^2}$	$\Delta\phi$	<i>D</i>	$\sqrt{\omega_i^2}$	$\Delta\phi$	<i>D</i>
1	5.9°	10.0°	~ <i>L</i>	5.4°	8.0°	~ <i>L</i>	6.7°	12.0°	~ <i>L</i>	5.8°	9.0°	~ <i>L</i>	6.0°	9.0°	~ <i>L</i>
2	3.1	5.0	<i>M</i>	2.7	6.5	~ <i>N</i>	2.2	4.5	~ <i>M</i>	2.7	5.0	~ <i>N</i>	1.9	3.5	~ <i>N</i>
3	2.3	4.0	~ <i>N</i>	2.0	4.0	<i>M</i>	2.0	3.5	~ <i>N</i>	1.6	3.5	~ <i>M</i>	0.0	3.0	~ <i>M</i>

ω_i^2 is the *i*th eigenvalue of the observed tensor of libration. $\Delta\phi$ is the width of the potential well at height 0.6 kcal/mole above the minimum. *D* is a symbol denoting the molecular axis to which the *i*th eigenvector of the libration tensor is closest; *L*: long axis, *M*: short axis, *N*: normal to molecular plane. Abbreviations: DMPH: *N,N'*-dimethyldihydrophenazine, PHT: 1,10-phenanthroline, DPDO: dibenzo-*p*-dioxin, TCNQ: 7,7,8,8-tetracyanoquinodimethane.

considerations concerning a solved structure as well as an aid in gaining more insight into the average dynamic behaviour of the molecule in question. In fact, in cases of reasonable thermal motion analyses a good correlation was observed between the r.m.s. libration amplitudes and the results of libration potential calculations. Moreover, a narrow (wide) libration potential is an evidence of tight (loose) packing and often a better one than a given set of short contacts. Therefore, it appears to us that the present approach, used in conjunction with a rigid-body motion analysis, usefully supplements conventional qualitative packing considerations. The above may not hold for structures in which strong interactions, not accounted for by the potential functions in Table 1, are present (*e.g.* hydrogen-bonded or ionic crystals).

The applicability to problems of orientational disorder is obvious from the above examples. However, it should be pointed out that the height of the barrier between two minima in a potential curve is sensitive to the choice of parameters and conclusions based on barriers of the order of kT (0.6 kcal/mole at room temperature) should be regarded with care. The results presented above for the naphthalene-TCNE complex (Williams & Wallwork, 1967) were used by us as a starting point for a constrained refinement of this disordered structure. These calculations will be reported elsewhere.

The above approach cannot be regarded as an accurate interpretative tool because many factors such as charge transfer energy, electrostatic and other long-range interactions are left out to an unknown extent. The potential functions used were fitted (Williams, 1966, 1967; Kuan *et al.*, 1970) mainly to structures in which many of the above interactions exist but their contribution may be different in each case. In addition, the assumption of uncorrelated motion, which is probably not too severe in the neighbourhood of the equilibrium position, certainly breaks down for large deviations from equilibrium and hence the values of energy in the region of high repulsion are probably grossly erroneous.

It would be interesting to extend the present approach to cases of significant screw motion where reliable screw tensors are available.

APPENDIX

Let atom i belong to the molecule of which the motion is to be simulated and let atom j belong to a neighbouring molecule. Further, let the displacement of atom i from its equilibrium position due to the motion which we simulate be δ , this being a small fixed known displacement, and let the instantaneous displacement of atom j from its equilibrium position be \mathbf{u} . The instantaneous interaction vector for this situation is therefore

$$\mathbf{r}_{ij} = \mathbf{r}_j + \mathbf{u} - \mathbf{r}_i - \delta \equiv \mathbf{r}_{ij} + \mathbf{u} - \delta. \quad (1)$$

Expanding the interatomic potential in a Taylor

series about the equilibrium interatomic vector \mathbf{r}_{ij} and dropping the subscripts, we get

$$\begin{aligned} V(|\mathbf{r}'|) &= V(|\mathbf{r}|) + \frac{\partial V}{\partial x_k} (u_k - \delta_k) + \frac{1}{2} \frac{\partial^2 V}{\partial x_k \partial x_l} (u_k - \delta_k) \\ & (u_l - \delta_l) + \dots = V(|\mathbf{r}|) + \frac{\partial V}{\partial x_k} (u_k - \delta_k) + \frac{1}{2} \frac{\partial^2 V}{\partial x_k \partial x_l} \\ & (u_k u_l + \delta_k \delta_l - u_k \delta_l - \delta_k u_l) + \dots \end{aligned} \quad (2)$$

where x_k , u_k and δ_k , $k=1,2,3$ are cartesian components of the vectors \mathbf{r}_{ij} , \mathbf{u} and δ respectively and the summation convention is employed.

In order to average (2) over all probable values of the displacement \mathbf{u} of atom j it is necessary to know in what way the probability distribution of \mathbf{u} depends on δ , *i.e.* we have to know in what way the atoms i and j are coupled. Neglecting this correlation we obtain for the average, assuming that $\partial V / \partial x_k = 0$,

$$\langle V(|\mathbf{r}'|) \rangle = V(|\mathbf{r}|) + \frac{1}{2} \frac{\partial^2 V}{\partial x_k \partial x_l} [\langle u_k u_l \rangle + \delta_k \delta_l] + \dots \quad (3)$$

We can regard (3) as a sum of the potential of atom i at equilibrium in the force field of its vibrating neighbour j :

$$V(|\mathbf{r}|) + \frac{1}{2} \frac{\partial^2 V}{\partial x_k \partial x_l} \langle u_k u_l \rangle + \dots$$

and of a term which arises from the displacement of atom i from its equilibrium position:

$$\frac{1}{2} \frac{\partial^2 V}{\partial x_k \partial x_l} \delta_k \delta_l. \quad (4)$$

Therefore, if correlation is neglected, the average motion of atom j merely influences the potential of atom i at the starting point of its simulated motion, *i.e.* at $\delta=0$. It follows that in the small displacement approximation it is only necessary to evaluate equation (4) if the absolute value of the lattice energy is of no particular interest. However, in the calculations described above we evaluate $V(x_k - \delta_k)$ exactly rather than

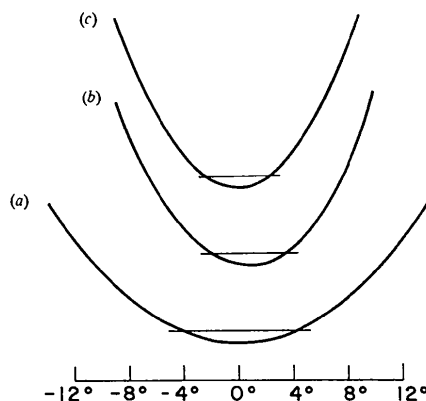


Fig. 7. Libration potentials of DMPH (in its complex with TCNQ). The corresponding libration r.m.s. amplitudes are: (a) 5.5, (b) 2.2 and (c) 2.0°.

by expanding it and terminating the series at the quadratic term.

Hence the stationary neighbour assumption is equivalent to the assumption of uncorrelated motion and implies an incorrect value of the energy at the starting point of the motion.

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* In Goldberg & Shmueli (1973a) there is an error in the legend to Table 3. Instead of *Fractional atomic coordinates* ($\times 10^4$) the legend should read *Fractional atomic coordinates of the heavy atoms* ($\times 10^4$) and of the hydrogen atoms ($\times 10^3$).

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The Structure of *anti*-Tricyclo[4,2,2,0^{2,5}]deca-3,9-diene-7,8-*endo*-dicarboxylic Anhydride

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The crystal and molecular structure of the title compound, $C_{12}H_{10}O_3$, has been determined by direct methods and refined by full matrix least-squares calculations. The crystals are monoclinic, space group $P2_1/c$, with $a = 6.385$ (1), $b = 21.922$ (2), $c = 6.622$ (1) Å, $\beta = 91.76$ (2)°, $Z = 4$. Intensities for 1487 independent reflexions were collected visually from Weissenberg photographs. The final R for 1010 observed reflexions is 0.088. Within experimental error the molecule has symmetry m . The geometry is in close agreement with the results found for bicyclo[2,2,2]octene-2,3-*endo*-dicarboxylic anhydride. The anhydride group is significantly non-planar as in other derivatives. The anisotropic temperature factors of the heavier atoms can be accounted for by a Schomaker–Trueblood rigid-body treatment; on this basis, corrections to the observed bond distances are about 0.006 Å.

Introduction

The structure of *anti*-tricyclo[4,2,2,0^{2,5}]deca-3,9-diene-7,8-*endo*-dicarboxylic anhydride (TRIC) has been determined as part of a systematic study of a series of chemically related compounds (Destro, Filippini, Gramaccioli & Simonetta, 1969, 1971; Filippini, Gramaccioli, Rovere & Simonetta, 1972).

The knowledge of an accurate experimental conformation of these molecules was considered necessary in view of theoretical work we are carrying out on an

extensive group of rigid molecules with internal strain (Gramaccioli, Simonetta & Suffritti, 1973; Filippini, Gramaccioli, Simonetta & Suffritti, 1973).

Experimental

Crystals of TRIC were obtained from reaction of cyclooctatetraene with maleic anhydride and recrystallized from benzene/light petroleum (Reppe, Schlichting, Klager & Toepfel, 1948).

Weissenberg photographs indicated the crystals to