check is carried out to determine whether it is hidden by any of the atoms in front of it. Any doing so are stored. Fast plotting procedures are used for unobscured (full circle) and totally obscured atoms (dashed circle). For partially hidden atoms only the unobscured part is drawn. The appropriate atom labels are drawn at the centre of the atoms. When the atom labels lie in an obscured position (see Fig. 1) they may be omitted.

Bonds are drawn as straight lines between atom centres from the edge of the nearer atom to the appropriate point on the further one. The bonds are not plotted at points where they are obscured by other atoms.

Stereoscopic views are obtained by plotting two clinographic projections on planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$ calculated by rotating the originally specified (hkl) plane through angles of $\pm s°$ (usually 3°). The new projection planes correspond to the left and right eye views as determined by consideration of the angles between the $\mathbf{d}^*(hkl)$ vector and the reciprocal cell axes.

The program has been written in Elliott Algol for the Elliott 503 Computer (8K central processor, 16K backing store) using a Calcomp plotter (100 steps/in, 300 steps/sec). The normal and stereoscopic views shown in Figs. 1 and 2 took $3\frac{1}{2}$ and 8 min respectively. This compares with about 70K storage required for Johnson's *ORTEP* and 60K for Cole & Adamson's program. The program described here is also about twice as fast as the latter.

Further information and copies of the program may be obtained from the authors at the above address.

We are grateful to the staff of Chelsea College Computer Centre for their help in the preparation of this program and one of us (D.C.P.) thanks the S.R.C. for a research studentship.

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Non-rigid-body thermal-motion analysis.

By J. D. DUNITZ and D. N. J. WHITE*, *Organic Chemistry Laboratory, Swiss Federal Institute of Technology,* 8006 *Zurich, Switzerland*

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The usual analysis of thermal-motion parameters, derived from X-ray diffraction data, in terms of rigid-body motions can be extended to include the effect of certain specified internal molecular motions.

Analysis of molecular thermal motion in terms of rigid-body libration and translation (Schomaker & Trueblood, 1968) sometimes leads to excellent agreement between the U_{ij} tensor components derived from X-ray analysis and those calculated from rigid-body thermal-motion analysis $(\langle \Delta U_{ij}^2\rangle^{1/2} \sim 1\text{–}2\times 10^{-3}$ Å^2); sometimes, however, the agreement is not so good $(\langle U_{ij}^2\rangle^{1/2} \sim 10^{-2}$ Å^2). In certain cases the poor quality of the agreement can plausibly be ascribed to internal molecular motions which invalidate the rigid-body assumption.

The general treatment of internal motions, given only the vibration tensors, which are sums of mean-square displacements, is impracticable for most molecules. However, we may sometimes be able to postulate certain kinds of motions and estimate their magnitude by including appropriate parameters in the least-squares equations. Obviously the mere addition of parameters to the least-squares treatment will decrease the value of the usual residual $Q=\sum w(U_{ij}^{\text{obs}}-U_{ij}^{\text{calc}})^2$ but carefully chosen parameters should be more effective than random choices.

Assume, for simplicity, that in Fig. 1, C librates about the axis AB. If the amplitude of libration is not too large the motion is along the unit vector $\mathbf{n}=\mathbf{m}\wedge\mathbf{a}/|\mathbf{m}\wedge\mathbf{a}|$ and its magnitude is the product of the root-mean-square libration amplitude Ω and the perpendicular distance, $R=|\mathbf{m}\wedge\mathbf{a}|/|\mathbf{a}|$, of C from the libration axis AB. We can now describe the motion of atom C in terms of the usual rigid-body contributions *plus* a non-rigid-body contribution. The observational equation for atom C is then, in the Schomaker–Trueblood (1968) notation.

$$U_{ij}=G_{ijkl}L_{kl}+H_{ijkl}S_{kl}+T_{ij}+\Omega^2R^2n_in_j \qquad (1)$$

or, in Cruickshank's (1956) notation the U_{ij} tensor can be expressed as

$$U_{ij}l_il_j=T_{ij}l_il_j+\omega_{ij}(\mathbf{l}\wedge\mathbf{r})_i(\mathbf{l}\wedge\mathbf{r})_j+\Omega^2R^2n_in_jl_il_j\,. \qquad (2)$$

More generally, several intramolecular librational axes $\mathbf{a}_j$ can be chosen so that each of them acts on one or more of the atoms constituting the molecule. The last term in (1) and (2) is then replaced by the appropriate sum over the various axes $\mathbf{a}_j$ which contribute to the motion of that atom. This treatment assumes that the motion of any atom arising from intramolecular motion can be approximated by compounding librational motions about prescribed vectors that have to be chosen by chemical intuition or guesswork.

Although several obvious objections may be raised against this procedure, it should provide in favourable cases a semiquantitative description of the molecular motions in the sense that a large motion should be manifested in a large value of the appropriate Ω and a substantial reduction

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* Present address: Chemistry Department, The University, Glasgow W.2., Scotland.

in Q, whereas an incorrectly chosen axis of librational motion should lead to a value of Ω not significantly different from zero.

Example 1: *Lithium purpurate dihydrate*

In this crystal structure analysis (Bürgi, Djuric, Dobler & Dunitz, 1972) the rigid-body treatment of the complex anion (Fig. 2) gave $\langle \Delta U_{ij}^2 \rangle^{1/2} = 0{\cdot}0022$ Å^2 compared with $\sigma(U_{ij}) \sim 0{\cdot}0015$ Å^2. Since the possibility of internal motions involving libration about the central N–C bonds had been raised, we decided to estimate the magnitudes of these two motions by the procedure described above. Our model permitted C(5), C(7), C(8), N(4), N(5), O(4), O(5), O(6) to librate about N(3)–C(6) and C(1), C(2), C(3), N(1), N(2), O(1), O(2), O(3) to librate about N(3)–C(4) and led to values of Ω that were zero within one standard deviation! As an alternative model we considered motion of the oxygen atoms perpendicular to the planes of the heterocyclic rings (such out-of-plane motions can be simulated as librations about a bond adjacent to the C–O bond in question, *i.e.* O(1) librates about N(1)–C(1), O(2) about N(2)–O(2), *etc.*). This model yielded values of Ω in the range 3–8°, significantly different from zero, and reduced $\langle \Delta U_{ij}^2 \rangle^{1/2}$ from 0·0022 to 0·0017 Å^2. We can conclude that the internal motions of largest amplitude in this molecule involve out-of-plane vibrations of the oxygen atoms rather than torsional vibrations about the central C–N bonds, as first supposed.

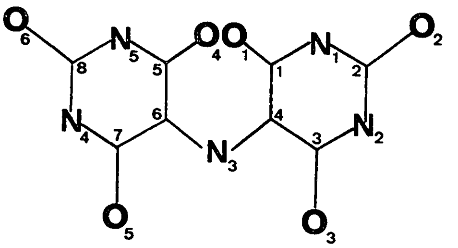

Fig. 2. Numbering of atoms in purpurate anion.

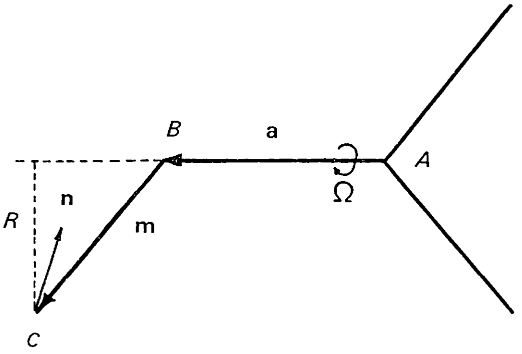

Fig. 1. Atom *C* is supposed to librate about the bond *AB*.

Example 2: *s-Trinitrobenzene in the* 1:1 *complex of s-trinitrobenzene and s-triaminobenzene* (*Iwasaki & Saito*, 1970)

Rigid-body analysis of the published thermal parameters gave $\langle \Delta U_{ij}^2 \rangle^{1/2} = 0{\cdot}0063$ Å^2. For this molecule the obvious intramolecular libration axes $\mathbf{a}_j$ are the three C–N bonds. which are crystallographically independent. Introduction of internal motions for the oxygen atoms gave Ω values of 14, 11 and 9° about the three C–N bonds and reduced $\langle \Delta U_{ij}^2 \rangle^{1/2}$ to 0·0048 Å^2.

Although there are certain pitfalls we believe that this kind of treatment, when applied with discretion, can yield useful semiquantitative descriptions of the more important internal motions of non-rigid molecules. A Fortran computer program for rigid-body thermal-motion analysis, incorporating this treatment as an option, is available on application to D.N.J.W.

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Debye–Waller factors for magnesium oxide.

By J. L. Lawrence. *School of Physical Sciences, University of St. Andrews, St. Andrews, Scotland*

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The Debye–Waller factors for magnesium oxide have been measured from X-ray diffraction data and have been found to be 0·30 ± 0·01 Å^2 and 0·34 ± 0·02 Å^2 for the magnesium and oxygen ions respectively.

The investigation of extinction effects in large crystals (Lawrence, 1972) requires a knowledge of the calculated structure factors for the crystal. The values of the Debye–Waller factors for magnesium oxide obtained by Togawa (1965). [B(magnesium) = 0·24 Å^2; B(oxygen) = 0·19 Å^2] from powder samples using copper radiation gave rise to unrealistic extinction effects and it was decided to redetermine the thermal parameters from a single-crystal experiment using molybdenum $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å).

A single crystal was cut from a large block of magnesium oxide and the integrated intensities measured on a Siemens four-circle diffractometer. The counting statistics on all in-