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Analysis of thermal vibrations in crystals: a warning.

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In crystal-structure determinations where experimental precision permits it is now usual to determine the deviation from the 'normal' (spherical) atomic scattering factor for each atom in the form

$$\exp -(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{23}kl+b_{31}lh)\ .$$

This factor, which may be due to thermal vibration, zero-point energy, bond anisotropy, etc., and may also include various non-random errors of observation or neglected corrections for absorption, dispersion, etc., is often referred to in a general way as representing the thermal ellipsoid for the atom in question, and its shape is discernable on Fourier projections or sections.

Assuming that the term is mainly due to vibrational effects, the b_{ij} may be interpreted in two ways.

(1) They may be used to determine the magnitudes and directions of the principal axes of *atomic* vibrations.

(2) They may be used to compute the values and directions of the three principal translational and three principal librational rigid-body vibrations of the *molecule*, all non-rigid-body vibrations being neglected.

We have shown elsewhere that neglect of intramolecular (non-rigid-body) vibrations is not justified. These may, in fact, be quite large compared with the rigid-body vibrational amplitudes. The problem of devising a programme by means of which both rigid-body and non-rigid-body vibrations may be computed directly from the b_{ij} is one that has not, as far as we know, been attempted, even for the simplest cases.

We have tackled the problem in another admittedly inadequate, but suggestive way (Lonsdale & Milledge, 1959, 1960; Lonsdale, Milledge & Rao, 1960; Lonsdale, 1961). We use the principal mean-square amplitudes for the atomic thermal ellipsoids to limit the possible values of the various (supposedly phase-independent) molecular rigid-body vibrations and then see what atomic (non-rigid-body) vibrations are left over at various temperatures, and whether these constitute reasonable proper distortional vibrations of the molecule as a whole.

In the course of our studies we have encountered two difficulties of which (to judge from recent publications) many workers are unaware.

(1) Independent sets of data may lead to sets of b_{ij} coefficients which apparently agree quite well, but which give very different sets of atomic thermal ellipsoids (different in both magnitude and direction of the principal axes). This is because the B_{ij} and their directions are extremely sensitive to the cross-terms $b_{ij}(i \neq j)$. *Except by taking two or more sets of independent experimental data and refining them separately, the extent of the uncertainty thus involved is not likely to be realized.*

(2) When the rigid-body vibrations are determined directly from the b_{ij}, it is usually assumed that any deviations of the principal vibrational translation and libration axes from the 'natural molecular axes' are due to 'experimental error'. In fact, the deviations (except for very symmetrical crystals, where averaging would in any case eliminate them) of the translational vibration axes from, for example, the L, M, N directions of a symmetrical aromatic molecule in a low-symmetry space group are likely to be *real*. Whether determination of those directions from the b_{ij} or from the thermal atomic ellipsoids will give the real values or will only give a computational artifact is another matter. Again it is likely that only examination and comparison of two or more independent sets of experimental data will indicate the degree of precision required for a trustworthy answer.

1. Conversion of the b_{ij} to directions and magnitudes of the atomic B_{ij}

We have recently compared two new sets of data for anthracene, both limited, but agreeing with each other to about $R_o = 0{\cdot}035$ in their common $|F|$s:

(*a*) 251 $F(hkl)$ with $\sin\theta < 0{\cdot}53$, observed by D. C. Phillips and refined by R. A. Sparks.

Table 1. *Two independent sets of b_{ij} for anthracene*

Atom		b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{31}
C(*A*)	(*a*)	0·0245 (12)	0·0412 (20)	0·0146 (7)	0·0003 (25)	−0·0024 (18)	0·0221 (18)
	(*b*)	0·0271	0·0444	0·0136	0·0012	−0·0044	0·0225
C(*B*)	(*a*)	0·0206 (10)	0·0328 (16)	0·0132 (7)	0·0032 (20)	−0·0013 (18)	0·0176 (15)
	(*b*)	0·0197	0·0317	0·0116	−0·0021	−0·0045	0·0147
C(*C*)	(*a*)	0·0150 (10)	0·0234 (15)	0·0107 (6)	−0·0002 (18)	−0·0023 (17)	0·0127 (15)
	(*b*)	0·0150	0·0242	0·0124	−0·0005	−0·0002	0·0147
C(*D*)	(*a*)	0·0160 (11)	0·0251 (14)	0·0129 (7)	0·0027 (19)	−0·0020 (17)	0·0146 (15)
	(*b*)	0·0158	0·0241	0·0130	−0·0010	−0·0062	0·0154
C(*E*)	(*a*)	0·0161 (10)	0·0204 (14)	0·0134 (7)	0·0007 (18)	0·0004 (14)	0·0178 (16)
	(*b*)	0·0144	0·0241	0·0126	−0·0022	0·0042	0·0144
C(*F*)	(*a*)	0·0181 (10)	0·0340 (16)	0·0133 (7)	−0·0007 (23)	0·0047 (18)	0·0173 (14)
	(*b*)	0·0189	0·0332	0·0146	0·0029	−0·0062	0·0190
C(*G*)	(*a*)	0·0219 (11)	0·0430 (18)	0·0135 (8)	0·0038 (26)	0·0089 (20)	0·0195 (17)
	(*b*)	0·0260	0·0468	0·0144	0·0032	0·0122	0·0228

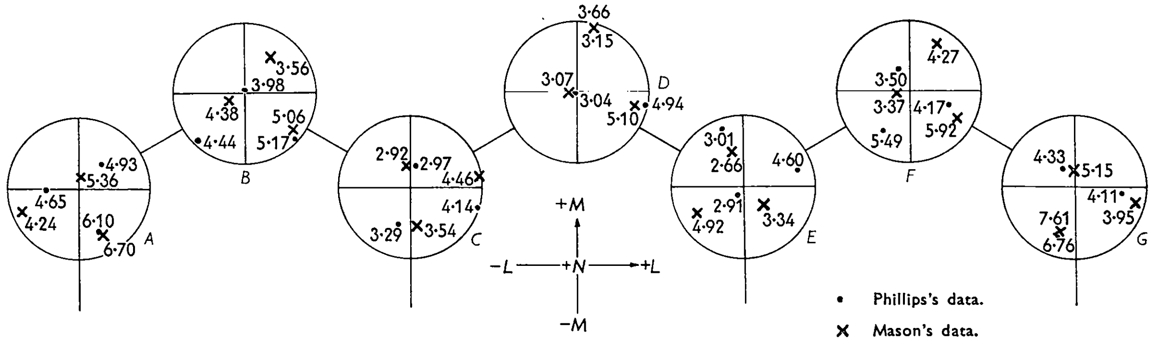

Fig. 1. Magnitudes and directions of principal B_{ij} from two independent sets of experimental $|F|$ values for anthracene, as calculated from the b_{ij} given in the Table.

(*b*) 120 $F(0kl)(h0l)(hk0)$, with 40 'less thans', observed by R. Mason and refined as a 3-dimensional set, using J. S. Rollett's programme. Fuller details will be published later.

These gave $R = 0{\cdot}036$ and $R = 0{\cdot}049$ respectively, with good agreement in positional parameters and the following agreement for the b_{ij} values (e.s.d. in brackets).

The e.s.d. for (*b*) have not been computed, but are certainly larger than for (*a*) and the refinement is capable of improvement. Nevertheless, R is less than 0·05 for both sets and most workers, we believe, would regard either as satisfactory and the agreement shown in Table 1 as good. Thus Cruickshank's (1956) analysis of the thermal vibrations of anthracene was carried out on more extensive data for which the experimental accuracy claimed was about 0·10 in $|F|$s, and which had refined to $R = 0{\cdot}11$, a reasonable limit for such data. Moreover, he used only the high-angle reflections, the $|F|$ values for which would certainly be the least accurate ($R = 0{\cdot}115$).*

When the two sets of b_{ij} given in Table 1 are converted into B_{ij}, they give the respective answers illustrated in Fig. 1. It is at once obvious that the B_{ij} magnitudes and directions both vary far more than might have been expected for sets of experimental data agreeing so well and refining to such low R-values. Doubt is at once cast on the accuracy of either set of deductions. If the B_{ij} deduced from the b_{ij} of Cruickshank's paper (and from various other sets of b_{ij} data for anthracene) are plotted in the same way, the discrepancies are quite remarkable, and the question at once poses itself as to whether some other way of determining the B_{ij} and/or the molecular vibrations may be more reliable.

2. Determination of the principal translational vibrations of the molecule

When we first began to consider the possibility of determining non-rigid-body vibrations by the prior elimination of the rigid-body vibrations, we accepted Cruickshank's (1957) statement that the evidence for anthracene is consistent with the supposition 'that the principal axes of T and ω coincide with the molecular axes' and that the apparent deviations of direction from the 'natural molecular axes' are probably due to experimental error, a statement which has been repeated by others in the case of other compounds. It seemed to us logical, therefore, to make this a prior assumption and to determine the B_{ij} amplitudes directly from the new experimental data for anthracene on this hypothesis. Analysis of the results on this and other compounds, however, soon convinced us that this hypothesis could not be true, and that the deviations of principal B_{ij} directions from those which would correspond with T and ω along and about the natural molecular axes were not random but (although with a very wide spread) systematic and real.

Further consideration indicated that this might have been expected. The r.m.s. amplitude of translational vibration of the molecule is likely to be influenced most by the acoustic, or elastic, waves which involve the concerted movements of *neighbouring* molecules. Diffuse Laue (stationary-crystal, characteristic wave-length) photographs, for example of sorbic acid (Lonsdale, Robertson & Woodward, 1941), succinic or adipic acid (Amorós *et al.*, 1957) show that when molecules are linked together in chains, for instance by hydrogen bonds along one direction, but are separated by van der Waals distances between chains, then longitudinal vibrations along the chain are comparatively negligible, but many sorts of interchain vibrations occur. The most important translational vibrations in all kinds of structures must be along directions governed by *lattice forces* rather than by the molecular geometry considered in isolation.

It is only when the principal molecular directions are also principal lattice directions, as for example in urea, hexamethylene tetramine or di-paraxylylene (Lonsdale, Milledge & Rao, 1960) that the principal translational vibration axes are likely to be closely related to *all* the principal molecular directions. In the case of diketopiperazine (Degeilh & Marsh, 1959; Lonsdale, 1961) the principal translational vibrations are towards neighbouring parallel molecules. This would correspond to

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* The high-angle reflections include, in general, many small $|F|$s which are not accurately measurable; they are also apt to contain non-random errors due to wrong scaling of upper layers or other faulty corrections of the experimental data; and they are most affected by crystal defects, distortions due to impurities etc. Low-angle reflections suffering from extinction may usually be detected and corrected or omitted, and of course bond anisotropy affects low-angle reflections more. But since bond anisotropy is itself a property of great interest the obvious treatment is to refine low, medium and high-order data (*a*) separately and (*b*) together, for some suitable substance for which really adequate data are available, to see what differences, if any, reveal themselves, and whether these may in fact reasonably be interpreted in terms of bond anisotropy at all for the particular substance concerned.

axes one of which (of *minimum* translation) is *in* the molecular plane and *along* a chain of molecules linked by H-bonds, the other two being inclined at 9·3° and −80·7° to the molecular normal. The librational vibrations are perhaps more likely to be closely related to the molecular geometry (axes of inertia); and the intramolecular vibrations certainly will be. Except in the case of highly-symmetrical crystals containing highly-symmetrical molecules, therefore, the resultant thermal ellipsoids probably will be orientated so that principal axes lie *between* those which would refer ω to the principal molecular axes and those corresponding with translation directions towards nearest parallel molecules. Since, in aromatic compounds, the molecular planes often make angles of about ±30° or less with one crystal plane (thus forming a pseudo-layer structure), the deviations of one of the three sets of B_{ij} directions from the molecular normal is not likely to be large (possibly about 15° or less), but it is important that this deviation should be recognized as real.

3. Alternative methods of determining B_{ij} directions

As has been mentioned earlier, Fourier sections and projections (especially difference syntheses) will often indicate atomic ellipsoid orientations. Whether these are likely to be more accurate than those deduced from the b_{ij} is a matter to be decided only by experience. Alternatively, determination of the Debye factors directly from the experimental data for two or three informed guesses at the atomic principal axis directions, thus 'sampling' the atomic vibration ellipsoids in various ways, may possibly give more reliable thermal information than the determination and subsequent conversion of b_{ij} values.

Certainly it is *not* safe to rely upon one determination only of a set of b_{ij} deduced from experimental data at one temperature, even for R-values as low as 0·05, unless the e.s.d. are smaller by an order of magnitude than those now usually accepted as reasonable.

Finally we would beg crystallographers not to mislead interested research workers in other disciplines by giving b_{ij} or B_{ij} values to 4 or 5 apparently significant figures (without proper qualification), unless and until they have repeated their measurements and refinements more than once, independently, and have proved experimentally that a claim to such accuracy is justified.

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The crystal structure of azodicarbonamide.

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Azodicarbonamide, $H_2N{-}CO{-}N=N{-}CO{-}NH_2$, is prepared by the oxidation of hydrazodicarbonamide in a potassium dichromate-sulfuric acid solution (Thiele, 1892). Hydrazodicarbonamide is obtained by the reaction of hydrazine sulfate and potassium cyanate (Thiele, 1892). Azodicarbonamide is insoluble in most common organic solvents and is only slightly soluble in water. Crystals were grown by slow cooling of a hot aqueous solution. They were found to be monoclinic with elongation in the direction of the a axis and showing the forms {011} and {101}. The crystals cleaved easily parallel to (101). Many of the crystals were double crystals by twinning on (001). This occurred in such a manner that the positive direction of the a axis was oppositely directed in the two parts.

The following unit-cell dimensions were obtained from rotation and Weissenberg photographs taken about the a and b axes (λ of Cu $K\alpha = 1{\cdot}5418$ Å):

$$a_0 = 3{\cdot}57 \pm 0{\cdot}01,\ b_0 = 9{\cdot}06 \pm 0{\cdot}02,\ c_0 = 7{\cdot}00 \pm 0{\cdot}02\ \text{Å};$$
$$\beta = 94°\ 50' \pm 15'.$$

The extinctions observed (hkl present in all orders, $h0l$ present only with $h+l=2n$, and $0k0$ present only with $k=2n$) uniquely determined the space group as $P2_1/n$. The calculated density for two centrosymmetric molecules of $C_2H_4N_4O_2$ per unit cell is 1·708 g.cm.$^{-3}$.

The intensity data for the structure determination were estimated visually from multiple-film equi-inclination Weissenberg photographs of the $0kl$ and $1kl$ reflections. Initial parameters of the projected structure were obtained easily from the sharpened $0kl$ Patterson projection by use of a reasonable model of the molecule. This initial arrangement was refined by least-squares and

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