

be incorporated in a table for use in the least-squares refinement procedure and only a single parameter need be used for the estimation of σ^2 .

Conclusion

It has been demonstrated that the major cause of covariance problems in the least-squares refinement of crystal structures has been caused by the use of incorrect least-squares equations and the insistence on weighting according to counting statistics. With the approach outlined in this paper it is possible to refine a centrosymmetric structure in a non-centrosymmetric space group. In such an application, if one starts from exactly centrosymmetric coordinates, refinement proceeds to a false minimum since the structure will stay centrosymmetric. However, if one is trying to test the validity of a structural parameter defining a rigid group of atoms, for example the angle which a plane of atoms makes with a symmetry axis, then an initial perturbation involving this parameter may be tested.

The problem of false minima is a necessary part of refining a crystal structure with a fixed weighting scheme (Rae, 1974). It is unrealistic to rely on the redefinition of the phase of $(F_o)_h$ to enable refinement to proceed. The contribution to the weighting scheme of $\langle |E_2|^2 \rangle$ and $\langle |E_3|^2 \rangle$ far outweighs the counting statistic contribution $\langle |E_1|^2 \rangle$ in all but the final refinement cycle since $\sum_h w_h |\Delta_i|^2 \gg 1$ with $w_h^{-1} = \langle |E_1|^2 \rangle$.

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On the Libration of 9, 10-Anthraquinone at Five Temperatures

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Potential energy profiles corresponding to libration of 9,10-anthraquinone about its molecular axes were constructed for the five structures derived from data which were collected at -170 , -112 , -72 , -12.5 and 20.5°C [Lonsdale, Milledge & El Sayed (1966). *Acta Cryst.* 20, 1–13]. These profiles were represented by fourth-degree least-squares polynomials, whereafter r.m.s. libration amplitudes and rigid rotator frequencies of 9,10-anthraquinone were evaluated in the quadratic approximation. The temperature dependence of the calculated quantities is in most cases close to that of the observed ones thus reproducing, by comparison with observed Raman frequencies, the pseudoharmonic behaviour of 9,10-anthraquinone. Calculated r.m.s. libration amplitudes are only qualitatively comparable to the experimental ones and appear to be somewhat too low. The present representation of energy profiles makes it possible to estimate conveniently the contribution of anharmonicity to the profile shape.

Introduction

The availability of semiempirical potential functions enables one to construct approximate potential energy

The point is made that the refinement is only as good as the weighting scheme. Because data with $|(F_o)_h| > |(F_c)_h|$ are weighted preferentially, scale constants should be refined on their own in a separate least-squares cycle in the initial refinement stages with $\langle |F_h|^2 \rangle = \sum_i f_i^2$ where f_i is the scattering factor for the i th atom in the crystal. The better the weighting scheme the more rapid and correct the convergence. The only extra computing time involved is in the actual multiplication of derivatives to form the matrix.

When refinement is complete $w_h^{1/2} \Delta_h$ values will enable a probability distribution to be evaluated. By multiplying w_h by the probability associated with the value of $w_h^{1/2} \Delta_h$ it should be possible to improve the refinement since the variance associated with the square of a normal distribution is half the variance associated with the normal distribution function itself.

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profiles corresponding to a specified type of molecular motion in the crystal. Such profiles were first shown by Shmueli & Goldberg (1973) to be a valuable tool for a critical examination of the librational motion indicated by an analysis of anisotropic thermal parameters. Thus, in cases of well behaved librational motion nearly parabolic potential wells were obtained while most

cases of suspiciously large libration were shown to correspond either to a probable orientational disorder or to an anharmonic behaviour of the motion.

The orientational disorder of naphthalene in its crystalline complex with tetracyanoethylene (Williams & Wallwork, 1967), indicated by the above study, was later confirmed by a constrained refinement of this structure (Shmueli & Goldberg, 1974).

The results of these calculations rest on the assumption that the environment of the molecule, the rotation of which is being simulated, is stationary. This assumption, which is in practice equivalent to the neglect of coupled molecular motion (Shmueli & Goldberg, 1973), is obviously a rather drastic one. However, encouraging correlations of the widths of such potential wells and corresponding r.m.s. libration amplitudes, as obtained in the above study, make it interesting to explore further the reliability of this simple approach.

In the present application five structures of 9,10-anthraquinone (Lonsdale, Milledge & El Sayed, 1966 *a, b*) are considered which correspond to data collected

at -170 , -112 , -72 , -12.5 and 20.5°C . For a similar temperature range, Raman spectroscopic results on 9,10-anthraquinone are also available (Miyazaki & Ito, 1973). It is intended, in this study, to calculate energy profiles corresponding to libration of 9,10-anthraquinone about its molecular axes and to represent them by polynomials in order to make an approximate quantitative treatment of these profiles feasible. The points of interest are: (a) a classical calculation of root-mean-squared libration amplitudes, (b) an estimation of the anharmonic contribution to the energy profile and (c) calculation of average frequencies of libration of the compound about the given directions.

It is hoped that this study will afford some insight into the approximation of fixed neighbours on which the calculations are based. Moreover, the use of results pertaining to several temperatures should make it possible to see whether the present method is sensitive enough to reflect the small structural changes (Lonsdale *et al.*, 1966) and the red shift of the Raman frequencies with increasing temperature (Miyazaki & Ito, 1973) which were observed in this compound.

Calculations and results

A schematic drawing of the 9,10-anthraquinone molecule is shown in Fig. 1. Crystal data and structural parameters were taken from the article of Lonsdale *et al.* (1966) and molecular tensors of inertia with their principal axes were evaluated for the five structures. The atomic coordinates were then transformed to the inertial systems of the molecule for subsequent calculations. Evaluation of energy profiles was carried out in exactly the same manner and with the same parameters

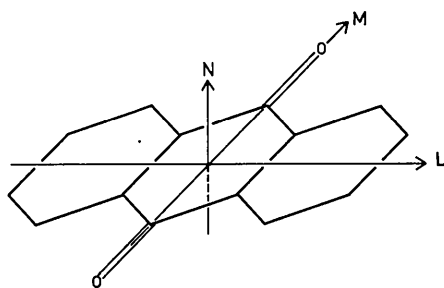


Fig. 1. The 9,10-anthraquinone molecule.

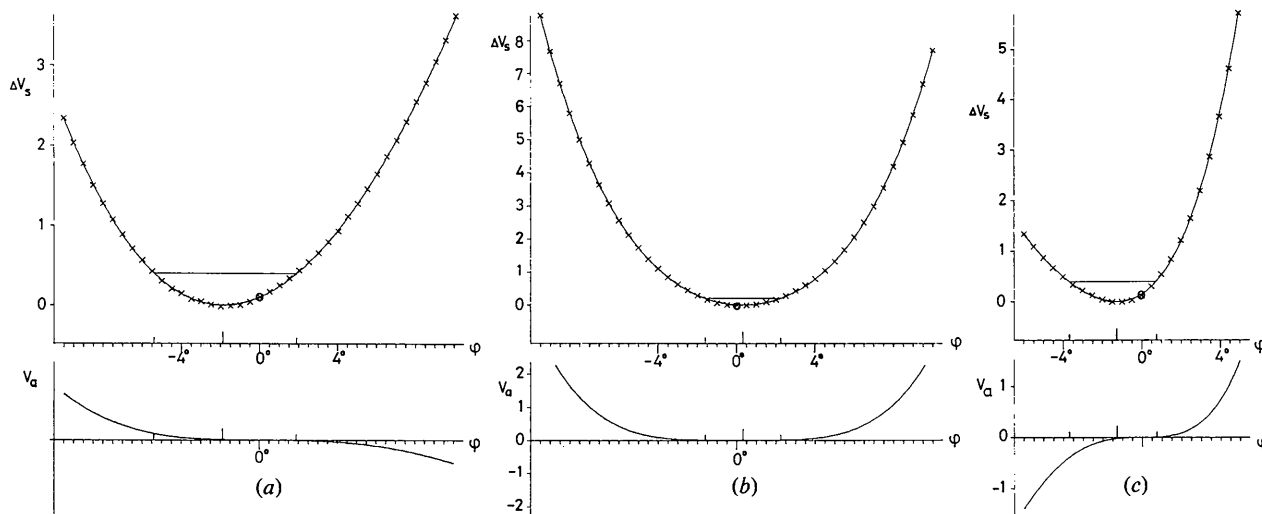


Fig. 2. Rotation potentials of 9,10-anthraquinone at -72°C . The upper graphs show the fitted relative energy $\Delta V_s = V_s - V_{\min}$ and the calculated energy values (\times) as a function of the angle of rotation, where V_s is given by equation (2) and V_{\min} is its minimum value. The lower graphs show the anharmonic part V_a [equation (3)] as a function of the angle of rotation. The horizontal lines are drawn at the height kT above the minima and the three marks above each of the ϕ axes denote the orientations corresponding to $\Delta V_s = kT$ and to $\Delta V_s = 0$. The energy is given in Kcal mole^{-1} units and angles are marked each 0.5° . The zero degree mark corresponds to the observed structure. Note that the scale of energy is not the same in the three graphs. (a) Rotation about L , (b) rotation about M , (c) rotation about N .

of potential functions as was described by Shmueli & Goldberg (1973). All interatomic distances not exceeding 7 Å, were included in the summation of atom-atom interactions in the present calculations. The 15 sets of energy values, obtained for rotation of anthraquinone about the *L*, *M* and *N* axes for the five temperatures were smoothed by least-squares polynomials of the form

$$V_s(\varphi) = a + b\varphi + c\varphi^2 + d\varphi^3 + e\varphi^4. \quad (1)$$

Equation (1) permits a separate estimation of the harmonic and most important anharmonic contributions to the energy profile. The anharmonic part was calculated as

$$V_a(\varphi) = d\varphi^3 + e\varphi^4. \quad (2)$$

Fig. 2 shows the results of these calculations for the structure determined from -72°C data. The three pairs of graphs shown are representative of those obtained for other temperatures insofar as the overall shapes of all the graphs obtained for a given direction and the deviations of their minima from the position corresponding to the observed structure are concerned. These deviations, averaged over the different temperatures for the *L*, *M* and *N* rotations, are -2.05 , 0.36 and -1.42° , the mean deviations from these values being 0.26 , 0.08 and 0.19° respectively.

Mean-squared libration amplitudes were evaluated assuming a classical Maxwell-Boltzmann distribution of the potential energy of the molecule which is supposed to librate according to the potential $V(\varphi) = c\varphi^2$, where *c* has the same meaning as in (1).

Thus

$$\langle \varphi^2 \rangle = \frac{\int_{-\infty}^{\infty} \varphi^2 \exp(-c\varphi^2/kT) d\varphi}{\int_{-\infty}^{\infty} \exp(-c\varphi^2/kT) d\varphi} = \frac{kT}{2c}. \quad (3)$$

Writing the above potential as $V(\varphi) = \frac{1}{2}(2c)\varphi^2$, the frequency of a rigid rotator representing the molecule and hindered by this potential is given by

$$\nu_R = \frac{1}{2\pi} \left(\frac{2c}{I} \right)^{1/2} \quad (4)$$

where *I* is the relevant moment of inertia. Combining (3) and (4) we obtain

$$\langle \varphi^2 \rangle = \frac{kT}{4\pi^2 I \nu_R^2}$$

which is the well-known equation of Cruickshank (1956) relating mean squared libration amplitude of a rigid molecule with the corresponding frequency of its libration.

These results are summarized in Table 1. In addition to the quantities defined above, the table also contains the experimental libration amplitudes of anthraquinone (Lonsdale *et al.*, 1966), referred to the molecular axes, the goodness of fit of the least-squares polynomials

to the calculated energy profiles and the half-widths of the wells at heights *kT* above their minima.

Table 1. Summary of the results

Symbols: *T* – temperature in K; $\langle (\Delta V)^2 \rangle^{1/2}$ – r.m.s. discrepancy of fit of the least-squares polynomial (1) to the calculated energy values, in kcal mole $^{-1}$; $c[\sigma(c)]$ – coefficient of φ^2 in (1) with standard deviation in units of the last decimal place, in kcal mole $^{-1}$ deg $^{-2}$; $\langle \varphi^2 \rangle^{1/2}$ – r.m.s. libration amplitude calculated from (3), in degrees; $\omega^{1/2}$ – experimental r.m.s. libration amplitude (Lonsdale *et al.*, 1966), in degrees; $\Delta\varphi_{1/2}$ – half-width of the well at the height *kT* (*k* – Boltzmann's constant) in degrees; ν_R – rigid rotator frequency calculated from (4), in cm $^{-1}$.

Rotation about *L*, φ : -10° to $+10^\circ$ in steps of 0.5°

<i>T</i>	$\langle (\Delta V)^2 \rangle^{1/2}$	$c[\sigma(c)]$	$\langle \varphi^2 \rangle^{1/2}$	$\omega_{11}^{1/2}$	$\Delta\varphi_{1/2}$	ν_R
103	0.015	0.0300 (3)	1.85	3.00	2.49	74
161	0.010	0.0266 (1)	2.45	4.04	3.26	70
201	0.011	0.0274 (1)	2.70	4.23	3.64	71
260.5	0.015	0.0252 (3)	3.20	4.52	4.32	68
293.5	0.013	0.0208 (2)	3.74	5.41	4.81	61

Rotation about *M*, φ : -10° to $+10^\circ$ in steps of 0.5°

<i>T</i>	$\langle (\Delta V)^2 \rangle^{1/2}$	$c[\sigma(c)]$	$\langle \varphi^2 \rangle^{1/2}$	$\omega_{22}^{1/2}$	$\Delta\varphi_{1/2}$	ν_R
103	0.021	0.1178 (4)	0.93	0	1.31	93
161	0.029	0.1120 (5)	1.20	0.97	1.68	91
201	0.036	0.1069 (6)	1.37	1.60	1.92	89
260.5	0.034	0.0983 (6)	1.62	0.85	2.26	85
293.5	0.032	0.0890 (6)	1.81	1.16	2.51	81

Rotation about *N*, φ : -6° to $+5^\circ$ in steps of 0.5°

<i>T</i>	$\langle (\Delta V)^2 \rangle^{1/2}$	$c[\sigma(c)]$	$\langle \varphi^2 \rangle^{1/2}$	$\omega_{33}^{1/2}$	$\Delta\varphi_{1/2}$	ν_R
103	0.014	0.1151 (10)	0.94	1.26	1.54	78
161	0.017	0.1175 (12)	1.17	1.98	2.02	79
201	0.018	0.1129 (13)	1.33	2.17	2.23	77
260.5	0.015	0.1050 (11)	1.57	2.67	2.67	74
293.5	0.018	0.1017 (13)	1.69	3.18	3.04	73

Discussion

The shapes of the smoothed energy profiles in the neighbourhood of their minima depend mainly on the quadratic term in (1), the contribution of the cubic and quartic terms being in general much smaller. As can be seen from Table 1 the dominant coefficient *c* decreases in most cases with increasing temperature which corresponds to a gradual flattening of the parabolic parts of the wells.

There is a similar but less pronounced tendency in the temperature dependence of the coefficients of the cubic and quartic terms in (1). For example, the values of *d* for the moderately anharmonic *L* rotation potentials are -46 , -42 , -44 , -43 and -40×10^{-5} kcal mole $^{-1}$ deg $^{-3}$ for the temperatures 103, 161, 201, 260.5 and 293.5 K respectively, while the values of *e* for the *M* rotation and for the same temperatures as above, are 62, 60, 57, 55 and 53×10^{-5} kcal mole $^{-1}$ deg $^{-4}$.

This behaviour of *c* is qualitatively consistent with the pseudoharmonic theory (Willis, 1969) which predicts a decrease of force constants and a corresponding decrease of frequencies with increasing temperature. The frequencies of libration of 9,10-anthraquinone, shown in Table 1, also follow this expected pattern and

their temperature dependence is similar to that observed by Miyazaki & Ito (1973). The values of the rigid rotator frequencies lie well within the range of the observed ones. Thus the values calculated for rotation about the M and L axes (Table 1) are remarkably close to the observed frequency ranges 92–82 cm^{-1} and 73–66 cm^{-1} (Miyazaki & Ito, 1973) respectively, the corresponding temperature range being 83–299 K. The polarizations of these two bands, as calculated by Miyazaki & Ito (1973), deviate by about 40° from the M and L axes and are closer to these directions than the polarizations assigned to the other three frequency bands (Table 1; Miyazaki & Ito, 1973). Nevertheless, it is difficult to draw quantitative conclusions from this apparent agreement of frequencies. Thus, the rigid rotator frequencies are only average values corresponding to the given three directions and moreover, as will be shown below, it is reasonable to expect that the curvatures of the wells (and hence the force constants) are exaggerated by the assumption of stationary neighbours. The correct average frequencies might therefore be somewhat lower.

The r.m.s. libration amplitudes calculated from (3) increase with increasing temperature for all three axes of libration considered (Table 1). However, their temperature dependence is stronger than a proportionality to $T^{1/2}$ owing to the above-mentioned pseudo-harmonic property of the coefficient c . These r.m.s. libration amplitudes can be only qualitatively compared to the experimental ones shown in Table 1. Apart from discrepancies which may be due to the assumption of stationary neighbours and to the admitted moderate accuracy of the experimental thermal parameters (Lonsdale, Walley & El Sayed, 1966), there are two factors which complicate the comparison.

Firstly, the experimental libration amplitudes about the L axes are most probably affected by the independent out-of-plane motion of the oxygen atoms (Lonsdale *et al.*, 1966) which, when ignored, probably exaggerates the apparent rigid libration ω_{11} . It is seen from Table 1 that the $\omega_{11}^{1/2}$ values are in fact consistently larger than the corresponding $\langle\varphi^2\rangle^{1/2}$ values. The influence of the anharmonic contribution appears to be rather small in this case [Fig. 2(a)]. Secondly, the considerable anharmonicity of the N -rotation potentials [Fig. 2(c)] is certainly responsible in part for the discrepancy between $\omega_{33}^{1/2}$ and the corresponding $\langle\varphi^2\rangle^{1/2}$ values (Table 1). The discrepancy between these values increases with temperature, which may perhaps be due in part to an absorption of the anharmonicity in the (formally quadratic) thermal parameters. It is worthwhile to note in this connexion that a calculation of energy profiles may be a useful guide when considering introduction of higher cumulants into the temperature factor (Johnson, 1969). The results for rotation about M cannot be conveniently compared with the corresponding experimental libration amplitudes because of the somewhat erratic behaviour of the latter.

Although the magnitudes of $\langle\varphi^2\rangle^{1/2}$ seem to be qualitatively reasonable, it is believed that they are somewhat too low even if the above-mentioned complications could be accounted for. As can be seen from equation (3), $\langle\varphi^2\rangle^{1/2}$ corresponds to the half width of a parabolic well at the height $kT/2$ above its minimum. On the other hand, the $\Delta\varphi_{1/2}$ values (Table 1), *i.e.* half-widths of the wells at the heights KT above minimum agree better with $\omega_{11}^{1/2}$ (while being consistently lower) and with $\omega_{33}^{1/2}$. This arbitrary criterion also appears to compare reasonably well with libration amplitudes in other applications (Shmueli & Goldberg, 1973). Since for a parabolic well $\langle\varphi^2\rangle^{1/2} = \Delta\varphi_{1/2}/\sqrt{2}$, it follows that $\langle\varphi^2\rangle^{1/2}$, which is an approximate but proper measure of an r.m.s. libration amplitude, appears to be an underestimate. This indication is in agreement with the results of a recent lattice-dynamical study by Cerrini & Pawley (1973) who compare rigid-body tensors derived from the Born-von Karman (correlated motion) and Einstein (independent motion, *i.e.* in practice, fixed neighbours) models with experimental values. The quantities derived by these authors from the Einstein model are in most cases underestimates of the experimental rigid-body-motion parameters of pyrene, obtained from neutron data. It is intended to examine further, by the present method, the extent of misrepresentation of the energy profiles by the stationary-neighbours assumption, performing the appropriate calculations for compounds with reliable thermal parameters and accurate positions of hydrogen atoms and comparing the results, where possible, with lattice-dynamical calculations.

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