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Analysis of Molecular Motion with Allowance for Intramolecular Torsion

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The one-parameter model of Dunitz & White [*Acta Cryst.* (1973), A29, 93–94] for the analysis of torsional degrees of freedom within an otherwise rigid body has been applied to data for a number of representative compounds. The model gives results not significantly different from those of more elaborate models for librations about bonds, even when the r.m.s. amplitudes of these librations are as great as 24°. The limitations of this kind of analysis and some of the problems in applying it are discussed.

Introduction

The rigid-body model (Cruickshank, 1956; Schomaker & Trueblood, 1968) has been extensively applied in the analysis of the motion of molecules in crystals. Two general approaches have been used. In the more common one (Cruickshank, 1956), followed in the present study, individual atomic vibration tensors are determined by suitable refinement of the diffraction data and are subsequently fitted to the rigid-body model by least squares. In the second approach (Pawley, 1966, 1972) the molecular rigid-body-motion parameters are found directly by a constrained least-squares refinement of the diffraction data; individual atomic vibration parameters are never determined.

The limitations of the rigid-body model have been extensively discussed (Johnson, 1970*a*, *b*; Maslen, 1970; Pawley, 1970; Willis & Pryor, 1975). Some of these limitations are inherent in the use of Gaussian ellipsoidal atomic parameters ('temperature factors'), the assumption of small ('infinitesimal') rotations, and the quadratic approximation that leads to the **T**, **L**, and **S** tensors, which suggest that applicability of the model would be limited to small-amplitude librations, no greater than perhaps 0·1 or 0·15 rad (6–9°), as well as to situations in which the potential function governing the motion is harmonic. Significant non-rigidity of the molecule will, of course, make the unqualified rigid-body model inapplicable; some modifications of the model that have been suggested for such situations are referred to in the following paragraph. Even if the molecule is reasonably rigid and the quadratic approximation is appropriate, the physical significance of the derived **T**, **L**, and **S** tensors may be limited by other effects. There may be systematic errors in the structure factors because of lack of correction for absorption or thermal diffuse scattering, or for other reasons. The individual atomic Gaussian parameters may, if derived from X-ray data not measured at high scattering angles, be systematically in error because of the neglect of bonding effects (Hirshfeld, 1976). Despite all these potential difficulties, such parameters derived from neutron or X-ray diffraction data can be, under appropriate circumstances, quite meaningful (*e.g.* Willis & Howard, 1975; Hirshfeld, 1976). Diffraction data measured at a single temperature do not, of course, permit the distinguishing of static from dynamic disorder, although measurements over a large temperature interval may provide strong clues (*e.g.* Baudour, Cailleau & Yelon, 1977).

A simple model for some molecules that are demonstrably not rigid is one that includes a rigid core with one or more attached groups, each itself internally rigid and participating in the motion of the core but also librating perceptibly relative to the core about a specified axis, usually a bond attaching the group to the core. Several approaches to the analysis of such non-rigid librations have been suggested (Chidambaram & Brown, 1973; Maslen, 1970; Baudour, 1972; Dunitz & White, 1973; Prince & Finger, 1973; Bennett, Hutcheon & Foxman, 1975), and more elaborate segmented- or coupled-rigid-body models have also been proposed (Johnson, 1967, 1970*a*; Schomaker, 1967).

In the present study, the appealingly simple model of Dunitz & White (1973) has been applied to the individual atomic vibration tensors derived for many seemingly appropriate molecules by primary least-squares analyses of X-ray or neutron diffraction structure factors. This model adds to the rigid-body model just one additional parameter for each non-rigid torsional mode, the corresponding mean-square amplitude of libration about the specified axis. The treatment is strictly valid only within the limits of applicability of the quadratic approximation, but as indicated below it is found to give results not significantly different from more elaborate treatments even when apparent internal torsional amplitudes are as large as 0·4 rad. All calculations were made with the computer programs *THMB* in Zürich or *THMI* in Los Angeles;

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Table 1. *Results of tests with the Dunitz–White model*

The compounds are identified by the number assigned them in the text. The different tests made on each compound are identified by letter. The improvement in fit when the group librations were permitted was highly significant by the *R*-ratio test (Hamilton, 1965) (better than 0·5%) for all compounds listed.

Compound	Test	Number of independent atoms	Librating group	R.m.s. group libration amplitude	R_{wU}	R.m.s. ΔU^{ij}	Average σ^{ij}
(I)	*A*	12	None	—	0·183	0·0094 Å^2	0·0058 Å^2
	B	12	CH_3	21·8 (0·9)°	0·081	0·0042	0·0058
			CH_3	20·4 (1·0)			
(II)	*A*	9	None	—	0·191	0·0097	—
	B	9	Central ring*	14·5 (0·4)	0·057	0·0033	—
(III)	*A*	18	None	—	0·293	0·0059	0·0027
	B	18	CH_3	24·7 (1·5)	0·229	0·0046	0·0027
			CH_3	20·8 (2·0)			
(IV*a*)	*A*	15	None	—	0·187	0·0046	0·0021
	B	15	CH_3	17·2 (1·0)	0·130	0·0032	0·0021
(V)	*A*	19	None	—	0·230	0·0081	0·0018
	B	19	$(CH_3)_3C$	10·9 (0·5)	0·126	0·0044	0·0018
			$(CH_3)_3C$	7·7 (0·7)			
			$(CH_3)_3C$	11·5 (0·6)			
(VI*a*)	*A*	14	None	—	0·074	0·0011	0·0005
	B	14	C_6H_9 ring	1·8 (0·4)	0·061	0·0009	0·0005
			C_6H_9 ring	2·6 (0·5)			
(VI*b*)	*A*	14	None	—	0·081	0·0015	0·0009
	B	14	C_6H_9 ring	2·1 (0·4)	0·061	0·0012	0·0009
			C_6H_9 ring	3·4 (0·4)			

* The libration amplitude listed for *p*-terphenyl (II) is relative to that of the outer ring.

these programs are described briefly in the Appendix. The results for a few representative compounds are presented here and summarized in Table 1. For convenience in reference, each compound is identified by a roman numeral; the different tests referred to for each compound are distinguished by letter.

Symbols and definitions

The following definitions are used:

U^{ij} = contravariant component of mean-square atomic vibration tensor in the crystal system, in Å^2;
σ^{ij} = estimated standard deviation of U^{ij};
w^{ij} = reciprocal of $(\sigma^{ij})^2$ if σ^{ij} is available; otherwise, 1·0;
Δ^{ij} = absolute value of $(U^{ij}_{\text{obs}} - U^{ij}_{\text{calc}})$, with U^{ij}_{calc} evaluated from the derived rigid-body and internal libration parameters;
$\sum$ implies summation over all atoms and all U^{ij};

$$R_{wU} = \left(\frac{\sum w^{ij} (\Delta^{ij})^2}{\sum w^{ij} (U^{ij}_{\text{obs}})^2} \right)^{1/2} .$$

The term 'fit' implies a qualitative assessment of the fit of the assumed model on the basis of R_{wU} and comparison of the r.m.s. Δ^{ij} with the r.m.s. or average σ^{ij}. Destro, Pilati & Simonetta (1977) have used a conventional unweighted *R* and suggested that a value smaller than 10% indicates a satisfactory fit. Burns, Ferrier & McMullan (1967) assessed the fit to Cruickshank's rigid-body model by comparing the size, shape, and orientation of the observed and calculated ellipsoids; this more elaborate procedure can become somewhat ambiguous when two of the eigenvalues are nearly the same, since the corresponding eigenvectors are then ill defined.

The quality of the data is estimated primarily from the conformity of the atomic vibration tensors (for atoms other than H) to Hirshfeld's (1976) rigid-bond test, with some account taken as well of the stated e.s.d.'s of these parameters. With data of the highest quality, the difference between the mean-square vibration amplitudes along the bonding direction for a pair of bonded atoms of comparable mass is no larger than 0·0010 Å^2. When the average e.s.d. of U^{ij} is not much larger than 0·0010 Å^2, this difference should be comparable with the e.s.d.; if the average e.s.d. of U^{ij} is many times larger, the data are manifestly unreliable.

Examples

(I) *Durene* (1,2,4,5-*tetramethylbenzene*)

Prince, Schroeder & Rush (1973) refined this structure with neutron diffraction data. They first determined individual atomic vibration tensors for the five independent C atoms and seven independent H atoms and attempted to apply the usual rigid-body model. However, the model proved inappropriate because of high-amplitude libration of the methyl groups. They then performed a constrained refinement, assuming that the methyl groups librated independently relative to a rigid core; third cumulants (Johnson, 1970*a*) were included because of the high amplitude of the methyl librations. The data are not of high quality but their fit to the rigid-bond test is about as good as their precision warrants. The average difference in mean-square vibration amplitude for the bonded atoms in the five unique C—C bonds is 0·0026 Å; the average e.s.d. of these differences is 0·0027 Å^2 (neglecting the covariances of the U^{ij}).

Application of the Dunitz–White model gave results not significantly different from those obtained with the more elaborate three-cumulant model, despite the very high libration amplitudes. The r.m.s. libration amplitudes calculated by the two methods, with their e.s.d.'s, are:

	Three-cumulant constrained refinement	Dunitz–White model
Methyl on C(2)	22·4 (0·5)°	21·8 (0·9)°
Methyl on C(4)	20·8 (0·6)	20·4 (1·0).

The overall molecular rigid-body tensors **L** and **T** also agreed within their estimated standard deviations. No correction was made in either analysis for the appreciable 'internal' vibrations of the H atoms (Johnson, 1970*a*; Hirshfeld, 1976). Even without these corrections, the fit of the Dunitz–White model is as good as the data permit (Table 1).

(II) *p-Terphenyl*

The high apparent libration amplitude of the central ring of this molecule at room temperature has recently been shown to be a consequence of static disorder (Baudour, Cailleau & Yelon, 1977). Nonetheless the individual atomic vibration tensors (Dejace, 1969; Rietveld, Maslen & Clews, 1970) can be analyzed as if they did result from molecular motion, as Dejace and Rietveld *et al.* showed. Baudour (1972) attempted a constrained refinement of Dejace's data in which he took into account explicitly the noncentrosymmetric character of the electron distribution resulting from the apparent high amplitude of libration. Despite the fact that the r.m.s. amplitude of this apparent libration approaches 0·3 rad, the Dunitz–White model gives results not significantly different from those of Baudour. The r.m.s. libration amplitudes are:

	Baudour's refinement	Dunitz–White model
Central ring	16·1 (0·2)°	16·6 (0·4)°
Outer ring	8·3 (0·2)	8·1 (0·4).

Analysis of the data of Rietveld *et al.* yields similar results.

(III) *Dinuclear copper*(II) *acetate monohydrate*

A neutron-diffraction study of this structure by Brown & Chidambaram (1973) started with a conventional refinement with Gaussian ellipsoidal vibration parameters for each of the 18 unique atoms. Then, because the methyl groups of the two independent acetate residues were undergoing very high torsional librations, two analyses of the motion in each acetate group separately were undertaken, first with Johnson's (1970*a*) segmented-body treatment and then with the model of Chidambaram & Brown (1973) for torsional oscillations of high amplitude. The data are of high quality by the rigid-bond test; the average difference of the mean-square vibration amplitudes for bonded pairs (not including H atoms) within the acetate groups is 0·0009 Å^2, with the average e.s.d. of these differences being 0·0008 Å^2. The corresponding figures for the six bonds around each Cu atom are 0·0011 and 0·0007 Å^2.

The r.m.s. libration amplitudes found with the present program are not significantly different from those reported by Brown & Chidambaram:

	Segmented-body analysis	Chidambaram–Brown model	Dunitz–White model
CH_3 on C(1)	23·2°	24·6 (2·1)°	24·7 (1·5)°
CH_3 on C(2)	22·5	23·6 (3·7)	20·8 (2·0).

The torsional amplitudes from the present program were not significantly different whether calculated with the acetate groups separately or with the entire complex. However, when calculations were made with the acetate groups separately, one eigenvalue of the overall **L** was negative for each group. Hence the amplitudes given above are for the calculation made for the complex as a whole, despite the fact that the complex is far from rigid, as indicated by the high value of R_{wU} even when the torsional oscillations are permitted. When the corrections to the C—H bond distances calculated with the present program (comprising the effects of both the overall molecular libration and the torsional motions of the methyl groups) are added to the 'raw' distances given by Brown & Chidambaram the average C—H distances become 1·123 and 1·101 Å, with a range of 0·033 Å for each group. These values are more physically reasonable than those calculated by any of the methods reported by Brown & Chidambaram, including a three-cumulant refinement (Johnson, 1970*a*).

(IV) *Methyl* α-D-*glucopyranoside and related compounds*

Careful neutron-diffraction structure analyses have been made of three related glycosides: methyl α-D-glucopyranoside (IV*a*) and methyl α-D-mannopyranoside (IV*b*) (Jeffrey, McMullan & Takagi, 1977), and methyl α-D-altropyranoside (IV*c*) (Poppleton, Jeffrey & Williams, 1975). Each molecule has a pyranose ring to which are attached a CH_3O- group on C(1), three HO— groups, and a $HOCH_2-$ group. The data are of high quality, the average difference in the mean-square vibration amplitudes for bonded atoms in the C—C and C—O bonds being for the three molecules 0·0010, 0·0004, and 0·0012 Å^2, respectively. Inspection of the vibration ellipsoids indicates that the methyl group in each molecule is librating with high amplitude about the $O-CH_3$ bond.

Application of the Dunitz–White model to a fifteen-atom fragment of each of these molecules (the pyranose ring, the five attached heavy atoms, and the methyl group) gave a striking improvement in fit over that obtained when each of these fragments was assumed to be rigid. The results for the glucose derivative (IV*a*) are summarized in Table 1; those for (IV*b*) and (IV*c*) were quite parallel, although the methyl-group libration amplitudes were somewhat larger, 19·9 (0·8)° and 24·4 (1·5)° respectively, than that for (IV*a*), 17·2 (1·0)°. The fit is still poor for the H atoms because no correction was made for the internal vibrations. Corrections to the apparent C—H distances in the methyl groups as a consequence of the methyl librations are large; the average C—H distances in the methyls change from 1·063 to 1·108 Å for the glucose derivative, from 1·054 to 1·113 Å for the mannose derivative, and from 1·055 to 1·139 Å for the altrose derivative. The last of these is clearly an overcorrection, attributable in part to the appreciably lower precision of the Gaussian parameters for the H atoms in this molecule and in part to the fact that the apparent libration is so large that the approximations in the model are even less valid than for the other compounds.

(V) *N-Methyl-N-benzyl*-2,4,6-*tris*(*tert-butyl*)*benzamide*

In the original structure analysis (Jungk & Schmidt, 1971) a modified rigid-body model (Hirshfeld & Rabinovich, 1966) incorporating a so-called center of libration was applied to various components of the molecule. The benzyl group was treated as a distinct unit. The three *tert*-butyl groups were found to have about the same translation tensor as the benzamide nucleus to which they are attached; each *tert*-butyl had its principal librational motion approximately about the bond attaching it to this nucleus. Thus the tris(*tert*-butyl)benzamide fragment seemed a good test for the Dunitz–White model; the O and N atoms were omitted, as they had been by Jungk & Schmidt. The r.m.s. libration amplitudes found here for the three *tert*-butyl groups, 10·9 (0·5), 7·7 (0·7) and 11·5 (0·6)°, agree well with those reported by Jungk & Schmidt (10·9, 8·5, and 11·5° respectively). The rigid-body tensors found for the core of this fragment and for the benzyl group treated separately also agree well with those reported earlier. When an attempt was made to fit a model incorporating all atoms of the molecule and permitting libration about the *N*-benzyl bond or the CH_2—phenyl bond, a negative mean-square amplitude was indicated for the former, implying (not surprisingly) that the motion of the benzyl group is more complicated than a simple predominant libration about one direction.

(VI) $\Delta^{1,1'}$-*Dicyclohexenyl ketone*

Holbrook & van der Helm (1975) determined the structures at −110°C of two crystalline forms of this substance, one colorless (VI*a*) and one made pink (VI*b*) by exposure to near-ultraviolet radiation. The structures are nearly identical, although the vibration ellipsoids are slightly larger for the pink form. The Dunitz–White model was applied to the data to see whether there would be any significant differences between the two molecules. The data are of high quality by the rigid-bond test, the average difference in mean-square vibration amplitude for bonded atoms being about 0·0006 Å^2 for the colorless form and 0·0010 Å^2 for the pink form. Each set fits the rigid-body model well; when internal librations of the cyclohexenyl rings about the bonds to the carbonyl group were permitted, r.m.s. amplitudes of 2–3°, with e.s.d.'s of 0·3–0·4°, were found in each molecule (Table 1). The improvement in fit was highly significant by the *R*-ratio criterion. Although the libration of the rings is slightly higher in the pink form than in the colorless form, the difference is not significant.

Discussion

Similar analyses have been made of data for many other compounds. Unfortunately, the quality of much of the data in the literature (especially those not derived from low-temperature measurements or high-angle refinements) is poor and erratic when judged by the rigid-bond test. Furthermore, although the simple Dunitz–White model has proved useful in examining the torsional amplitudes of many groups, for a good fit with groups as large as phenyl a more general wagging motion may often be needed, to the extent that the rigid-group approximation is valid at all. (Frequently, the rigid-bond test fails much more severely for some of the bonds in a phenyl group than for other bonds in the same molecule.) For groups such as nitro, carboxylate, carboxymethyl, and carboxamide, for which nominal r.m.s. amplitudes varying from 7 to 24° have been found in different compounds, there are also often appreciable apparent motions not allowed for by the model with a single torsional degree of freedom.

Among the problems in making tests with published data are that there are four common (and several uncommon) definitions of ellipsoidal anisotropic 'temperature factors' (not always stated in publications or deposited tables, and sometimes stated incorrectly) and that errors in lists of such parameters are more easily overlooked by authors than are errors in positional parameters, in part because there is no independent check on errors in 'temperature factors', especially when they are given in dimensionless form. Despite all these problems, analysis of internal degrees of freedom in molecules can under favorable circumstances provide valuable data for correlation with and extension of intramolecular and intermolecular potential functions (*e.g.* Baudour *et al.*, 1977).

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APPENDIX

The computer programs *THMB*, written for a CDC 6600, and, *THMI*, the adaptation for an IBM 360/91, are extensive revisions of a versatile program, *THMA*, written by Huber-Buser (1974). They are applicable to a molecule of any (crystallographic) point symmetry, with as many as fifteen different internally librating groups, which may have some atoms in common. The programs have many options and some internal checks; the latest versions permit calculation along interatomic directions of the mean-square vibration amplitudes for all pairs of atoms in the molecule, a generalization of Hirshfeld's (1976) rigid-bond test (Rosenfield, Trueblood & Dunitz, 1978). The programs do not yet permit input of the full variance–covariance matrix for the U^{ij}; neglect of covariances (which are never published and are not available in deposited supplementary tables) may lead to small errors, especially in non-orthogonal systems (Hirshfeld & Shmueli, 1972; Küppers & Scheringer, 1973).

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