## Summary and concluding remarks

Three general types of intermolecular approach are distinguished for dimers of these flat aromatic molecules: coplanar with optional sliding motion, edge-to-plane and edge-to-edge. The presence of net atomic charges has a strong effect on both dimer and crystal structures. A coplanar approach allows the shortest distance between molecular centers and is favored by dispersion attraction as the molecular area increases. A sliding motion will lower the Coulombic energy of coplanar molecules. Edge-plane orientations are favored by electrostatic interaction between adjacent molecules and this orientation predominates in all three directions in the benzene crystal, where the molecules pack in quasi-c.c.p. fashion. However, naphthalene and anthracene utilize edge-plane interaction primarily only within quasi-h.c.p. layers. In these two structures, about 80% of the intermolecular energy originates within layers and only about 20% between layers.

## References

BARTELL, L. S., HARSANYI, L. & VALENTE, E. J. (1989). *J. Phys. Chem.* **93**, 6201-6205.

BATTAGLIA, M. R., BUCKINGHAM, A. D. & WILLIAMS, J. H. (1981). *Chem. Phys. Lett.* **78**, 421-423.

BUCKINGHAM, A. D. & FOWLER, P. W. (1983). *J. Chem. Phys.* **79**, 6426-6428.

BUCKINGHAM, A. D. & FOWLER, P. W. (1985). *Can. J. Chem.* **63**, 2018-2025.

CARSKY, P., SELZLE, H. L. & SCHLAG, E. W. (1988). *Chem. Phys.* **125**, 165-170.

CHAPLOT, S. L., LEHNER, N. & PAWLEY, G. S. (1982). *Acta Cryst.* B**38**, 483-487.

COX, S. R. & WILLIAMS, D. E. (1981). *J. Comput. Chem.* **2**, 304-323.

FRISCH, M., BINKLEY, J. S., SCHLEGEL, H. B., RAGHAVACHARI, K., MELIUS, C. F., MARTIN, R. L., STEWART, J. J. P., BOBROWICZ, F. W., ROHLFING, C. M., KAHN, L. R., DEFREES, D. J., SEEGER, R. A., WHITESIDE, R. A., FOX, D. J., FLEUDER, E. M. & POPLE, J. A. (1988). *Program GAUSSIAN*86. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, USA.

GAVEZZOTTI, A. (1989). *J. Am. Chem. Soc.* **111**, 1835-1843.

HALL, D., STARR, T. H., WILLIAMS, D. E. & WOOD, M. K. (1980). *Acta Cryst.* A**36**, 494.

HALL, D. & WILLIAMS, D. E. (1975). *Acta Cryst.* A**31**, 56-58.

HURST, G. J. B., FOWLER, P. W., STONE, A. J. & BUCKINGHAM, A. D. (1986). *Int. J. Quant. Chem.* **29**, 1223-1239.

HWANG, J.-K. & WARSHEL, A. (1987). *Biochemistry*, **26**, 2669-2673.

KOLLMAN, P. & VAN GUNSTEREN, W. F. (1987). *Methods Enzymol.* **154**, 430-449.

LIU, S. & DYKSTRA, C. E. (1986). *Chem. Phys.* **107**, 343-349.

NATKANIEC, I., BELUSHKIN, A. V., DYCK, W., FUESS, H. & ZEYEN, C. M. E. (1983). *Z. Kristallogr.* **163**, 285-293.

POLITZER, P., LAURENCE, P. R. & JAYASURIYA, K. (1985). *Environ. Health Perspect.* **61**, 191-202.

PRICE, S. L. & STONE, A. J. (1987). *J. Chem. Phys.* **86**, 2859-2868.

SHI, X. & BARTELL, L. S. (1988). *J. Phys. Chem.* **92**, 5667-5673.

STEED, J. M., DIXON, T. A. & KLEMPERER, W. (1979). *J. Chem. Phys.* **70**, 4940-4946.

STERNLICHT, H. (1964). *J. Chem. Phys.* **40**, 1175-1188.

VALENTE, E. J. & BARTELL, L. S. (1984). *J. Chem. Phys.* **80**, 1451-1457.

VENANZI, C. A. & BUNCE, J. D. (1986). *Int. J. Quantum Chem. Quantum. Biol. Symp.* **12**, 69-87.

WAAL, B. W. VAN DE (1984). *Acta Cryst.* A**40**, 306-307.

WARSHEL, A. (1981). *Acc. Chem. Res.* **14**, 284-290.

WILLIAMS, D. E. (1974). *Acta Cryst.* A**30**, 71-77.

WILLIAMS, D. E. (1980). *Acta Cryst.* A**36**, 715-723.

WILLIAMS, D. E. (1988). *Program PDM*88. Quantum Chemistry Program Exchange, Indiana Univ., USA.

WILLIAMS, D. E. (1991*a*). *PCK*91. *A Crystal Molecular Packing Analysis Program.* Chemistry Department, Univ. of Louisville, USA.

WILLIAMS, D. E. (1991*b*). *Reviews in Computational Chemistry* II, edited by K. B. LIPKOWITZ & D. B. BOYD, pp. 219-271. New York: VCH Publishers.

WILLIAMS, D. E. & STARR, T. H. (1977). *J. Comput. Chem.* **1**, 173-177.

---

*Acta Cryst.* (1993). A**49**, 10-22

# Internal Vibrations of a Molecule Consisting of Rigid Segments. I. Non-interacting Internal Vibrations

BY XIAO-MIN HE

*ES76 Biophysics Branch, National Aeronautics and Space Administration, Space Science Laboratory, Marshall Space Flight Center, AL* 35812, *USA*

AND B. M. CRAVEN

*Department of Crystallography, University of Pittsburgh, Pittsburgh, PA* 15260, *USA*

(*Received* 30 *September* 1991; *accepted* 11 *May* 1992)

## Abstract

For molecular crystals, a procedure is proposed for interpreting experimentally determined atomic mean square anisotropic displacement parameters (ADPs) in terms of the overall molecular vibration together with internal vibrations with the assumption that the molecule consists of a set of linked rigid segments.

0108-7673/93/010010-13$06.00

The internal librations (molecular torsional or bending modes) are described using the variable internal coordinates of the segmented body. In paper I of this two-part report, it is assumed as a zero-order approximation that the internal vibrations about the linkage axes between pairs of segments are uncorrelated with each other and with the overall molecular rigid-body vibrations. As a first-order approximation, the possibility that each internal vibration can be correlated with the external vibrations is also considered. An important feature of this approach is that the internal librations are required to give zero contribution to the overall momentum of the molecule at all times, so the internal coordinates must be orthogonal to the external ones. Also, each of the internal librations involves the motion of *all* atoms in the molecule. The resulting internal vibrational parameters are invariant to the choice of reference segment. With this procedure, the experimental ADPs obtained from crystal structure determinations involving six small molecules (*sym*-trinitrobenzene, adenosine, tetracyanoquinodimethane, benzamide, α-cyanoacetic acid hydrazide and *N*-acetyl-L-tryptophan methylamide) have been analyzed. As a consequence, vibrational corrections to the bond lengths and angles of the molecule are calculated as well as the frequencies and force constants (with e.s.d.'s) for each internal torsional or bending vibration. Compared with other models used for describing internal vibrations, there are differences in how the total ADP is partitioned between the internal and overall molecular vibrations.

## 1. Introduction

The information concerning molecular dynamical behavior that is obtained from a crystal structure determination is extensive but incomplete. The Bragg intensities can be used to determine the six anisotropic displacement parameters (ADPs) for each atom and from these the mean square (m.s.) amplitudes of atomic displacement can be obtained. However, because of the space and time averaging that is inherent in the diffraction experiment, we cannot determine directly how the vibration of one atom is correlated with the vibrations of the others in the crystal. It is necessary to postulate a model for the correlated motions of atoms in crystals and then to test the model, for example, by comparing calculated ADPs with observed values.

The lattice-dynamical model of Born and von Karman (described by Willis & Pryor, 1975) provides the most generalized approach. Although computationally intensive, the model has been used successfully in studies of the crystal structure of benzene (Filippini & Gramaccioli, 1989) and other aromatic hydrocarbons. Application to other classes of crystal structure depends on the development of an appropriate force field involving a set of atomic charges and atom–atom potential functions.

For molecular crystals, the rigid-body model (Cruickshank, 1956; Schomaker & Trueblood, 1968) has been the most widely applied. Here, it is assumed that the major contribution to the observed ADPs are from lattice vibrations in which the molecule behaves rigidly. All internal vibrational modes of the molecule are neglected. To use this model, there are geometrical constraints on the molecule as pointed out by Johnson (1970*a*). Thus the atoms of the rigid body must not all lie on a conic section such as a circle or two coplanar straight lines. In general, the atomic ADPs can be fitted to the rigid-body model by a linear least-squares procedure to obtain values for all but one of the elements of the molecular translational (**T**), librational (**L**) and cross (**S**) tensors (the trace of **S** usually being constrained to zero). The importance of the **L** tensor is that it allows bond lengths and angles to be corrected for molecular librations (Johnson, 1970*a*). These corrections are typically 0.005 Å and 0.2° and therefore may be very significant for accurately determined crystal structures.

Some molecules are better treated by assuming that they consist of a sequence of linked rigid segments with the segments in relative motion (Johnson, 1970*b*; Dunitz & White, 1973). The internal modes of vibration are usually torsional librations about axes that are chemical bonds linking the rigid segments. The riding approximation (Busing & Levy, 1964) is assumed to govern the internal motion of a segment with respect to its neighbors. Thus the internal motion of a given atom is the sum of m.s. displacements derived from each of the internal librations that affect that atom. These segmented-body models were first formulated so that the internal vibrations were uncorrelated with the overall rigid-body motion. More recently, the model has been modified so that such correlations can be taken into account (Dunitz, Schomaker & Trueblood, 1988). However, a difficulty remains because, if the vibrational correlation is in fact significant, the m.s. internal libration of segments about a fixed torsional axis cannot be separated from the component of the overall molecular m.s. libration about the same axial direction.* With the revised model, significant correlation of external and internal vibrations have been reported in a few crystal structures, including *N*-acetyl-L-tryptophan methylamide (Souhassou *et al.*, 1991).

---

* This effect is not to be confused with the correlation of variables as defined by the correlation matrix obtained in a least-squares-fitting procedure. For biphenyl, there will be complete correlation in the least-squares model between the overall molecular libration about the molecular long axis (symmetrical) and the internal relative libration of the phenyl groups about the same axis (antisymmetrical). However, no physical correlation of these two motions is required because they have different symmetry coordinates and distinct intrinsic frequencies of vibration.

He & Craven (1985) have proposed a segmented-body model in which the internal vibrations are treated as so-called quasinormal modes. These are similar to the normal modes of internal vibration of an isolated molecule except that high-frequency bond-stretching and bond-angle-bending vibrations are frozen and only torsional librations about selected chemical bonds are permitted. Thus, if there are $n$ internal axes of torsional vibration, there will be $n$ quasinormal modes, each constructed as a linear combination of the $n$ permitted torsions. In this model, it is assumed that there is no correlation between the overall rigid-body motion and the quasinormal vibrations. However, each quasinormal mode involves the correlated motion of all atoms in the molecule.

In its original formulation, the model was inconvenient to use in some respects. It was necessary to specify all the internal modes of the molecule, although most of them were subsequently frozen. Also, it was necessary to store and invert matrices of the approximate size $(3N)^2$, $N$ being the number of atoms in the molecule. This imposes computational limits on the size of the molecule that can be treated. Therefore, we have developed an improved procedure that avoids these difficulties. A similar procedure has been described by Noguti & Go (1983) in connection with molecular dynamical studies of proteins.

As before, on the basis of chemical intuition we must decide how the molecule is to be constituted as a sequence of rigid segments. We can then define variable internal coordinates to describe each of the internal vibrations of the molecule. We consider each variable internal coordinate to be either a bond torsional displacement or a bending of the molecule at a selected bond angle. The successive steps in the calculations are as follows. Firstly, we derive equations of motion for the molecule with respect to the moving frame of the global center. Secondly, following the procedure of Eckart (1935), we eliminate six variables, thereby effectively requiring that the overall linear and angular momenta due to internal vibrations are zero. Thirdly, we recast these equations to set up the matrix that transforms the internal angular displacements into atomic linear displacements in a Cartesian coordinate system. Fourthly, we construct the inverse of the G matrix for the segmented-body system as would be used in a subsequent normal-mode analysis (Wilson, Decius & Cross, 1955). Details of the fourth and subsequent steps will be described in paper II of this report. At present, we are concerned only with the first three steps. These form the basis for our proposed new procedure in which the internal vibrations of the molecule about each internal axis are assumed to be uncorrelated with each other. Thus, the total ADP for each atom is the sum of m.s. amplitudes from the overall rigid-body motion and from the separate vibrations about each of the internal axes. As a subsequent modification of this procedure, we also consider the possible correlation of the external vibration with each of the internal vibrations of the molecule.

Differences from the models of Johnson (1970*b*) and Dunitz & White (1973) are that, firstly, the internal vibrations in the new approach do not involve riding motion and, secondly, the amplitudes of the internal vibrations are mass weighted and conform to the Eckart (1935) conditions concerning zero contribution to the overall linear and angular momentum from the internal vibrations, so that the internal coordinates are orthogonal to the external ones. Thirdly, in the vibration about each internal axis, *all* atoms in the molecule are in motion.

## 2. Internal coordinates of segmented bodies

We restrict ourselves to discussing only harmonic vibrations. Our aim here is to introduce a coordinate system that splits the kinetic energy of the segmented-body system into the sum of two parts, one describing the external vibrations and the other the internal vibrations. This is possible if we assume that the change of moment of inertia of the entire system owing to internal vibrations is negligible and that the Coriolis terms can be neglected. In addition, if we assume that the potential energy of the entire system can be partitioned in a similar way, then the Hamiltonian of the entire system is split and orthogonality between internal and external coordinates can be achieved. Under these conditions, which we consider as a zero-order approximation, an atom is considered to act as a point mass in the moving frame of the molecular center of mass as though it is in an inertial frame. The external vibrations of the molecule will be treated in terms of the well known rigid-body model (Schomaker & Trueblood, 1968) and will not be discussed further. In § 4, we consider a first-order approximation in which we retain the same coordinate system but allow correlation between the external and internal vibrations.

Our first concern is to find a set of coordinates for describing the internal vibrations of the molecule. We assume that the molecule consists of $N$ atoms grouped into $N_s$ rigid segments interconnected by joints, each of which allows the relative angular vibration of the two adjacent segments (Fig. 1). We consider only the special case in which the interconnections form a topographical tree. Thus, there will be a unique path or sequence of segments and joints in going from a given segment to any other segment. For a system with $N_s$ segments there must be $N_J = N_s - 1$ joints. We number the segments and joints purely for ease of indexing and arbitrarily choose segment one, $B_1$, as the reference segment. We can then define a pathway $P_i$ for the $i$th segment, $B_i$, as the listing of the segments and joints in going from $B_i$ to the reference segment $B_1$. If the number of segments in a given pathway is $k$, the number of joints in the pathway must be $k-1$. For the reference segment, the segment and joint numbers that specify the path are simply 1 and 0, respectively.

In a moving Cartesian frame fixed on the molecular center of mass (global center), we use $\mathbf{r}_\alpha$ ($\alpha = 1, 2, 3, \ldots, N$) to represent the position vector of atom $\alpha$ located in one of the segments. Because of the rigidity of the various segments, there are many geometric constraints on the set of $\mathbf{r}_\alpha$. Furthermore, as will be shown later, there are additional conditions governing the set of $\mathbf{r}_\alpha$ that ensure that the internal vibrations do not change the overall momenta. It is convenient to deal with these restrictions by defining a set of internal coordinates to describe the internal vibrations. We allow two kinds of internal coordinates $\varphi$. If the internal vibration is a torsional twist of the molecule, then the variable internal coordinate is a bond-torsion angle $A$–$B$–$C$–$D$ where atoms $A$ and $D$ belong to different rigid segments and the twist is about the axis $B$–$C$. If the internal vibration is a molecular bending, the variable internal coordinate is a bond angle $A$–$B$–$C$ where atoms $A$ and $C$ belong to different rigid segments and the motion is about an axis through the bridging atom $B$ and normal to the plane $A$–$B$–$C$. Now we set out to find the coordinate transformation relating the infinitesimal linear atomic displacements $d\mathbf{r}_\alpha$ ($\alpha = 1, 2, 3, \ldots, N$) and the infinitesimal angular displacements $d\varphi_a$ ($a = 1, 2, 3, \ldots, N_J$).*

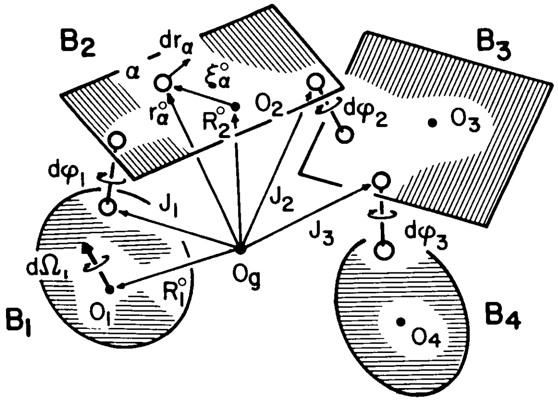

Fig. 1. Diagram representing a molecule with four rigid segments, $B_1$, $B_2$, $B_3$ and $B_4$, and three flexible joints. Angular displacements at the joints are $d\varphi_1$, $d\varphi_2$ and $d\varphi_3$. Vectors are shown originating from the molecular center of mass ($O_g$) and from the centers of mass of the segments ($O_i$). A typical atom $\alpha$ is shown together with vectors defining the atomic position and internal rectilinear displacement.

For any atom $\alpha$ fixed in segment $B_i$, the infinitesimal displacement $d\mathbf{r}_\alpha$ from its equilibrium position $\mathbf{r}_\alpha^0$ due to internal motions can be expressed as

$$d\mathbf{r}_\alpha = \sum_{a\in P_i} \mathbf{n}_a^0 \times (\mathbf{r}_\alpha^0 - \mathbf{J}_a^0)\, d\varphi_a + d\boldsymbol{\Omega}_1 \times (\mathbf{r}_\alpha^0 - \mathbf{R}_1^0) + d\mathbf{R}_1, \quad (1)$$

where $\mathbf{R}_1^0$ is the position vector of the center of mass of the reference segment $B_1$ with respect to the global origin; $d\mathbf{R}_1$ and $d\boldsymbol{\Omega}_1$ are the infinitesimal linear- and angular-displacement vectors, respectively, of the reference segment $B_1$ with respect to the moving frame of the molecule; $\mathbf{n}_a^0$ is a unit vector along the direction of the $a$th internal vibrational axis; $\mathbf{J}_a^0$ is the equilibrium position vector of a point on the $a$th internal axis defined with respect to the global origin.

On the right-hand side of (1) the first term represents the displacement of atom $\alpha$ with respect to the center of mass of the reference segment $B_1$ due to a series of internal librations in the path $P_i$; the second and third terms represent the displacements of atom $\alpha$ due to the angular and linear movement of the reference segment with respect to the moving frame of the molecule.

Equation (1) expresses $d\mathbf{r}_\alpha$ in terms of a linear combination of the $N_J$ variables $d\varphi_1, \ldots, d\varphi_{N_J}$ as required, except that there are six extra variables on the right-hand side, namely the components of $d\boldsymbol{\Omega}_1$ and $d\mathbf{R}_1$. With the requirement that the $d\mathbf{R}_\alpha$ satisfy the conditions specified by

$$\sum_{i=1}^{N_s} \sum_{\alpha\in B_i} m_\alpha \mathbf{r}_\alpha^0 \times d\mathbf{r}_\alpha = 0, \quad (2)$$

$$\sum_{i=1}^{N_s} \sum_{\alpha\in B_i} m_\alpha\, d\mathbf{r}_\alpha = 0, \quad (3)$$

these six extra variables are eliminated as independent variables. These are the conditions described by Eckart (1935) and discussed by Wilson, Decius & Cross (1955) in § 11-1. They are nearly but not exactly equivalent to the conditions requiring that the total angular and linear moments of the internal vibrations with respect to the moving frame of the global center should be zero.

Replacing $d\mathbf{r}_\alpha$ in (2) and (3) by the expression in (1) gives a system of equations that can be solved (see Appendix 1) to obtain the six components of $d\boldsymbol{\Omega}_1$ and $d\mathbf{R}_1$ as given in

$$d\boldsymbol{\Omega}_1 = \sum_{a=1}^{N_J} \boldsymbol{\theta}_a\, d\varphi_a, \quad (4)$$

$$d\mathbf{R}_1 = \sum_{a=1}^{N_J} \boldsymbol{\kappa}_a\, d\varphi_a, \quad (5)$$

where $\boldsymbol{\theta}_a$ and $\boldsymbol{\kappa}_a$ are $3\times 1$ matrices (vectors).

For any atom $\alpha$ in segment $B_i$, if we introduce the symbol $\delta_{ai} = 1$ when $a \in P_i$ and $\delta_{ai} = 0$ otherwise, then

---

* For ease of description, we assume that only one variable internal coordinate occurs at each joint. Hence the number of these coordinates is $N_J$. For practical calculations using the computer program *EKRT* (written by the authors), this restriction does not apply.

if we replace $\mathbf{d\Omega}_1$ and $\mathbf{dR}_1$ in (1) by (4) and (5) we obtain the final result,

$$\mathbf{dr}_\alpha = \sum_{a=1}^{N_J} [\delta_{ai}\mathbf{n}_a^0 \times (\mathbf{r}_\alpha^0 - \mathbf{J}_a^0) + \boldsymbol{\theta}_a \times (\mathbf{r}_\alpha^0 - \mathbf{R}_1^0) + \boldsymbol{\kappa}_a]\, d\varphi_a. \tag{6}$$

The system of equations given in (6) can be cast in matrix notation as

$$\mathbf{y} = \mathbf{A\Phi}, \tag{7}$$

where **A** is the $3N \times N_J$ matrix that transforms small angular displacements about the $N_J$ internal libration axes into the Cartesian linear displacements for the $N$ atoms. The elements of the $N_J \times 1$ column matrix $\mathbf{\Phi}$ are $\Delta\varphi_a$ for $a = 1, 2, 3, \ldots, N_J$ and the elements of the $3N \times 1$ column matrix $\mathbf{y}$ can be written as $\Delta r_{x\alpha}, \Delta r_{y\alpha}, \Delta r_{z\alpha}$ for $\alpha = 1, 2, 3, \ldots, N$.

## 3. Calculation of mean square atomic displacements

If a normal-mode analysis of the segmented-body vibrations were to be carried out, it would be necessary at this point to calculate the relative magnitudes and signs for $\Delta\varphi_a$ $(a = 1, 2, 3, \ldots, N_J)$ for each internal normal mode, that is, the polarization vector for each mode. However, we are presently concerned only with the simpler model in which the angular displacements $\Delta\varphi_a$ are assumed to be independent of each other. Thus the diadics describing the mean square amplitudes of these vibrations can be written as the diagonal matrix

$$\langle \mathbf{\Phi}\ \mathbf{\Phi}^T \rangle = \begin{bmatrix} \langle(\Delta\varphi_1)^2\rangle & 0 & \cdots & 0 \\ 0 & \langle(\Delta\varphi_2)^2\rangle & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \langle(\Delta\varphi_{N_J})^2\rangle \end{bmatrix}. \tag{8}$$

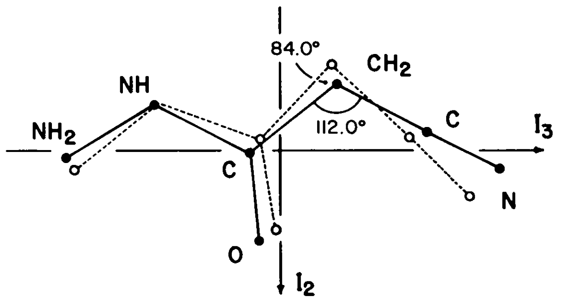

Fig. 2. A molecule of $\alpha$-cyanoacetohydrazide shown with atoms in their mean positions (connected by solid bonds) and with the molecule undergoing an internal C–C–C bending vibration with atomic displacements calculated from the matrix **A**. It should be noted that all atoms are moving during the vibration. The angular displacement is greatly exaggerated to display the pattern of atomic displacements. The molecule, which is approximately planar except for the H atoms, is viewed normal to the best least-squares plane.

The Cartesian atomic linear displacements associated with the vibration about the $a$th axis are determined from the $a$th column in **A**. Thus each column in **A** can be used to construct a diagram such as Fig. 2, which shows all atoms in the $\alpha$-cyanoacetohydrazide molecule displaced in a molecular bending mode. Mean square amplitudes of atomic displacements for libration about the $a$th axis can also be obtained from products of elements taken from the $a$th column of **A**. Thus for the third atom $(\alpha = 3)$, the contribution to the atomic ADP in a Cartesian system is obtained as

$$\begin{aligned} \Delta U_{11} &= \langle u_{xa,3} u_{xa,3} \rangle = \langle A_{7,a}^2 (\Delta\varphi_a)^2 \rangle \\ &= A_{7,a}^2 \langle (\Delta\varphi_a)^2 \rangle \\ \Delta U_{22} &= \langle u_{ya,3} u_{ya,3} \rangle = A_{8,a}^2 \langle (\Delta\varphi_a)^2 \rangle \\ \Delta U_{33} &= \langle u_{za,3} u_{za,3} \rangle = A_{9,a}^2 \langle (\Delta\varphi_a)^2 \rangle \\ \Delta U_{12} &= \langle u_{xa,3} u_{ya,3} \rangle = A_{7,a} A_{8,a} \langle (\Delta\varphi_a)^2 \rangle \end{aligned}$$

and so on. If there are two or more internal vibrations, their contributions to the ADP are summed. In a more generalized form, we can construct a diadic for any atom as

$$\Delta U_{ij}^\alpha = \langle \Delta r_{i\alpha} \Delta r_{j\alpha} \rangle = \langle y_p y_q \rangle = \sum_{a=1}^{N_J} A_{pa} A_{qa} \langle (\Delta\varphi_a)^2 \rangle, \tag{9}$$

where $i, j = 1, 2, 3$, $p = 3(\alpha - 1) + i$ and $q = 3(\alpha - 1) + j$.

As it is assumed that there is no correlation of motions between the internal and external motions, the total ADP is additive. Hence, we modify the tensor expression (7) of Schomaker & Trueblood (1968) to include the internal vibrations as

$$U_{ij}^\alpha = G_{ijkl}^\alpha L_{kl} + H_{ijkl}^\alpha S_{kl} + T_{ij} + A_{pa} A_{qa} \langle (\Delta\varphi_a)^2 \rangle, \tag{10}$$

where $p$ and $q$ are as in (9) and the Einstein convention for summation is applied. It can be seen that (10) is linear not only with respect to the components of the tensors **T**, **L** and **S**, which describe the overall rigid-body vibrations, but also with respect to the m.s. amplitudes of the internal angular displacements $\langle (\Delta\varphi_a)^2 \rangle$. Therefore, using observational equations based on (10), these variables can be determined by a noniterative least-squares-fitting procedure.

## 4. Inclusion of terms for the correlation of the internal and external vibrations

In § 2, as a zero-order approximation, we assumed complete separability of the Hamiltonian and described a system in which the internal coordinates are orthogonal to the external coordinates. However, when there is significant coupling of internal and external modes, this approximation becomes inadequate, although the orthogonality of the coordinates is retained. As a first-order approximation, we retain the same coordinate system and introduce terms to describe the vibrational correlations between the internal and external modes. This is analogous to the modification of the procedure of Dunitz & White (1973) carried out by Dunitz, Schomaker & Trueblood (1988).*

We introduce six new variables for each internal vibration, namely $\langle t_x \Delta\varphi_a \rangle$, $\langle t_y \Delta\varphi_a \rangle$, $\langle t_z \Delta\varphi_a \rangle$ and $\langle \lambda_x \Delta\varphi_a \rangle$, $\langle \lambda_y \Delta\varphi_a \rangle$, $\langle \lambda_z \Delta\varphi_a \rangle$, where $t_x$, $\lambda_x$ *etc.* are Cartesian components of the overall rigid-body translation and libration with respect to the molecular inertial axes. As Dunitz, Schomaker & Trueblood (1988) have pointed out, for libration about an internal axis we can determine only $\langle (\lambda^{\parallel} + \Delta\varphi_a)^2 \rangle$, where $\lambda^{\parallel}$ is the component of the overall libration with respect to the axis of the internal libration. In the expansion

$$\langle (\lambda^{\parallel} + \Delta\varphi_a)^2 \rangle = \langle (\lambda^{\parallel})^2 \rangle + \langle (\Delta\varphi_a)^2 \rangle + 2\langle \lambda^{\parallel} \Delta\varphi_a \rangle,$$

the first term $\langle (\lambda^{\parallel})^2 \rangle$ generally can be estimated from the components of **L** and this gives rise to an estimate of the sum of the second and third terms but not their individual values. For calculations in the molecular inertial axial system, with the introduction of the six variables listed above, $\langle (\Delta\varphi_a)^2 \rangle$ is no longer an independent variable and is therefore omitted from the least-squares-fitting procedure. After least-squares estimates are obtained for $\langle \lambda_x \Delta\varphi_a \rangle$, $\langle \lambda_y \Delta\varphi_a \rangle$, $\langle \lambda_z \Delta\varphi_a \rangle$, we carry out a transformation to local Cartesian axes in which one axis is coincident with the axis of $\varphi_a$. In this way we obtain $\langle (\Delta\varphi_a)^2 \rangle + 2\langle \lambda^{\parallel} \Delta\varphi_a \rangle$ as the component of the transformed correlation terms about the axis $\varphi_a$. By addition of $\langle (\lambda^{\parallel})^2 \rangle$, we obtain $\langle (\lambda^{\parallel} + \Delta\varphi_a)^2 \rangle$. For the details of calculating the ADPs when there are physical correlations present between the external and internal vibrations, see Appendix 2. For an example in which these correlations are considered, see § 6(*f*). For the other examples presented in § 6, when physical correlation terms were introduced into the vibrational analysis, the improved agreement between observed and calculated ADPs was found to be insignificant in terms of the *R*-value-ratio test (Hamilton, 1974).

### 5. Bond-distance and bond-angle corrections, vibrational frequencies and force constants

A crystal structure refinement determines the mean atomic positions averaged with respect to the thermal displacements but, as pointed out by Busing & Levy (1964), the interatomic distances calculated from these positions are foreshortened. The valence angles thus calculated are also affected (Scheringer, 1978). Estimated corrections owing to thermal vibrations depend on the nature of the correlations in the atomic displacements. With the procedure that we propose, the correlation terms between all the atomic linear displacements can be calculated using a modified version of (9). Thus

$$\langle \Delta r_{i\alpha} \Delta r_{j\beta} \rangle = \langle y_p y_q \rangle = \sum_{a=1}^{N_J} A_{pa} A_{qa} \langle (\Delta\varphi_a)^2 \rangle, \quad (11)$$

where $i, j = 1, 2, 3$, $p = 3(\alpha - 1) + i$ and $q = 3(\beta - 1) + j$, the difference from (9) being that $p$ and $q$ can take any value from 1 to $3N$. With the correlation terms derived from (11), appropriate corrections for bond distances and angles can be calculated as indicated by He & Craven (1985) and Scheringer (1978).

Trueblood & Dunitz (1983) have provided examples of the estimation of internal vibrational frequencies and force constants using the expressions

$$\langle (\Delta\varphi_a)^2 \rangle = (h/8\pi^2 I\nu) \coth (h\nu/2kT) \quad (12)$$

$$f = 4\pi^2 I\nu^2. \quad (13)$$

For torsional librations of an atomic group with small mass, such as a methyl group, Trueblood & Dunitz (1983) make the approximation that the rest of the molecule effectively possesses an inertia of infinity and is not involved in motion. The appropriate moment of inertia, $I$, is that of the moving group only. However, this simplification does not apply when there is a relative motion of molecular segments that have comparable mass. Under these circumstances, according to the model we propose, $I$ is the reduced moment of inertia involving the two parts of the molecule on each side of the particular internal axis of vibration.

### 6. Applications of the model

A computer program *EKRT* has been written and is available from the authors. In this program, observational equations based on (10) are set up and a least-squares fit to the experimental ADPs is carried out. The observational equations have weights $w = \sigma^{-2}(U_{ij})$ derived from the crystal structure refinement. Calculated results include the estimated components of the molecular vibration tensors ($T_{ij}$, $L_{ij}$, $S_{ij}$) and the m.s. amplitudes of the internal displacements $\langle (\Delta\varphi_a)^2 \rangle$. A listing of the elements of the **A** matrix is also provided. Alternatively, $\langle (\Delta\varphi_a)^2 \rangle$ for each internal vibration can be substituted by the six correlation variables as described in § 4. The calculations are with respect to Cartesian axes taken along the directions of the principal moments of inertia of the molecule and with respect to the molecular center of

---

* It should be pointed out that, in the treatment of Dunitz, Schomaker & Trueblood (1988), no attempt is made to orthogonalize the internal and the external coordinates. Therefore, the coupling terms in their approach are at least partly due to the nonorthogonality of the chosen coordinates.

mass as origin. The $x$ axis corresponds to the maximum moment of inertia or the normal to the mass-weighted best least-squares plane through the molecule. The $z$ axis corresponds to the minimum moment of inertia or the mass-weighted best least-squares line through the molecule. In the following examples, the model is used to fit ADPs only for the nonhydrogen atoms of the molecule. Atoms bonded to an H atom are assigned a mass including that of the H atom. We made use of our auxilliary program *UINS* for analyzing the differences between observed and calculated ADPs. Principal values of these differences (positive or negative) and their directions are obtained with respect to Cartesian axes chosen appropriately for each atom. We can then evaluate and if necessary revise the assumed segmented body model. Another of our auxilliary programs, *MSD*, was used to test for nonrigidity of the bonds within segments taken to be rigid (Harel & Hirshfeld, 1975).

### (*a*) *sym-Trinitrobenzene*

We have chosen this example because it was also used by Dunitz & White (1973) when they proposed their procedure for describing internal vibrations. The ADPs for *sym*-trinitrobenzene (Fig. 3) are derived from the room-temperature study of the 1:1 crystal complex with *sym*-triaminobenzene (Iwasaki & Saito, 1970). The X-ray intensities for the structure determination were estimated by eye from Weissenberg photographs. In this molecule, the benzene ring was found to be planar. The nitro groups at C1, C3 and C5 make dihedral angles 9.9, 0.9 and 5.9° with respect to the plane of the benzene ring.

With the assumption that the molecule vibrates as a rigid body, the observed ADPs were fitted with $R_w = 0.161$, GOF = 3.57.* There was considerably improved agreement ($R_w = 0.097$, GOF = 2.21) when the model included uncorrelated internal torsional librations about the three C–N bonds. The m.s. amplitudes of libration were 240 (24), 138 (20) and 76 (25) deg$^2$ for C1-N1, C3-N2 and C5-N3, respectively. These values are close to those reported by Dunitz & White (1973), which were 14, 11 and 9° in root mean square amplitude or 196, 121 and 81 deg$^2$.

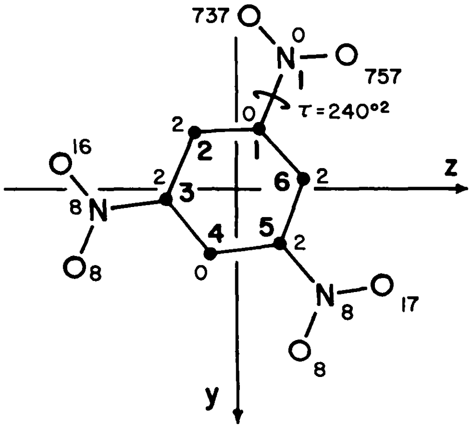

Fig. 3. M.s. out-of-plane displacements ($\Delta U_{11}$, units Å$^2 \times 10^{-4}$) owing to the internal torsional libration $\langle\tau^2\rangle = 240$ deg$^2$ about the C1-N1 bond in *sym*-trinitrobenzene. The molecule is shown referred to Cartesian axes along the directions of the principal moments of inertia.

In Fig. 3, we show the contributions to $U_{11}$ for all atoms due to the libration $\tau_1$ about the C1-N1 axis. We find similar patterns of m.s. displacement for the other two internal librations (not shown in Fig. 3) and, since these motions are uncorrelated, the total internal displacements are obtained as the sum of all three. In Fig. 3, it can be seen that the displacements of atoms O1 and O2 are large compared with those of the other two nitro groups and those in the benzene ring are negligible. Such a pattern of displacements is consistent with the moment of inertia of the nitro group about the C–N axis being small compared with that of the rest of the molecule (37.1 *vs* 818.4 dalton Å$^2$ for C1-N1). According to the Dunitz & White procedure, the internal displacements due to $\tau_1$ would be zero for all atoms except O1 and O2. Consequently, for *sym*-trinitrobenzene, our procedure and that of Dunitz & White (1973) give results in good agreement.

Using (14) and (15), we obtain frequencies 52 (3), 68 (5) and 93 (16) cm$^{-1}$ for the nitro groups at C1, C3 and C5, respectively, giving a weighted average of 57 cm$^{-1}$. The corresponding force constants are 11 (1), 19 (3) and 36 (12) with a weighted average of 12 J mol$^{-1}$ deg$^{-2}$.

### (*b*) *Adenosine*

The crystal structure of adenosine (Fig. 4) has been determined from neutron diffraction data collected at 123 K (Klooster, Ruble, Craven & McMullan, 1991). Assuming a two-segment model with internal torsion $\tau$ about the glycosidic bond N9-C1′, we obtain $R_w = 0.100$ and GOF = 2.32 and m.s. amplitude 14.7 (19) deg$^2$ for $\tau$. Principal values for the overall molecular translation are 0.0107, 0.0086 and 0.0069 Å$^2$ and for the libration they are 0.4, 1.1 and 4.7 deg$^2$. With the same two-segment model and using the procedure of Dunitz & White (1973), the agreement is very similar ($R_w = 0.102$ and GOF = 2.47). However, the m.s. amplitude for $\tau$ is smaller [5.1 (9) deg$^2$ assuming that the ribose group is the reference segment] and the m.s. amplitudes of the overall vibrations are slightly different (0.0115, 0.0085 and 0.0071 Å$^2$ for the translations and −0.1, 0.8 and

---

* $R_w = [(\sum w\Delta^2)/(\sum wU_{ij}^{\rm obs})]^{1/2}$ and $\mathrm{GOF} = [(\sum w\Delta^2)/(m-n)]^{1/2}$, where the summation is over the independent components of the ADP and over the atoms in the molecule. Also, $w = \sigma^{-2}U_{ij}^{\rm obs}$, $\Delta = U_{ij}^{\rm obs} - U_{ij}^{\rm cal}$ and $m - n$ is the number of degrees of freedom in the least-squares fit.

6.8 deg$^2$ for the librations). Unlike the previous example ($a$), the rigid segments in adenosine both have a considerable moment of inertia about the internal torsion axis (453.6 and 847.6 dalton Å$^2$ for adenine and ribose, respectively).

In the case of adenosine, the two procedures give different results because they involve patterns of internal atomic displacements that are different. The least-squares fitting to the observed ADPs gives very similar overall agreement but there are significant differences in how the calculated ADP is partitioned between the internal and external contributions.

For the internal libration in adenosine, we obtain a frequency of 47 (3) cm$^{-1}$ and a force constant 76 (10) J mol$^{-1}$ deg$^{-2}$. Further details of the analysis of ADPs for adenosine are given by Klooster *et al.* (1991). They also report an analysis of ADPs from the room-temperature study of Lai & Marsh (1972), which was based on X-ray diffraction data. At room temperature, the m.s. amplitude of the internal libration increases to 36.1 deg$^2$. However, there are no significant changes in the frequency or the force constant.

### ($c$) 7,7,8,8-*Tetracyanoquinodimethane* (*TCNQ*)

The ADPs for the TCNQ molecule come from the crystal structure determination of the 1:1 complex with $p$-terphenyl using neutron diffraction data collected at room temperature (Lisensky, Johnson & Levy, 1976). The ADPs for TCNQ were analyzed assuming a segmented body and using the *ORSBA* computer program (Johnson, 1970$b$). The molecule (Fig. 5) lies on a crystallographic center of symmetry so that there is no correlation between overall rigid-body librational and translational motion and therefore the components of the cross tensor **S** are all zero.

If we assume that the entire molecule is rigid, after fitting the ADPs for non-H atoms we obtain $R_w$ = 0.114 and GOF = 7.75. We then assumed model *I* in which the molecule consists of three rigid segments: the central ring; the pair of cyano groups together with the bridging atom C4; the equivalent centrosymmetrically related segment involving C4′ [see Fig. 5($b$) for the atomic nomenclature]. Model I gave a considerable improvement in the agreement ($R_w$ = 0.030 and GOF = 3.06) but was unacceptable. A negative m.s. amplitude was obtained for the principal value

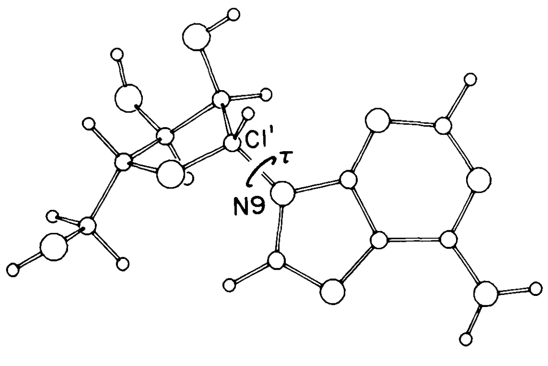

Fig. 4. The molecule of adenosine in the conformation observed in the crystal structure. The internal torsional libration is about the C1′-N9 bond, which links the ribose group (upper left) and the adenine group (lower right). Circles of decreasing size represent O, N, C and H atoms.

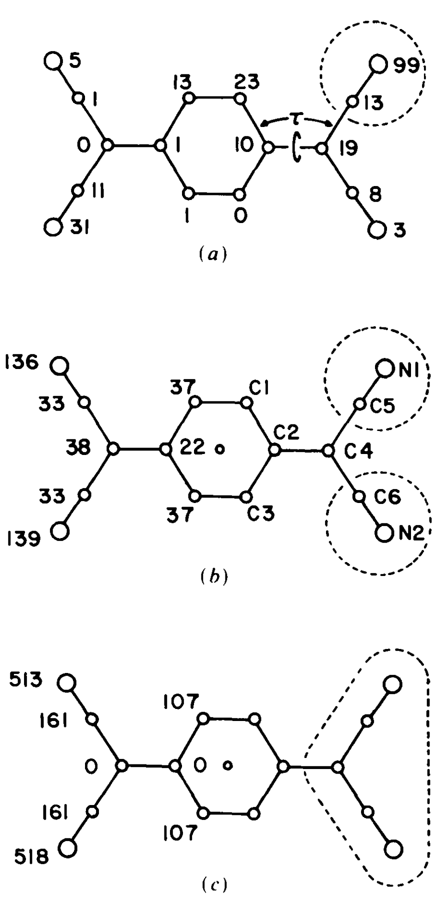

Fig. 5. The molecule of tetracyanoquinodimethane (TCNQ), which lies on a crystallographic center of symmetry. Total m.s. amplitudes were determined from the ADPs by least-squares fitting of a segmented-body model. The atomic out-of-plane displacements shown here ($\Delta U_{11}$, units Å$^2$ × 10$^{-4}$) involve only the contribution of the internal vibrations. ($a$) Out-of-plane atomic displacements due to torsional libration of one of the cyano groups (C5-N1, upper right) about the C2-C4 bond as axis. ($b$) Sum of out-of-plane m.s. atomic displacements obtained if a five-segment model is assumed in which there are independent torsional librations of the four cyano groups about axes C2-C4 (or C2′-C4′). The angular displacement $\langle\tau^2\rangle$ = 27 (7) deg$^2$ has the same value for cyano groups unrelated by crystallographic symmetry. The resultant displacement is thus the sum of four patterns, each as is shown in ($a$). ($c$) Sum of out-of-plane m.s. atomic displacements obtained assuming a three-segment model in which pairs of cyano groups are rigidly joined. One such segment is outlined by the dashed line. As in ($a$) and ($b$), the cyano groups are assumed to be librating about the axes C2-C4 or C2′-C4′. The pattern of displacements is notably different from that shown in ($b$).

of the overall libration about the molecular long axis. Also, there was almost a complete negative least-squares correlation between this overall libration and the internal torsional vibrations about the axes C2-C4 and C2′-C4′. Although a model of type I was not described by Lisensky *et al.* (1976), they would presumably have encountered similar results. They considered a model (which we call II), in which each cyano group forms a rigid segment riding independently on C4 or C4′. They report a m.s. amplitude of 18.5 $\text{deg}^2$ for the overall libration about the $z$ axis, an out-of-plane bending of 12.0 and 6.5 $\text{deg}^2$ for the C5-N1 and C6-N2 groups, respectively, and an in-plane motion of 11.8 and 10.0 $\text{deg}^2$ for the same groups. We tested this model with the difference that we neglected fitting the ADPs for the H atoms. We also tested a model (III) that involved all the internal vibrations of II together with an in-plane bending of angles C1-C2-C3 and C1′-C2′-C3′. Model III gave slightly better agreement than II but was rejected because the additional bending modes were not significant (1.4$\sigma$). Model II gave $R_w = 0.024$ and GOF = 2.49. The largest least-squares correlation was −0.71 between the overall translation $T_{22}$ and libration $L_{11}$. There is good agreement with the value given by Lisensky *et al.* (1976) for the m.s. amplitude of the overall libration about the molecular long axis. However, our estimates are slightly larger for the m.s. amplitudes of the internal vibrations and slightly smaller for the overall translations.

In an effort to understand why model I failed whereas II did not, we compared the out-of-plane components of the internal motions. In Fig. 5(*a*), we show the contributions to $U_{11}$ for all atoms from the internal torsion ($\tau_1$) of C5′-N1′ about the axis C2′-C4′ that occurs in model II. Although not required by crystal symmetry, the torsion ($\tau_2$) of C6′-N2′ about the axis C2′-C4′ has the same m.s. amplitude and thus gives the same pattern of displacements except for a molecular reflection operation. Since there are also torsional vibrations affecting the cyano groups C5-N1 and C6-N2 and all four torsions are assumed to be uncorrelated, we must sum the four sets of m.s. amplitudes to obtain the total contribution to $U_{11}$ of the internal out-of-plane displacements (Fig. 5*b*). In Fig. 5(*c*), we show the corresponding result for summing the two torsional modes that occur in model I. In this case there are only two torsions because pairs of cyano groups are in the same rigid segment. Because the pattern of displacements in Fig. 5(*c*) resembles that which would be obtained for the overall rigid-molecule libration about the $z$ axis, we conclude that this is the explanation for the strong least-squares correlations obtained with model I. Although it might be expected that the effect of allowing independent motion of all cyano groups would be small, in fact the pattern of out-of-plane displacements becomes quite different, as shown in Fig. 5(*b*).

### (*d*) *Benzamide*

The crystal structure of benzamide has recently been determined from neutron diffraction data collected at 15 and 123 K (Gao, Jeffrey, Ruble & McMullan, 1991). Assuming the molecular framework to be rigid, we obtain $R_w = 0.060$ and GOF = 1.82 for the ADPs at 15 K. Several models for the internal libration were tested, all involving torsion ($\tau$) of the amide group with respect to the benzene ring (Fig. 6*a*). As in the case of TCNQ, there is a strong least-squares correlation (here −0.93) between $\tau$ and the overall libration about the molecular long axis, $L_{33}$. The best agreement ($R_w = 0.043$ and GOF = 1.28) was obtained by introducing an additional in-plane bending of the two segments ($\theta$ in Fig. 6*a*). M.s. amplitudes for $\langle\tau^2\rangle = 26\ (5)$ and $\langle\theta^2\rangle = 3.3\ (10)\ \text{deg}^2$ are significant in terms of their e.s.d.'s. For the internal vibrations $\tau$ and $\theta$, the frequencies are 79 (16) and 137 (41) $\text{cm}^{-1}$, respectively. The overall libration about the molecular long axis is small [$L_{33} = 0.8\ (11)\ \text{deg}^2$]. With the same vibrational model, ADPs at 123 K give $R_w = 0.036$ and GOF = 1.93 with $\langle\tau^2\rangle = 25\ (14)$, $\langle\theta^2\rangle = 1.2\ (24)$ and $L_{33} = 13\ (3)\ \text{deg}^2$. As shown by the larger e.s.d.'s, at the higher temperature the least-squares fitting is less successful in separating the internal and external vibrations for benzamide.

We have made further calculations in studying the relationship between the internal and external librations $\tau$ and $L_{33}$. As can be seen from Fig. 6, the pattern of out-of-plane displacements owing to $\tau$ are

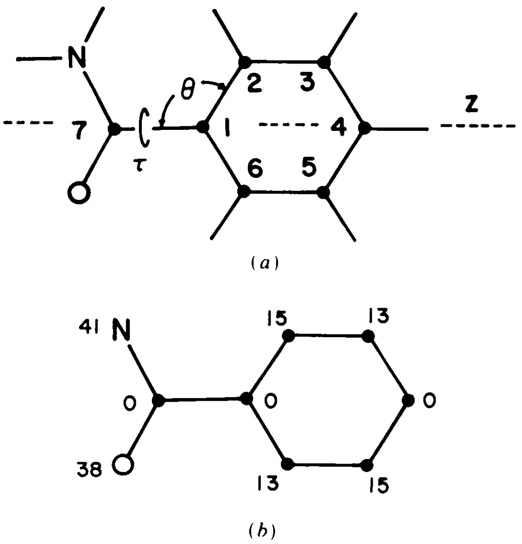

Fig. 6. The molecule of benzamide showing C atoms as filled circles. (*a*) The molecule is assumed to consist of two rigid segments (the amide group and the benzene group) that are involved in torsion $\tau$ about the C1-C7 bond and bending $\theta$ of the C2-C1-C7 bond angle. (*b*) Out-of-plane m.s. atomic displacements ($\Delta U_{11}$, units $\text{Å}^2 \times 10^{-4}$) owing to the internal torsional libration $\tau$, which is found to have a m.s. angular displacement of 26 (5) $\text{deg}^2$ at 15 K.

similar to those expected for an overall libration about the same molecular axis. Therefore, we took $U_{ij}^{\text{cal}}$ values for the $\tau$ vibration only, as obtained from the ADPs at 15 K (see Fig. 6*b*), and fitted them, assuming the complete molecular framework to be rigid. Retaining the original weighting scheme, we obtained an apparently significant libration $L_{33} = 5.2\,(4)\ \text{deg}^2$. However, the agreement was poor ($R_w = 0.20$ and GOF = 2.18). We also carried out a fit assuming the complete segmented-body model but using as observations the $U_{ij}^{\text{cal}}$ values from only the rigid-body motion. We then obtained $\langle\tau^2\rangle = -1.1\,(6)$ and $L_{33} = 1.0\,(1)\ \text{deg}^2$ with $R_w = 0.006$ and GOF = 0.15. Thus the value of $L_{33}$ is recovered without significant change, while the m.s. amplitude for $\tau$ becomes marginally negative. We conclude that, at 15 K with ADPs small and accurately determined, the segmented-body model reliably indicates the presence of the internal torsion.

### (*e*) *α-Cyanoacetohydrazide*

The crystal structure of α-cyanoacetohydrazide (Fig. 2) has been determined from neutron diffraction data collected at 15 K (Nanni, Ruble, Jeffrey & McMullan, 1986). Neglecting the H atoms and assuming the molecular frame to be vibrating as a rigid body, we obtained $R_w = 0.046$ and GOF = 2.37.* No segmented-body model could be found in which there was a significant out-of-plane internal vibration. The best fit ($R_w = 0.036$ and GOF = 1.94) was obtained assuming a two-segment model having an in-plane bending vibration ($\theta$) with a m.s. displacement 2.8 (8) deg$^2$. This is the bending mode that is shown in Fig. 2 with an exaggerated displacement.

### (*f*) *N-Acetyl-L-tryptophan methylamide*

Souhassou *et al.* (1991) have determined the crystal structure of this peptide (Fig. 7) from X-ray diffraction data collected at 103 K and they have also analyzed the ADPs using the procedure of Dunitz & White (1973) including the effects of coupling of the overall and internal vibrations (Dunitz, Schomaker & Trueblood, 1988). With the simple rigid-body model, Souhassou *et al.* (1991) calculated ADPs giving $R_w = 0.21$ and GOF = 4.20. With the inclusion of internal torsional librations about each of the three bonds at C3 (Fig. 7), there was no significant improvement in the agreement. However, when correlations were introduced between each internal torsion and the overall molecular vibrations, the agreement was significantly improved ($R_w = 0.12$ and GOF = 2.46).

In a parallel set of calculations with our procedure (assuming the zero-order and then the first-order approximation, § 4), we obtained similar results. Including the correlation terms, the agreement was $R_w = 0.126$ with GOF = 2.90, but with somewhat different values for the vibrational parameters. We obtain principal values 7.5, 2.4, 1.3 deg$^2$ for the overall libration **L**, larger than the values 4.38, 3.70, −0.26 deg$^2$ reported by Souhassou *et al.*, while our values for the correlation parameters are somewhat smaller. Thus, for $\langle(\Delta\tau_1)^2\rangle + 2\langle\lambda^{\parallel}\Delta\tau_1\rangle$ we obtain 11.4 deg$^2$ compared with 25.8 deg$^2$ reported by Souhassou *et al.*

By trial and error we have obtained a model using our procedure that gives considerably improved agreement ($R_w = 0.086$ and GOF = 2.00). The only difference from the model assumed by Souhassou *et al.* (1991) is the replacement of the internal torsion of the tryptophan about the C3-C6 axis by a bending ($\theta$) of the C6-C7-C10 bond angle (see Fig. 7). With this model, one of the principal values of the overall libration **L** becomes non-positive-definite (−0.4 deg$^2$), but not significantly so. It can be seen from Table 1 that each of the three internal modes of vibration is significantly coupled with the overall molecular vibrations, both translational and librational. We find that, for some atoms, the correlation terms make large contributions to the calculated ADP (see Appendix 2). Thus, after transformation to the molecular inertial axes, atom O2 has $U_{11}^{\text{obs}} = 0.0211\ \text{Å}^2$ in good agreement with $U_{11}^{\text{cal}} = 0.0212\ \text{Å}^2$. The latter includes contributions of 0.0095 Å$^2$ from the overall molecular vibrations, −0.0312 Å$^2$ from $\langle t_y\Delta\tau_2\rangle$ and 0.0527 Å$^2$ from $\langle\lambda_y\Delta\tau_2\rangle$. The m.s. amplitudes of

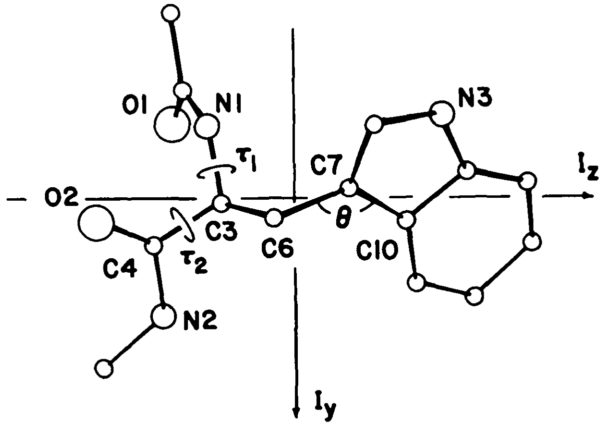

Fig. 7. The molecular structure of *N*-acetyl-L-tryptophan methylamide determined by Souhassou *et al.* (1991) shown with respect to the molecular inertial axes with origin at the molecular center of mass. The projection is down $I_x$, which is the normal to the mass-weighted best plane through the atoms of the molecule. The vibrational analysis [§ 6(*f*); Table 1] assumes that there are four rigid segments consisting of C3-C6, the acetyl group at N1, the methylamide group at C4 and the tryptophan at C7. The internal vibrations consist of torsions $\tau_1$ about C3-N1 (making an angle 12° with $I_y$), $\tau_2$ about C3-C4 (making an angle 32° with $I_z$) and the bending $\theta$ about the normal to the plane C6-C7-C10 (making an angle 38° with $I_x$).

---

* There is a typographical error in Table 4 of Nanni *et al.* (1986). The value of $U_{12}$ for atom H5 should be −0.0006 Å$^2$.

Table 1. *Molecular vibrational analysis for N-acetyl-L-tryptophan methylamide*

The analysis is based on the anisotropic mean square ADPs reported by Souhassou *et al.* (1991) in their Table 3. Calculations are with respect to the molecular principal inertial axes with the origin at the molecular center of mass. The molecular model (Fig. 7) involves the overall vibrations with tensors describing the translational (**T**) and librational (**L**) vibrations and their correlation (**S**) and three internal vibrations ($\tau_1, \tau_2$ and $\theta$), each of which is assumed to be correlated with the overall translational and librational vibrations. The variables are in units Å$^2$, deg$^2$ or deg Å.

(*a*) Overall vibrations

$$\mathbf{T}=\begin{bmatrix} 0.0138\,(9) & 0.0011\,(7) & 0.0011\,(7) \\ & 0.0055\,(8) & 0.0036\,(7) \\ & & 0.0057\,(12) \end{bmatrix}$$

$$\mathbf{L}=\begin{bmatrix} 4.3\,(4) & -1.0\,(4) & 1.5\,(3) \\ & -0.2\,(5) & -0.3\,(3) \\ & & 7.8\,(6) \end{bmatrix}$$

$$\mathbf{S}=\begin{bmatrix} -0.035\,(20) & -0.032\,(6) & -0.010\,(6) \\ 0.048\,(9) & -0.11\,(20) & 0.024\,(10) \\ -0.172\,(16) & 0.004\,(16) & 0.046 \end{bmatrix}$$

(*b*) Correlations of the overall and internal vibrations

Here $t_x$ and $\lambda_x$ refer to the amplitude of overall translation and libration about the inertial axis $I_x$ (and similarly for $y$ and $z$) and $\Delta\varphi$ refers to the amplitude of the appropriate internal vibration ($\tau_1, \tau_2$ or $\theta$).

| | $\langle t_x\Delta\varphi\rangle$ | $\langle t_y\Delta\varphi\rangle$ | $\langle t_z\Delta\varphi\rangle$ |
|---|---|---|---|
| $\tau_1$ | −0.27 (12) | −0.72 (12) | 0.59 (17) |
| $\tau_2$ | 0.72 (12) | −0.03 (11) | 0.10 (7) |
| $\theta$ | −0.06 (5) | 0.25 (4) | 0.08 (2) |
| | $\langle \lambda_x\Delta\varphi\rangle$ | $\langle \lambda_y\Delta\varphi\rangle$ | $\langle \lambda_z\Delta\varphi\rangle$ |
| $\tau_1$ | 11 (3) | −11 (3) | −1 (2) |
| $\tau_2$ | 2 (2) | 18 (2) | 0 (2) |
| $\theta$ | 1.2 (4) | 4.4 (7) | −2.8 (9) |

(*c*) M.s. librational amplitudes about the internal axes

Here $\lambda^{|}$ is the amplitude of the overall molecular libration **L** about a selected internal vibrational axis, $\varphi$.

| | $\langle(\Delta\varphi)^2\rangle+2\langle\lambda^{|}\Delta\varphi\rangle$ | $\langle(\lambda^{|})^2\rangle$ | $\langle(\lambda^{\|}+\Delta\varphi)^2\rangle$ |
|---|---|---|---|
| $\tau_1$ | 23.2 | 0.1 | 23.3 |
| $\tau_2$ | 19.4 | 5.7 | 25.0 |
| $\theta$ | 4.2 | 3.7 | 7.9 |

vibration about the three internal vibration axes (Table 1) are predominantly internal in nature only for $\tau_1$.

## 7. Discussion

We find very similar agreement between observed and calculated ADPs for a given segmented molecular model irrespective of whether we use our procedure or other procedures in the calculations. In such comparisons, we also find that the resultant vibrational corrections to molecular bond lengths and angles are very similar. The primary difference in the various procedures is found in the partitioning of the total ADP with respect to the contributions of the internal and overall vibrations. The aim in formulating our procedure was to set up a coordinate system in which the internal coordinates are orthogonal to the external coordinates. Under these circumstances, the results are invariant to the choice of reference segment. When significant coupling occurs between internal and external vibrations, our zero-order approximation breaks down. Under the first-order approximation, if our assumption remains valid concerning the separability of kinetic energy for the two kinds of motion, then the orthogonality of the coordinate system is preserved. However, interaction terms become important in the potential energy.

It would be desirable to have an objective test for evaluating how well different procedures or molecular models describe the molecular vibrations. Such a test is difficult to devise because chemical intuition must always be invoked in setting up the molecular model. However, it is worth emphasizing that a necessary condition for ensuring the physical significance of a model is that the resulting m.s. amplitude matrix must be positive-definite. This is not a condition that is guaranteed by the least-squares fitting. In the case of a molecule with one internal vibration $\varphi$, the m.s. amplitude matrix can be written as

$$\begin{bmatrix} \mathbf{T} & \mathbf{S} & \langle \mathbf{t}\Delta\varphi\rangle \\ \mathbf{S}^T & \mathbf{L} & \langle \boldsymbol{\lambda}\Delta\varphi\rangle \\ \langle \mathbf{t}\Delta\varphi\rangle^T & \langle \boldsymbol{\lambda}\Delta\varphi\rangle^T & \langle \Delta\varphi^2\rangle \end{bmatrix},$$

where the superscript $^T$ denotes the transpose. To evaluate the eigenvalues of this $7\times 7$ matrix, all its elements must be determined. Unfortunately, with Bragg diffraction data, this is possible only under special circumstances when the molecule has crystallographic point symmetry of certain kinds, such as $\bar{1}$ or $m$. Otherwise, [**S**] has one degree of indeterminancy (Schomaker & Trueblood, 1968). In the case of TCNQ [see § 6(*c*), above], the molecule has site symmetry $\bar{1}$, so that $[\mathbf{S}]=0$. With our procedure, assuming that the internal and external vibrations are uncorrelated, we have $\langle \mathbf{t}\Delta\varphi\rangle = \langle \boldsymbol{\lambda}\Delta\varphi\rangle = 0$, so that [**T**] and [**L**] must each be positive-definite and each $\langle\Delta\varphi^2\rangle$ must be positive. We found that model II satisfied these conditions but model I did not and therefore I was rejected. In the general case, although the m.s. amplitude matrix is not completely determined, it must be symmetric and thus a model giving one or more negative diagonal terms should be rejected. A model should be regarded with suspicion if an off-diagonal term is unusually large compared with the geometric mean of the two corresponding diagonal terms.

The procedure that we have outlined for the analysis of internal molecular vibrations should be widely useful, but it is subject to certain limitations. Firstly, to deal with flexible cyclic molecules, it is necessary to introduce constraints on the internal vibrations that are associated with ring closure. These will be described in part II of our report. Present applications of our procedure using program *EKRT* are restricted to molecules that lack a cyclic configuration of segments.

Secondly, we have not allowed for bond stretching as an internal vibration because the m.s. amplitudes for most vibrations of this kind are likely to be smaller than the e.s.d.'s in the observed ADPs. There are important exceptions, such as the stretching of covalent bonds involving hydrogen. H-atom vibrations can be studied in detail for crystal structures that have been determined from neutron diffraction. Our procedure can be applied in such studies, but first the m.s. amplitude of stretching along the bond must be estimated, for example by making use of the non-rigid-bond test (Harel & Hirshfeld, 1975). It is a good approximation to attribute all the stretching motion to the light H atom and to subtract this m.s. amplitude from the hydrogen ADP. When this was done in the case of $\alpha$-cyanoacetohydrazide at 15 K [see § 6(*e*), above], and when H atoms were included in the analysis, we obtained a fit with $R_w = 0.059$ and GOF = 3.12. However, this procedure is cumbersome and, to deal with the H atoms, the number of internal vibrations must increase considerably. We believe that the internal vibrations of H atoms can be estimated more conveniently and directly by subtracting from the hydrogen ADPs the contribution calculated from the motion of the molecular frame (Johnson, 1970*b*).

Thirdly, our procedure is not suitable for crystal structures in which molecular interactions are so strong that the rigid-body approximation becomes inappropriate. The crystal structure of *N*-acetyl-L-tryptophan methylamide [Souhassou *et al.*, 1991; see also § 6(*f*)] provides an example in which there appears to be a significant mixing of internal and external vibrations. In this case, the effect might be attributed to the irregular shape of the molecule (Fig. 7), which requires an interlocking pattern for the molecular packing. The presence of a three-dimensional hydrogen-bonding network might be another important factor. Because these are quite common structural characteristics, it is to be expected that the mixing of internal and external vibrations is an effect that will be reported more frequently in future. Further studies are needed of crystal structures involving strong molecular interactions to explore the limitations of the existing procedures for analysis of ADPs.

This work was supported by NIH grants HL-20350, GM-39513 and CA-19616 and also by NASA through contracts NAS 8-37301 and NAS 8-38785. We are grateful to Dr Allen Edmundson for his encouragement during the early stages of this research and also to Mrs Joan Klinger for technical support.

## APPENDIX 1

### Elimination of $d\boldsymbol{\Omega}_1$ and $d\mathbf{R}_1$

If one substitutes the expression for $d\mathbf{r}_\alpha$ from (1) in (2) and (3), one obtains

$$\sum_{i=1}^{N_s}\left\{\sum_{\alpha\in B_i} m_\alpha\mathbf{r}_\alpha^0\times\left[\sum_{a\in P_i}\mathbf{n}_a^0\times(\mathbf{r}_\alpha^0-\mathbf{J}_a^0)\,d\varphi_a\right]\right.$$
$$+\sum_{\alpha\in B_i} m_\alpha\mathbf{r}_\alpha^0\times d\boldsymbol{\Omega}_1\times(\mathbf{r}_\alpha^0-\mathbf{R}_1^0)$$
$$\left.+\sum_{\alpha\in B_i} m_\alpha\mathbf{r}_\alpha^0\times d\mathbf{R}_1\right\}=0 \qquad (A1)$$

and

$$\sum_{i=1}^{N_s}\left\{\sum_{\alpha\in B_i} m_\alpha\left[\sum_{a\in P_i}\mathbf{n}_a^0\times(\mathbf{r}_\alpha^0-\mathbf{J}_a^0)\,d\varphi_a\right]\right.$$
$$\left.+\sum_{\alpha\in B_i} m_\alpha\, d\boldsymbol{\Omega}_1\times(\mathbf{r}_\alpha^0-\mathbf{R}_1^0)+\sum_{\alpha\in B_i} m_\alpha\, d\mathbf{R}_1\right\}=0. \quad (A2)$$

It may be noted that

$$\sum_{\alpha\in B_i} m_\alpha\mathbf{r}_\alpha^0\times(d\boldsymbol{\Omega}_1\times\mathbf{r}_\alpha^0)=\mathbf{I}_i^0\,d\boldsymbol{\Omega}_1$$

and similarly

$$\sum_{\alpha\in B_i} m_\alpha\mathbf{r}_\alpha^0\times\left[\sum_{\alpha\in B_i}\mathbf{n}_a^0\times\mathbf{r}_a^0\,d\varphi_a\right]=\mathbf{I}_i^0\sum_{a\in P_i}\mathbf{n}_a^0\,d\varphi_a,$$

$$\sum_{\alpha\in B_i} m_\alpha\mathbf{r}_\alpha^0=m_i\mathbf{R}_i^0,\qquad \sum_{i=1}^{N_s} m_i=M,$$

$$\sum_{i=1}^{N_s} m_i\mathbf{R}_i^0=0,$$

where $m_i$ and $\mathbf{I}_i^0$ are the mass and the moment-of-inertia tensor of segment $B_i$ with respect to the global origin; $\mathbf{R}_i^0$ is the equilibrium position vector of the center of mass for segment $B_i$ with respect to the global origin; $M$ is the total mass of the molecule. Thus ($A$1) and ($A$2) reduce to

$$\sum_{i=1}^{N_s}\left\{\mathbf{I}_i^0\sum_{a\in P_i}\mathbf{n}_a^0\,d\varphi_a+m_i\mathbf{R}_i^0\right.$$
$$\left.\times\left[\sum_{a\in P_i}\mathbf{J}_a^0\times\mathbf{n}_a^0\,d\varphi_a\right]+\mathbf{I}_i^0\,d\boldsymbol{\Omega}_1\right\}=0 \qquad (A3)$$

and

$$\sum_{i=1}^{N_s}\left\{-m_i\mathbf{R}_i^0\times\left[\sum_{a\in P_i}\mathbf{n}_a^0\,d\varphi_a\right]+m_i\left[\sum_{a\in P_i}\mathbf{J}_a^0\times\mathbf{n}_a^0\,d\varphi_a\right]\right\}$$
$$-M\,d\boldsymbol{\Omega}_1\times\mathbf{R}_1^0+\mathrm{M}\,d\mathbf{R}_1=0. \qquad (A4)$$

These equations can be solved numerically using a digital computer for the six components of $d\boldsymbol{\Omega}_1$ and $d\mathbf{R}_1$. Since these equations are linear with respect to $d\boldsymbol{\Omega}_1$, $d\mathbf{R}_1$ and the $d\varphi_a$ the solutions must take the form of (4) and (5).

## APPENDIX 2

### Contribution to the ADP from the correlation of the external and internal vibrations

The equations given here are obtained by an extension of the procedure described by Johnson (1970*a*). If we write $(A_x, A_y, A_z)$ as the terms from the atomic displacement matrix **A** [(7)] corresponding to the displacements of atom $\alpha$ owing to the internal vibration about the $a$th axis then, in the molecular inertial axial system, for atom $\alpha$ we have

$$\begin{bmatrix}\Delta U_{11}\\ \Delta U_{22}\\ \Delta U_{33}\\ \Delta U_{12}\\ \Delta U_{13}\\ \Delta U_{23}\end{bmatrix} = \begin{bmatrix}2A_x & 0 & 0\\ 0 & 2A_y & 0\\ 0 & 0 & 2A_z\\ A_y & A_x & 0\\ A_z & 0 & A_x\\ 0 & A_z & A_y\end{bmatrix}\begin{bmatrix}\langle t_x\Delta\varphi_a\rangle\\ \langle t_y\Delta\varphi_a\rangle\\ \langle t_z\Delta\varphi_a\rangle\end{bmatrix}. \qquad (A5)$$

Similarly, if $(x, y, z)$ are the positional coordinates (in Å) of atom $\alpha$ with respect to the molecular center of mass as origin, we have

$$\begin{bmatrix}\Delta U_{11}\\ \Delta U_{22}\\ \Delta U_{33}\\ \Delta U_{12}\\ \Delta U_{13}\\ \Delta U_{23}\end{bmatrix} = \begin{bmatrix}0 & 2zA_x & -2yA_x\\ -2zA_y & 0 & 2xA_y\\ 2yA_z & -2xA_z & 0\\ -zA_x & zA_y & xA_x-yA_y\\ yA_x & zA_z-xA_x & -yA_z\\ yA_y-zA_z & -xA_y & xA_z\end{bmatrix}$$

$$\times\begin{bmatrix}\langle \lambda_x\Delta\varphi_a\rangle\\ \langle \lambda_y\Delta\varphi_a\rangle\\ \langle \lambda_z\Delta\varphi_a\rangle\end{bmatrix}. \qquad (A6)$$

We introduce here a local Cartesian system $(x', y', z')$ with its $z'$ axis parallel to the internal libration axis $\mathbf{n}_a^0$. Then $(A6)$ will take the form

$$\begin{bmatrix}\Delta U_{11}\\ \Delta U_{22}\\ \Delta U_{33}\\ \Delta U_{12}\\ \Delta U_{13}\\ \Delta U_{23}\end{bmatrix} = \begin{bmatrix}0 & 2zA_x & -2yA_x\\ -2zA_y & 0 & 2xA_y\\ 2yA_z & -2xA_z & 0\\ -zA_x & zA_y & xA_x-yA_y\\ yA_x & zA_z-xA_x & -yA_z\\ yA_y-zA_z & -xA_y & xA_z\end{bmatrix}$$

$$\times[\mathbf{B}]\begin{bmatrix}\langle \lambda_{x'}\Delta\varphi_a\rangle\\ \langle \lambda_{y'}\Delta\varphi_a\rangle\\ \langle \lambda_{z'}\Delta\varphi_a\rangle\end{bmatrix}, \qquad (A7)$$

where [**B**] is a $3\times 3$ transformation matrix from local atomic axes $(x', y', z')$ to the molecular inertial axes $(x, y, z)$. As is pointed out by Dunitz, Schomaker & Trueblood (1988), $\langle(\Delta\varphi_a)^2\rangle$ and $\langle\lambda_{z'}\Delta\varphi_a\rangle$ (or $\langle\lambda^{\parallel}\Delta\varphi_a\rangle$ in their notation) are inseparable. Only the sum $\langle(\Delta\varphi_a)^2\rangle + 2\langle\lambda_{z'}\Delta\varphi_a\rangle$ can be determined. One approach is to omit $\langle\lambda_{z'}\Delta\varphi_a\rangle$ and to determine the apparent value of $\langle(\Delta\varphi_a)^2\rangle$ together with the five correlation terms $\langle t_x\Delta\varphi_a\rangle$, $\langle t_y\Delta\varphi_a\rangle$, $\langle t_z\Delta\varphi_a\rangle$, $\langle\lambda_{x'}\Delta\varphi_a\rangle$, $\langle\lambda_{y'}\Delta\varphi_a\rangle$. An alternate approach (used in program *EKRT*) is to omit $\langle(\Delta\varphi_a)^2\rangle$ and to determine the six correlation terms given in $(A5)$ and $(A6)$. By using the inverse matrix $[\mathbf{B}]^{-1}$, the three librational terms can then be transformed to obtain $\langle\lambda_{x'}\Delta\varphi_a\rangle$, $\langle\lambda_{y'}\Delta\varphi_a\rangle$ and an apparent value for $\langle\lambda_{z'}\Delta\varphi_a\rangle$. Whichever approach is used, it must be remembered that the apparent $\langle(\Delta\varphi_a)^2\rangle$ or $2\langle\lambda_{z'}\Delta\varphi_a\rangle$ is actually the sum $\langle(\Delta\varphi_a)^2\rangle + 2\langle\lambda_{z'}\Delta\varphi_a\rangle$.

### References

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142-146.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 754-756.

Dunitz, J. D., Schomaker, V. & Trueblood, K. N. (1988). *J. Phys. Chem.* **92**, 856-867.

Dunitz, J. D. & White, D. N. J. (1973). *Acta Cryst.* **A29**, 93-94.

Eckart, C. (1935). *Phys. Rev.* **47**, 552-558.

Filippini, G. & Gramaccioli, C. M. (1989). *Acta Cryst.* **A45**, 261-263.

Gao, Q., Jeffrey, G. A., Ruble, J. R. & McMullan, R. K. (1991). *Acta Cryst.* **B47**, 742-745.

Hamilton, W. A. (1974). *International Tables for X-ray Crystallography*, Vol IV, p. 288. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Harel, M. & Hirshfeld, F. L. (1975). *Acta Cryst.* **B31**, 162-172.

He, X.-M. & Craven, B. M. (1985). *Acta Cryst.* **A41**, 244-251.

Iwasaki, F. & Saito, Y. (1970). *Acta Cryst.* **B26**, 251-260.

Johnson, C. K. (1970*a*). *Crystallographic Computing*, edited by F. R. Ahmed, pp. 207-228. Copenhagen: Munksgaard.

Johnson, C. K. (1970*b*). In *Thermal Neutron Diffraction*, edited by B. T. M. Willis, pp. 132-160. Oxford Univ. Press.

Klooster, W., Ruble, J. R., Craven, B. M. & McMullan, R. K. (1991). *Acta Cryst.* **B47**, 376-383.

Lai, T. F. & Marsh, R. E. (1972). *Acta Cryst.* **B28**, 1982-1989.

Lisensky, G. C., Johnson, C. K. & Levy, H. A. (1976). *Acta Cryst.* **B32**, 2188-2197.

Nanni, R. G., Ruble, J. R., Jeffrey, G. A. & McMullan, R. K. (1986). *J. Mol. Struct.* **147**, 369-380.

Noguti, T. & Go, N. (1983). *J. Phys. Soc. Jpn*, **52**, 3283-3288.

Scheringer, C. (1978). *Acta Cryst.* **A34**, 428-431.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63-76.

Souhassou, M., Lecomte, C., Blessing, R. H., Aubry, A., Rohmer, M. M., Wiest, R., Bénard, M. & Marraud, M. (1991). *Acta Cryst.* **B47**, 253-266.

Trueblood, K. N. & Dunitz, J. D. (1983). *Acta Cryst.* **B39**, 120-133.

Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography.* Cambridge Univ. Press.

Wilson, E. B., Decius, J. B. & Cross, P. C. (1955). *Molecular Vibrations.* New York: McGraw-Hill.