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THE INTERPRETATION OF ATOMIC DISPLACEMENT PARAMETERS.

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Abstract Modern crystal structure determination provides not only the atomic arrangement but also a set of quantities known as Gaussian displacement parameters (ADP's), which contain information about averaged displacements of atoms from their mean positions. These quantities can be analysed in terms of simple models to yield conclusions about the rigid-body motion of molecules, about large-amplitude internal motions, and about the nature of any disorder that may be present in the crystals. Rotation barrier heights derived from such analyses are in good agreement with values obtained by other physical methods.

ATOMIC MOTION IN CRYSTALS

Contrary to opinions overheard at this Conference, the atoms in a crystal are not stationary; in fact, they move appreciably about their mean positions. From diffraction studies, one can obtain information not only about the mean atomic positions but also about the probability density functions (pdf's) of the atoms resulting from their time-averaged motion, averaged again over all unit cells in the crystal. In small-molecule crystallography, the atomic pdf's are usually taken as trivariate Gaussian probability functions:

$$D(\mathbf{X}) = (2\pi)^{-3/2}(\det \mathbf{U}^{-1})^{1/2} \exp(-\mathbf{X}^{T}\mathbf{U}^{-1}\mathbf{X}/2)$$

where $\mathbf{X}$ is a vector and $\mathbf{U}^{-1}$ is the inverse of the second-moment matrix $\mathbf{U}$. The equi-probability surfaces of this pdf

are ellipsoids, and its second moment in an arbitrary direction defined by a unit vector **n** is $\mathbf{n}^T\mathbf{U}\mathbf{n}$, corresponding to the mean-square displacement amplitude (MSDA) in that direction. For organic crystals at room temperature, typical MSDA's are around 0.05 to 0.1 $Å^2$, corresponding to root-mean-square (rms) displacements in the range 0.25 to 0.3 Å. At 100 K, the MSDA's would be reduced to about a third of their room-temperature values.

Because the weak scattering power of hydrogen atoms precludes the use of too many parameters in the description of their motion, hydrogen pdf's are generally taken as isotropic. The six components of **U** may be termed anisotropic Gaussian displacement parameters (ADP's), and they are routinely obtained, together with the mean atomic positions, for thousands of crystal structure analyses every year. In fact, crystallographers use a considerable part of their computing resources in calculating these quantities. The main outcome, it would seem, consists of the familiar ORTEP diagrams[1] of crystal structures, where the atoms are represented by "vibration ellipsoids". Apart from this, ADP's are not, apparently, regarded as being of any particular interest. At any rate, they have more or less disappeared from the published literature, most journals having decreed that ADP's be relegated to "supplementary material", a highly uncertain fate. Sometimes the information can be recovered with little inconvenience, expense, and delay, but sometimes it is practically irretrievable. In most published accounts of crystal structure analyses, the **U** matrices are contracted into scalars, variously described as isotropic or equivalent U's.This indiscriminate degradation of the information contained in the **U**'s is a great pity. Hard-won

knowledge about atomic motion in crystals is simply being thrown away.

The atomic "temperature factor" is the Fourier transform of the pdf, and for the above Gaussian D(**X**) it becomes

$$T(\mathbf{h}) = \exp(-2\pi^2 \mathbf{h}^T \mathbf{U} \mathbf{h})$$

where **h** is the reciprocal lattice vector (of length $2\sin\theta/\lambda$). In principle, additional terms (higher cumulants) required for the description of non-Gaussian pdf's can also be determined by including suitable parameters in the least-squares refinement. However, these higher terms are likely to be important only when the second moments are large, and hence when the scattering from the atom in question falls off rapidly with scattering angle. Thus, it is just when the higher terms are important that they become almost impossible to measure.

PROBLEMS IN INTERPRETING ADP'S

The ADP's associated with a given atomic centre refer to the motion of an averaged atom and not to the motion of any individual one. The motions of the individual atoms are highly correlated, and the ADP's provide no information whatsoever about the nature of these correlations. An important part of the information necessary to describe the atomic motions is therefore not available directly.

In the mean-field model, we assume that the motion of the averaged atom is governed by an effective potential imposed by its averaged environment. Given a suitable force-field, this potential can be calculated by summing all relevant interatomic interactions when one atom (or

molecule) is displaced, all other atoms (or molecules) being held at their mean positions.

Although rigorous conclusions about crystal or molecular vibrations cannot be derived from the ADP's alone, it is often possible to reproduce the observed ADP's with the help of simple models involving correlated motions of groups of atoms. The assumption that a given molecule or atomic grouping behaves as a rigid body in the crystal is perhaps the simplest way of introducing such correlations. Indeed, ADP's have been used for many years in this way to estimate rigid-body translational and librational motion of molecules in crystals[2,3] as well as torsional amplitudes for internal molecular motions.[4,5]

THE RIGID-BODY MODEL

To describe the translation motion of a rigid body we require six numbers, the components $\langle t^i t^j \rangle$ of a symmetric matrix **T**, analogous to **U** for the motion of a single atom. Similarly, the librational motion can be described by a symmetric matrix **L** with components $\langle \lambda^i \lambda^j \rangle$. If the libration axes are required to intersect at a point, the rigid-body motion is completely described by **T** and **L**, but in the general case additional parameters are needed to allow for the quadratic correlation between the pure translational and pure librational motions.[3] The additional parameters, nine in number, are of the form $\langle \lambda^i t^j \rangle$ and form the elements of a new matrix **S**, which is unsymmetric. The elements of **T** and **L** (and of **S**, where necessary) are found by a linear least-squares fit to the observed ADP's, except that the diagonal

elements of **S** cannot be obtained completely in this way; only their differences. Where the assumption of reasonable molecular rigidity seems justified, the model usually reproduces the observed **U**'s within their experimental precision.

INTERNAL MOLECULAR MOTION

For every pair of atoms A,B in a perfectly rigid grouping, the MSDA's of both atoms must be exactly equal along the interatomic vector:

$$\Delta(A,B) \equiv \mathbf{n}^T\mathbf{U}_A\mathbf{n} - \mathbf{n}^T\mathbf{U}_B\mathbf{n} = 0$$

where **n** is the unit vector along A,B. Note that the converse does not hold; Δ will be zero (in first approximation) if the relative motion of the atoms is perpendicular to the A,B direction. This condition provides a simple method of testing whether the ADP's obtained for a particular grouping are compatible with rigid-body motion.[6] Since bond-stretching vibrations typically have negligible amplitudes compared with other internal motions, this condition should also be valid for bonded pairs of atoms even in non-rigid molecules. Thus, evaluation of $\Delta(A,B)$ over all bonded pairs of atoms can give a useful estimate of the overall quality of the ADP's.[7]

Inspection of the matrix of Δ values can reveal relative motion of rigid subgroups; within the subgroups the Δ values should not differ significantly from zero, while relative motion of the subgroups will be manifested by much larger values of some of the inter-group Δ's. An example is given in Table 1, where Δ values for triphenylphosphine

oxide in its orthorhombic crystal modification at 100 K[8] are shown. The triangles labelled A,B,C contain Δ values for the three phenyl groups (Figure 1); the three blocks AB,AC,BC contain Δ values for pairs of atoms belonging to different rings. The estimated standard deviations of the Δ's are about 7 units. Thus, the rings themselves can be regarded as being essentially rigid. On the other hand, there is clear evidence of significant motion of the rings relative to one another, especially of ring A relative to rings B and C.

TABLE I Matrix of Δ values (in units of 10^{-4} A^2) for triphenylphosphine oxide at 100 K. Each Δ is the mean-square displacement amplitude (MSDA) of the atom at the head of the column minus the MSDA for the atom at the left of the row, both MSDA's being taken along the interatomic vector. Atoms C1-C6 comprise ring A, C7-C12 ring B, C13-C18 ring C.

ATOM	C18	C17	C16	C15	C14	C13	C12	C11	C10	C9	C8	C7	C6	C5	C4	C3	C2	C1	P1
O1	0	-8	-15	-6	-8	-19	18	8	10	35	32	9	2	-15	-22	9	48	-10	-20
P1	33	31	23	25	31	10	38	32	22	31	35	22	29	25	16	24	41	13	
C1	48	28	-2	-11	-5	-9	40	44	11	-5	-3	0	11	5	5	10	21		
C2	15	5	-23	-44	-46	-34	-73	-89	-100	-77	-57	-61	-2	-7	5	-6			
C3	49	26	-22	-45	-38	-20	-21	-31	-74	-78	-57	-42	-11	-22	2				
C4	56	12	-53	-59	-34	-25	36	67	12	-31	-29	-15	-10	-16					
C5	14	-32	-78	-68	-41	-47	-25	2	-25	-40	-29	-33	-11						
C6	17	-10	-34	-32	-18	-30	-50	-34	-51	-49	-32	-44							
C7	35	42	23	20	19	3	2	-1	0	1	-6								
C8	19	13	-19	-23	-23	-36	8	-9	-9	1									
C9	19	12	-27	-32	-30	-36	5	-5	-3										
C10	27	44	13	4	-1	-12	-5	-8											
C11	-2	21	1	-3	-5	-17	-7												
C12	6	24	4	-1	-1	-11													
C13	7	16	13	7	3														
C14	0	5	7	2															
C15	-8	-13	-11																
C16	2	4																	
C17	-5																		

A

B

C

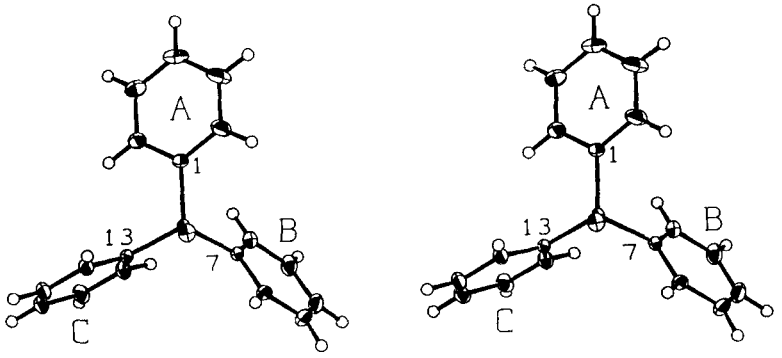

FIGURE 1.Stereoview of triphenylphosphine oxide (orthorhombic modification) at 100 K showing ring labels and atoms numbered 1,7 and 13.

For flexible molecules like triphenylphosphine oxide with reasonably large torsional motions of more or less rigid groups, the magnitudes of such motions can be estimated by a slight modification of the **T,L,S** analysis.[4] An additional parameter $\langle\phi^2\rangle$, a mean-square torsional amplitude, is added for each group suspected of undergoing appreciable torsional motion. The torsional axis needs to be specified in advance, and, in the simplest version, all correlations between the internal motion and the overall motion are neglected.

For the triphenylphosphine oxide molecule mentioned above, the $\langle\phi^2\rangle$ values for the three rings are 42 deg^2 (A), 5 deg^2 (B), and 7 deg^2 (C) at 100 K; the eigenvalues of the **L** matrix are between 3.2 and 4.8 deg^2. Thus, there is no

doubt that ring A has a much larger torsional motion than the other two rings. For large amplitude motions, the approach described here yields results not significantly different from those obtained by more elaborate methods.[5] However, when the torsional motion is not much larger than the overall libration, neglect of the correlations can lead to misleading results.[9]

MEAN-SQUARE AMPLITUDES AND POTENTIAL ENERGY

For a particle in a one-dimensional harmonic potential, the classical Boltzmann distribution of displacements is

$$p(x) = (2\pi kT/f)^{1/2} \exp(-fx^2/2RT)$$

a Gaussian with second moment $\langle x^2 \rangle = RT/f$. For many crystals the second moments of the atomic pdf's are indeed approximately proportional to T over a wide range. At sufficiently low and high T, however, deviations from the linear dependence are to be expected. At low T, the Boltzmann averaging must be made over the energy levels of a quantized harmonic oscillator, leading to

$$\langle x^2 \rangle = (h/8\pi^2\mu\nu) \coth(h\nu/2RT)$$

where ν is the frequency and μ the reduced mass (or, for a rotational oscillation, the moment of inertia, I). For $h\nu \gg 2RT$, this reduces to

$$\langle x^2 \rangle = h/8\pi^2 \mu\nu$$

the zero-point motion, and for $h\nu \ll 2RT$ we obtain the linear dependence derived above for the classical oscillator. The temperature dependence of $\langle x^2 \rangle$ for classical and quantum averaging is shown in Figure 2. If $\langle x^2 \rangle$ remains nearly constant over an appreciable range of T, this is a good

indication that it arises mainly from static disorder among two or more sites and not from genuine vibration. From measurements at a single temperature, it is often hard to decide between these possibilities.

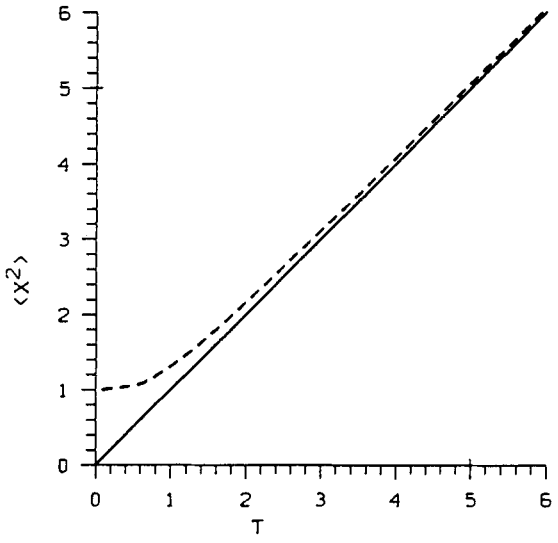

FIGURE 2. Mean-square vibration amplitude $\langle x^2 \rangle$ (units of $h/8\pi^2\mu\nu$) versus temperature (units of $h\nu/2R$) for a one-dimensional harmonic oscillator. The linear dependence shown by the full line is based on the assumption of a classical Boltzmann distribution; the dashed curve corresponds to a quantized distribution.

At sufficiently high temperature, deviations from linear dependence are expected because of the general softening of the potential as the crystal expands. Such deviations have been observed in a temperature-dependence study of naphthalene.[10]

For a sinusoidal potential, classical Boltzmann

averaging leads to a distribution of angular displacements given by

$$p(\phi) = N \exp\{-B(1 - \cos n\phi)/2RT\}$$

where B is the barrier height and N is a normalization factor. Figure 3 shows $\langle\phi^2\rangle$ for this distribution for n = 5 as a function of RT/B, as obtained by numerical integration.[11]

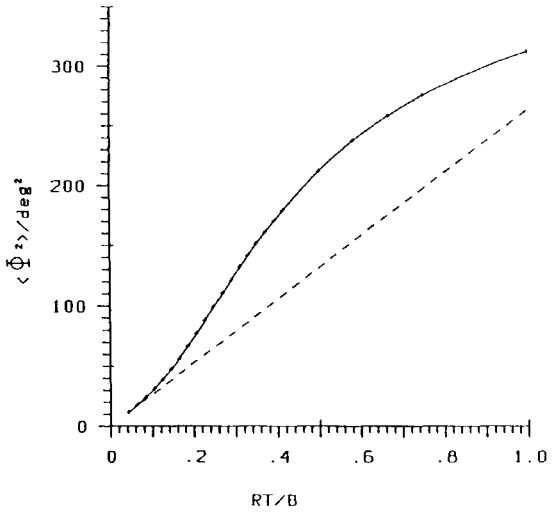

FIGURE 3. Full curve: Mean-square libration amplitude $\langle\phi^2\rangle$ versus temperature for a fivefold periodic sinusoidal potential with barrier height B. Dashed curve: $\langle\phi^2\rangle$ for harmonic oscillator potential with the same quadratic force constant. At very low temperature, both curves should be raised slightly to allow for the zero-point motion, as indicated in Figure 2.

From an observed value of $\langle\phi^2\rangle$ for a given librating group in a crystal and a knowledge of the temperature at which the measurements were made, we can thus obtain the rotation barrier B. This has been done for a series of

metallocenes[11], for which extensive diffraction data are available over a wide temperature range, and for which barriers to rotation of the cyclopentadienyl rings have also been estimated by nuclear magnetic resonance (mainly from ^1H spin-lattice relaxation times), by incoherent quasi-elastic neutron scattering (IQENS), and by Raman and infrared spectroscopy. The best diffraction data are for triclinic ferrocene[12], where there are four symmetry-independent cyclopentadienyl rings. Table 2 shows that the derived barriers decrease slightly with temperature and also vary somewhat from ring to ring. The first trend can be explained by the thermal expansion of the crystal, which leads to an increase in intermolecular distances; the variation from ring to ring is also probably genuine, arising from differences in the packing of the individual rings. The barrier heights agree astonishingly well with those derived from NMR and IQENS, considering that the latter values refer to averages over a considerable temperature range and that differences among the individual rings are not resolved by the spectroscopic methods.

MEAN-SQUARE DISPLACEMENTS AND PHASE TRANSFORMATIONS

Another area where a knowledge of atomic ADP's and their temperature dependence might be of interest is that of phase transformations, particularly those involving conformational isomerizations. Preliminary data are available for the three known crystal modifications of dimethyl-3,6-dichloro-2,5-dihydroxyterephthalate,

TABLE II Barriers to ring rotation (in kJ mol^{-1}, esd's in parentheses) in triclinic ferrocene.

	X-ray		
	101K	123K	148K
Ring 1	7.6(7)	6.4(4)	5.9(5)
Ring 2	12 (2)	10.2(5)	10 (2)
Ring 3	8.4(6)	6.8(7)	7.0(6)
Ring 4	9 (2)	8.5(8)	8 (1)

	Other		
NMR	7.5(8)[a]	10.3(5)[b] 11 (2)	8.3[c]
IQENS	9[d]		

a) C.H. Holm and J.A. Ibers, J.Chem.Phys., 30, 885 (1959).
b) A. Kubo, R. Ikeda and D. Nakamura, Chem. Lett. Japan 1981, 1497.
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which differ in the orientation of the carbomethoxy group. The temperature-dependence of $\langle\phi^2\rangle$ for this group was measured for all three polymorphs.[13] The one that transformed into the others at high temperature showed the largest increase in $\langle\phi^2\rangle$; the results could be interpreted to yield a plot of a one-dimensional reaction coordinate, portraying "in an approximate way the energy dependence on ϕ

at a defect in the crystal and in a still more approximate way the energy profiles for the phase transformation".

CONCLUSIONS

In this article I have attempted to show that analysis of ADP's from diffraction studies can yield quantitative information about the rigidity of molecules and molecular fragments in crystals, about the nature and degree of rigid-body molecular motions, and even about internal motions of supposedly rigid fragments in non-rigid molecules. With the aid of a few rather simple additional assumptions, it is then in principle possible to derive quantities such as force constants or rotation barriers that are normally associated with the realm of spectroscopic methods. A more detailed discussion of many of these points has been given elsewhere[14].

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