

$$A_h = \frac{2}{\pi} [\text{arc cos } r - r\sqrt{1-r^2}]$$

$$B_h = 0. \quad (35)$$

$$J(s) = \sqrt{\frac{\pi}{2}} F(\pi s) \left[ 1 - \frac{1}{2\sqrt{1+\pi^2 s^2}} + \frac{\pi s}{1+\pi^2 s^2} \right] \quad (36)$$

corresponding to

$$\{I_h\} = \left( \frac{1+\pi s}{1+\pi^2 s^2} \right)^2,$$

$$A_h = \exp(-2|r|)$$

$$B_h = 2r \exp(-2|r|)$$

[for  $F(z)$  see equation (19)].

Values of  $A_h$  and  $B_h$  were calculated from  $J(s)$ , using equations (32) and (33) for various upper limits  $s_0$  (the lower limits were taken as  $-s_0$  for simplicity) and compared with  $A_h$  and  $B_h$  calculated from  $\{I_h\}$  with the same truncation, and with the theoretical values. It was found that the optimum value of  $s_0$  depends on the rate at which  $J(s)$  is approaching  $1/\sqrt{s}$ , as could be expected. For the first two test functions (Figs. 7 and

8), calculations with  $s_0=3$  give already a reasonably good agreement, which means that for such types of distribution a truncation at  $s_0 \approx 1.5b_s$  is admissible. For the last test function (Figs. 9 and 10) a somewhat higher limit ( $s_0=6$ ) had to be used, but since this function is rather unlikely to occur in practice [it has been chosen only to demonstrate the applicability of equation (33)] this can be regarded as a limiting case. One can thus expect that, in most of the cases,  $s_0$  values between  $1.5b_s$  and  $3b_s$  will be admissible.

The author is indebted to Dr H. Tompa for stimulating discussions during the course of this work, and to Mr J. P. Pauwels for technical assistance.

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## The Rigid-Body Vibrations of Molecules in Crystals

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The rigid-body analysis of the thermal vibrations in seventeen molecular structures has been performed. Parameters are proposed for judging the validity of the rigid-body model by means of an atom-by-atom comparison. It is concluded that the model has a wider range of applicability than might be expected.

### Introduction

Since Cruickshank (1956*a*) first introduced the idea, it has become fairly common practice at the end of a molecular crystal structure determination to analyse the anisotropic temperature parameters on the assumption that the molecule is rigid. Often the purpose is no more than the correction of bond lengths (Cruickshank, 1956*b*), and only occasionally has the assumption of rigidity been critically examined. As part of a larger programme of work, it was decided in this laboratory to undertake a survey of suitable molecular structures in order to determine, if possible, the range of validity of the rigid-body approximation. Chosen for analysis were published structures that had been refined to an  $R$  index of 0.1 or better, and that not only stated unambiguously the form of their temperature factors but also quoted estimated errors for all temperature parameters. It is surprising, but re-

grettably true, that published structures can be found from which it is impossible to determine unequivocally what particular form of temperature factor has been used. No structure containing atoms heavier than oxygen was considered, since it was felt that wide disparities in atomic masses might prejudice the validity of the approximation.

### Procedure

A program (JMTRFAC) was written for the IBM 1620 computer to perform the rigid-body analysis. All published temperature factors were first written in the standard form

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

and were then transformed to  $U_{ij}$  referred to orthogonal crystal axes defined by the unit vectors  $\hat{\mathbf{b}} \times \hat{\mathbf{c}}^*$ ,  $\hat{\mathbf{b}}$ ,  $\hat{\mathbf{c}}^*$ . The transformation equations are:

$$\begin{aligned}
2\pi^2 U_{11} &= (a \sin \gamma)^2 b_{11} + \Theta^2 (c \operatorname{cosec} \gamma)^2 b_{33} + ac \Theta b_{13}, \\
2\pi^2 U_{22} &= (a \cos \gamma)^2 b_{11} + b^2 b_{22} + (c \cos \alpha)^2 b_{33} + \\
&\quad bc \cos \alpha b_{23} + ac \cos \alpha \cos \gamma b_{13} + ab \cos \gamma b_{12}, \\
2\pi^2 U_{33} &= (c \operatorname{cosec} \gamma)^2 \Phi^2 b_{33}, \\
4\pi^2 U_{23} &= c \operatorname{cosec} \gamma \Phi \{a \cos \gamma b_{13} + b b_{23} + 2c \cos \alpha b_{33}\}, \\
4\pi^2 U_{13} &= \Phi \{a c b_{13} + 2(c \operatorname{cosec} \gamma)^2 \Theta b_{33}\}, \\
4\pi^2 U_{12} &= 2a^2 \sin \gamma \cos \gamma b_{11} + 2c^2 \cos \alpha \operatorname{cosec} \gamma \Theta b_{33} + \\
&\quad bc \operatorname{cosec} \gamma \Theta b_{23} + ac (\sin \gamma \cos \alpha + \\
&\quad \cos \gamma \operatorname{cosec} \gamma \Theta) b_{13} + ab \sin \gamma b_{12},
\end{aligned}$$

where

$$\Theta = \cos \beta - \cos \alpha \cos \gamma,$$

and

$$\Phi^2 = 1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma.$$

These equations do not reduce in the monoclinic case to those of Rollett & Davies (1955) owing to a different choice of rectangular axes. This intermediate step of transforming to rectangular axes defined by the crystal is not necessary, and Waser (1955) has shown how to proceed directly from the triclinic axes to rectangular axes defined by the molecule or by individual ellipsoidal atoms. It is really a matter of individual taste.

The  $U_{ij}$  so obtained were transformed to molecular axes chosen to coincide with the inertial axes of the molecule with origin at the centre of mass. The directions of these inertial axes are the eigenvectors of the inertia matrix

$$\mathbf{K} = \begin{pmatrix} \Sigma m(y^2 + z^2) - \Sigma mxy & -\Sigma mxz \\ -\Sigma mxy & \Sigma m(z^2 + x^2) - \Sigma myz \\ -\Sigma mxz & -\Sigma myz & \Sigma m(x^2 + y^2) \end{pmatrix},$$

where the coordinates are relative to the rectangular axes. In forming the various moments and products of inertia, each atom was given a mass proportional to its atomic weight. It may be worth pointing out that the inertial axes are also defined by the eigenvectors of another matrix

$$\mathbf{K}' = \begin{pmatrix} \Sigma mx^2 & \Sigma mxy & \Sigma mxz \\ \Sigma mxy & \Sigma my^2 & \Sigma myz \\ \Sigma mxz & \Sigma myz & \Sigma mz^2 \end{pmatrix}.$$

This is the matrix that occurs in the determination of the best molecular plane (Schomaker, Waser, Marsh & Bergman, 1959) and is easily shown to have the same eigenvectors as the inertia matrix,  $\mathbf{K}$ . When referred to these inertial axes, the  $U_{ij}$  will be labelled  $U_{ij}^o$  and referred to as the observed ellipsoid.

The  $\mathbf{T}$  and  $\omega$  tensors representing the vibrations and librations of the best rigid body to fit the  $U_{ij}^o$  were then calculated by least squares, and from these the  $U_{ij}^c$ , defining what we shall refer to as the calculated ellipsoid, were obtained. The procedure of Cruickshank (1956a) was followed exactly throughout. At this stage we have an observed and a calculated ellipsoid for each atom, and a detailed comparison of these, with respect to size, shape and relative orientation,

should enable reasonable conclusions to be drawn about the rigidity of the molecule. In order to get data for such a comparison the eigenvalues and eigenvectors of the individual  $\mathbf{U}^o$  and  $\mathbf{U}^c$  matrices were calculated, the eigenvalues being arranged in order of increasing size in each. In addition, the matrix  $\mathbf{R}$  was found which rotates the calculated ellipsoid so that its axes coincide with those of the observed ellipsoid, the ordering of the eigenvalues being unaltered. All this yields some thirty-three numbers per atom, and the practical difficulty arises of presenting the comparison in intelligible, yet reasonably succinct, form. It was finally decided to use comparison parameters derived from the thirty-three numbers and defined in the following way.

#### (a) Size

The sum of the eigenvalues, being an invariant, is suitable for specifying the size of an ellipsoid. For the observed and calculated ellipsoids these invariants are denoted by  $U^o$  and  $U^c$  respectively, and their difference  $U^o - U^c$  is listed together with  $U^o$  in Table 1. Also listed, in parenthesis, is the estimated error  $\sigma(U^o)$  calculated using the published e.s.d.'s of the  $b_{ij}$ .

#### (b) Shape

The actual geometrical shape of an ellipsoid is specified by its three semi-axes which are the inverse square-roots of the eigenvalues. Partly for simplicity, and partly in order to exaggerate the shape, it was decided in the present work to use the eigenvalues themselves, and in order to get a single shape parameter the stratagem was adopted of regarding the ordered triad of eigenvalues as a vector, which was normalized to unit length. If  $\mathbf{s}^o$  and  $\mathbf{s}^c$  are the shape vectors of the observed and calculated ellipsoids, then a single shape-correlation factor was chosen to be  $S = 2(1 - \mathbf{s}^o \cdot \mathbf{s}^c) \times 10^4$ . Since, for small angles,  $\cos \theta = 1 - \frac{1}{2}\theta^2$ , this shape-correlation factor is essentially the square of the angle between the two individual shape vectors, suitably scaled.

#### (c) Orientation

If the orthogonal matrices which diagonalize the  $\mathbf{U}^o$  and  $\mathbf{U}^c$  matrices are  $\Lambda^o$  and  $\Lambda^c$  respectively, then  $\tilde{\Lambda}^o \mathbf{U}^c \Lambda^o$  is the symmetric matrix representing the calculated ellipsoid referred to the principal axes of the observed ellipsoid. If now  $\mathbf{R}$  is the orthogonal matrix required to complete the diagonalization of  $\mathbf{U}^c$  in this representation, then  $\tilde{\mathbf{R}} \tilde{\Lambda}^o \mathbf{U}^c \Lambda^o \mathbf{R} = \tilde{\Lambda}^c \mathbf{U}^c \Lambda^c$  and we have  $\mathbf{R} = \tilde{\Lambda}^o \Lambda^c$ . This rotation matrix was evaluated for every atom. Since the elements of such a rotation operator have the general form  $R_{ik} = \cos \theta \delta_{ik} + (1 - \cos \theta) n_i n_k - \sin \theta \epsilon_{ikm} n_m$ , where  $n_i$  are the direction cosines of the line about which the rotation takes place and  $\theta$  is the amount of the rotation (Jeffreys & Jeffreys, 1956), it follows that the trace of the rotation matrix is simply  $1 + 2 \cos \theta$ , and the single parameter  $\theta$  so obtained was deemed suitable to indicate the agreement in orienta-

tion of the  $U^o$  and  $U^c$  ellipsoids. A difficulty arose, however, in those cases where the angle turned out to be very large, and where an inspection of the elements of  $\mathbf{R}$  showed that this very large rotation could more appropriately be decomposed into a permutation of the principal axes of  $U^c$  together with a smaller rotation. In every such case the smallest possible angle of rotation has been quoted (in degrees, for convenience of visualization), and the entry in Table 1 supplemented with a statement of the permutation. Thus (132) means that axis 1 has become axis 3, that axis 3 has become axis 2 and axis 2 has become axis 1. This re-ordering of the axes implies, of course, a re-ordering of the eigenvalues of  $U^c$  and hence a revised shape vector,  $s^c$ . These new shape vectors have been used to give revised shape comparison parameters which are all larger than those previously obtained.

The observed and calculated ellipsoids for each atom in each molecule were systematically compared using the above parameters. The comparison was deemed unsatisfactory if (a)  $U^o - U^c > 3\sigma(U^o)$ , or (b)  $S > 200$ . No unequivocal level of acceptability is possible with the orientation parameter  $\theta$  because this angle has little physical significance when the ellipsoids have an approximately circular section perpendicular to the rotation axis. Each such case was considered on its own merits and the corresponding acceptable large  $\theta$  values are asterisked in the table. For all other atoms the acceptability level of  $\theta$  was fixed at  $30^\circ$ . Atoms deemed unsatisfactory are labelled NR in Table 1. The comparison was deemed satisfactory if (a)  $U^o - U^c \leq 2\sigma(U^o)$ , (b)  $S \leq 150$ , and (c) either  $\theta \leq 25^\circ$ , or its larger value could be satisfactorily accounted for as explained above. Such atoms are labelled R. Atoms which are neither satisfactory nor unsatisfactory are labelled with a question mark. The particular comparison parameters which exceed the prescribed values are italicized in Table 1. These criteria are, of course, subjective in large measure, but, on the basis of our careful study of *all* the data, we believe them to be realistic.

With the individual atoms classified in this way, each molecule was then examined as a whole and a decision made as to its compatibility or otherwise with the rigid-body hypothesis. Judgment must be exercised in this matter, since it would be unreasonable to demand that every atom of a complex molecule satisfy the above criteria. In Table 1 the molecules are arranged roughly in order of decreasing rigidity. In the first section are those which we judge to be compatible with the rigid-body hypothesis; in the last section are those which we judge to be incompatible; while in the middle section are those about which legitimate doubts could be raised.

### Discussion

Molecules will be referred to by their number in the table for brevity. Of the molecules deemed rigid as a whole, the first two need no comment since every atom has comparison parameters which are well inside the

prescribed tolerances. Molecules 3 and 4 each have one atom with an unacceptable size parameter, these being  $3.1\sigma$  and  $3.8\sigma$  respectively, clearly not bad enough to justify regarding the molecule as non-rigid. Molecules 5 and 6 are the separate parts of the quinhydrone complex. These were analysed separately but are listed together although 6 is unequivocally rigid while 5 has one atom with an unsatisfactory orientation angle. The corresponding atom in 6 actually has a larger angle, but a nearly circular section of the  $U^c$  ellipsoid makes this larger angle acceptable. Molecule 7 was accepted as rigid despite one unsatisfactory orientation angle since this was only  $37^\circ$ .

All the molecules 8–11 in the second section have such a proportion of both questionable and unsatisfactory atoms as to make it impossible to regard them as unequivocally rigid. On the other hand, the overall agreement is not so bad that they can definitely be said to be non-rigid. Slight changes in the size, shape and orientation criteria would tend to shift them into the definitely-rigid group, and consequently their exact status must be regarded as doubtful.

For the remaining six molecules in the third section, the proportion of unsatisfactory atoms is sufficiently high to warrant their being labelled as unequivocally non-rigid.

In addition to those molecules listed another four structures were processed. In three of these the analysis led to negative diagonal elements in the  $\mathbf{T}$  and  $\omega$  tensors which are physically unacceptable. In the fourth, salicylic acid (Sundaralingam & Jensen, 1965), the  $U_{22}^o$  of atom O(1) turned out to be negative. This disconcerting result was readily traced to an obvious misprint in the original paper, where  $b_{12}$  has accidentally been given the same numerical value as  $b_{33}$ .

### Conclusions

It must be emphasized that in the present work rigid-body librations about the centre of mass of the molecule have been used. No attempt was made to refine the centre of libration for those molecules not possessing a centre of symmetry, as suggested by Pawley (1963), and this should be borne in mind when interpreting the results. It is possible that some of the molecules might better fit the rigid-body model if a different centre of libration were used, but we do not feel that this would materially affect the classification in Table 1. In particular, it is difficult to envisage any very great improvement in the case of the markedly non-centrosymmetric molecule 3.

The main conclusion to be drawn from the present work is that the simple Cruickshank model fits a wide variety of organic molecules much better than could reasonably be expected. That a molecule like chrysene should behave as a rigid-body is perhaps not surprising in view of its condensed-ring architecture, but the goodness of fit for molecules 1, 3 and 4 is hardly to be expected from an examination of their structural for-

Table 1. Size, shape, and orientation parameters for thermal ellipsoids in seventeen molecular structures

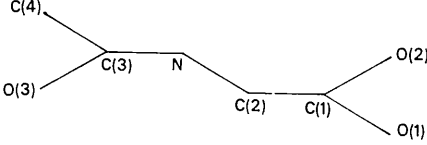
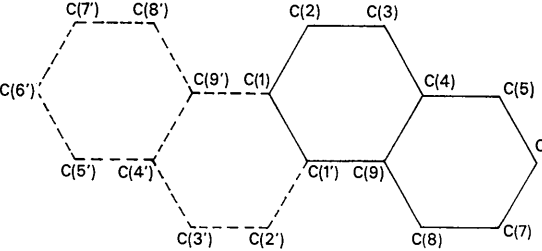
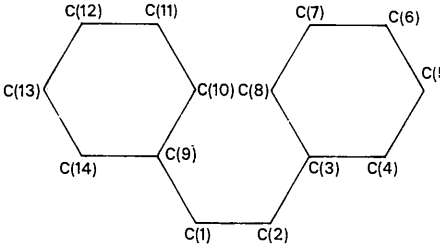
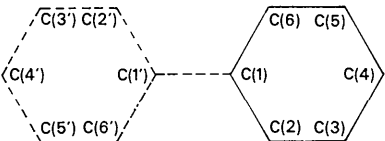
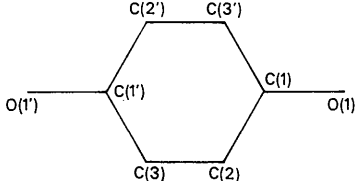
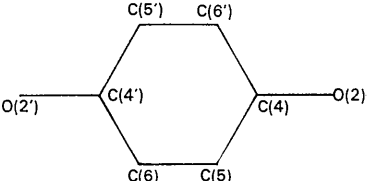
	Atom	$U^o$ ( $\text{\AA}^2 \times 10^4$ )	$U^o - U^c$ ( $\text{\AA}^2 \times 10^4$ )	( $\sigma$ )	S	$\theta$ ( $^\circ$ )	
1. <i>N</i> -Acetylglycine (Donohue & Marsh, 1962)	C(1)	1084	20	(78)	1	10	R
	C(2)	1154	-34	(95)	20	13	R
	C(3)	1106	38	(95)	15	3	R
	C(4)	1595	1	(189)	12	6	R
	N	1113	-5	(84)	17	9	R
	O(1)	1353	-32	(77)	29	8	R
	O(2)	1670	117	(98)	7	7	R
	O(3)	1399	101	(92)	29	7	R
							
2. Chrysene (Burns & Iball, 1960)	C(1)	1397	45	(28)	2	17	R
	C(2)	1445	-14	(29)	6	8	R
	C(3)	1726	-26	(34)	14	7	R
	C(4)	2034	-18	(41)	6	7	R
	C(5)	2079	-4	(41)	7	5	R
	C(6)	1923	3	(38)	3	8	R
	C(7)	1557	-28	(31)	15	7	R
	C(8)	1699	-2	(34)	0	11	R
	C(9)	1619	44	(32)	49	8	R
							
3. <i>cis,cis</i> -1,2,3,4-Tetraphenylbutadiene (Karle & Dragonette, 1965)	C(1)	1544	-54	(89)	56	6	R
	C(2)	1531	-38	(89)	18	7	R
	C(3)	1380	-280	(89)	36	4	NR
	C(4)	1809	32	(89)	8	13	R
	C(5)	2151	152	(89)	6	12	R
	C(6)	1982	-105	(89)	40	6	R
	C(7)	2094	123	(89)	11	8	R
	C(8)	1776	23	(89)	2	8	R
	C(9)	1548	-165	(89)	3	6	R
	C(10)	2000	139	(89)	31	5	R
	C(11)	2166	64	(89)	6	6	R
	C(12)	2242	76	(89)	4	19	R
	C(13)	2082	78	(89)	34	37*	R
	C(14)	1750	-50	(89)	8	7	R
							
4. Bicyclohexylidene (Sasvári & Löw, 1965)	C(1)	1171	-107	(28)	64	14	NR
	C(2)	1500	33	(31)	26	10	R
	C(3)	1619	-2	(33)	97	3	R
	C(4)	1716	30	(36)	1	10	R
	C(5)	1657	4	(36)	5	14	R
	C(6)	1524	42	(32)	20	35 (1,2)*	R
							
5. Quinhydrone (Sakurai, 1965) (1) Hydroquinone	O(1)	1502	48	(43)	74	16	R
	C(1)	1059	-23	(43)	79	30	?
	C(2)	1156	22	(43)	27	8	R
	C(3)	1071	-47	(43)	45	14	R
							
6. (2) Quinone	O(2)	1457	44	(43)	23	10	R
	C(4)	1122	17	(43)	16	34*	R
	C(5)	1167	-9	(43)	11	5	R
	C(6)	1112	-51	(43)	25	15	R
							

Table 1 (cont.)

	Atom	$U^o$ ( $\text{\AA}^2 \times 10^4$ )	$U^o - U^c$ ( $\text{\AA}^2 \times 10^4$ )	( $\sigma$ )	$S$	$\theta$ ( $^\circ$ )		
7. 1,8-Bisdehydro-[14]annulene (Bailey & Mason, 1966)								
		C(1)	1226	-36	(65)	4	37	NR
		C(2)	1508	-11	(71)	33	8	R
		C(3)	1543	-30	(73)	50	10	R
		C(4)	1402	8	(68)	19	22	R
		C(5)	1470	80	(68)	95	13	R
		C(6)	1580	15	(78)	16	16	R
		C(7)	1482	-27	(76)	14	10	R
8. 3-3-Bi-2-isoxazoline (Bednowitz, Fankuchen, Okaya & Soffer, 1966)								
		C(1)	1763	-17	(44)	7	54	NR
		C(2)	2118	-84	(69)	32	28	?
		C(3)	2674	41	(77)	11	29	?
		N(4)	2284	32	(62)	109	11	R
		O(5)	2832	27	(63)	27	16 (1,2)	R
9. [2.2]Paracyclophane (Coulter & Trueblood, 1963)								
		C(1)	1878	-105	(43)	86	55 (2,3)*	?
		C(2)	1695	-3	(38)	33	30	?
		C(3)	1863	52	(43)	96	26	?
		C(4)	1861	74	(44)	121	28*	R
		C(5)	1720	22	(41)	76	13	R
		C(6)	1842	36	(44)	81	45	NR
		C(7)	1819	37	(43)	116	16 (1,2)	R
		C(8)	1879	-112	(46)	239	45 (2,3)	NR
10. Phenylcyclobutenedione (Wong, Marsh & Schomaker, 1964)								
		C(1)	1679	-24	(29)	8	46	NR
		C(2)	2041	-100	(34)	29	47*	?
		C(3)	2082	-106	(38)	161	23	?
		C(4)	2190	38	(43)	164	24 (2,3)	?
		C(5)	1840	18	(30)	25	25	R
		C(6)	1460	43	(27)	42	49 (2,3)*	R
		C(7)	1460	61	(27)	4	38*	?
		C(8)	1824	14	(33)	42	11	R
		C(9)	1793	-43	(30)	19	32*	R
		C(10)	2593	-19	(30)	82	11	R
		O(1)	2421	69	(28)	323	28	NR
		O(2)	2202	48	(25)	34	23	R
11. Cytosine-5-acetic acid (Marsh, Bierstedt & Eichhorn, 1962)								
		N(1)	1019	-51	(36)	1	14	R
		C(2)	941	-44	(37)	30	24	R
		N(3)	999	-12	(35)	194	9	?
		C(4)	852	-34	(35)	76	46 (2,3)*	R
		C(5)	888	61	(35)	22	23	R
		C(6)	1083	63	(40)	110	26	?
		O(7)	1311	64	(37)	257	21	NR
		N(8)	1201	-39	(40)	66	6	R
		C(9)	1037	59	(41)	1	14	R
		C(10)	930	-94	(36)	203	23	NR
		O(11)	1141	-28	(30)	535	27 (1,2)	NR
		O(12)	1335	32	(35)	9	35	NR

Table 1 (cont.)

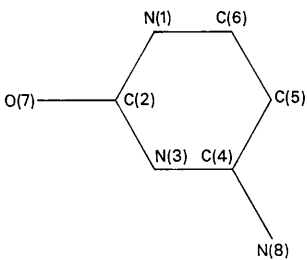
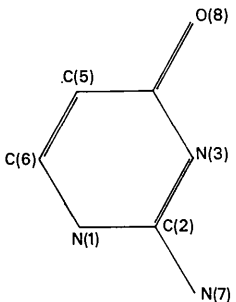
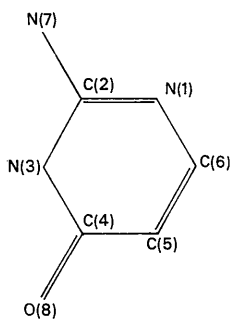
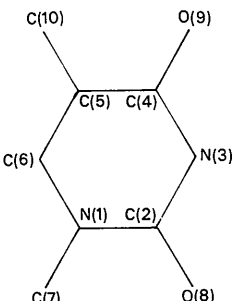
	Atom	$U^o$ ( $\text{\AA}^2 \times 10^4$ )	$U^o - U^c$ ( $\text{\AA}^2 \times 10^4$ )	( $\sigma$ )	$S$	$\theta$ ( $^\circ$ )	
12. Cytosine (Barker & Marsh, 1964)							
	N(1)	879	-16	(18)	22	18	R
	C(2)	821	-17	(21)	15	28	?
	N(3)	810	10	(16)	133	26	?
	C(4)	868	13	(21)	95	10	R
	C(5)	1012	94	(22)	57	13	NR
	C(6)	961	43	(22)	239	36 (2,3)	NR
	O(7)	1048	-74	(16)	35	6	NR
	N(8)	1140	-52	(21)	36	11	?
13. Isocytosine (Sharma & McConnell, 1965) (A)							
	N(1)	1678	118	(14)	32	14	NR
	C(2)	1403	-44	(16)	43	17	?
	N(3)	1317	-117	(11)	38	16 (2,3)	NR
	C(4)	1335	-107	(12)	16	29	NR
	C(5)	1685	91	(16)	50	28 (1,2)	NR
	C(6)	1812	123	(18)	60	24 (2,3)	NR
	N(7)	1945	46	(16)	28	22	?
	O(8)	1720	-110	(11)	68	13	NR
14. (B)							
	N(1)	1565	49	(12)	25	39	NR
	C(2)	1323	-119	(12)	39	24	NR
	N(3)	1318	-75	(10)	16	31	NR
	C(4)	1404	-32	(14)	0	43	NR
	C(5)	1635	68	(15)	54	7 (1,2)	NR
	C(6)	1649	72	(15)	17	23	NR
	N(7)	1873	-2	(15)	188	36 (1,2)	NR
	O(8)	1805	39	(10)	11	19	NR
15. 1-Methylthymine (Hoogsteen, 1963)							
	N(1)	1776	46	(31)	15	25	R
	C(2)	1808	46	(31)	7	13	R
	C(3)	1754	76	(29)	118	34 (2,3)*	?
	C(4)	1572	-164	(31)	267	35 (2,3)	NR
	C(5)	1678	-104	(37)	3	44	NR
	C(6)	1784	77	(40)	65	37*	R
	C(7)	2316	130	(28)	58	14	NR
	O(8)	2635	435	(27)	131	15	NR
	O(9)	1826	-270	(21)	139	41 (1,2)*	NR
	C(10)	2110	-273	(33)	8	32	NR

Table 1 (cont.)

Atom	$U^o$ ( $\text{\AA}^2 \times 10^4$ )	$U^o - U^c$ ( $\text{\AA}^2 \times 10^4$ )	( $\sigma$ )	$S$	$\theta$ ( $^\circ$ )	
16. Cytidine (Furberg, Peterson & Rømming, 1965)						
C(6)	1136	-62	(43)	261	25 (2,3)	NR
C(2)	1037	38	(40)	238	44 (2,3)	NR
C(4)	1154	131	(44)	263	24	NR
C(5)	1327	139	(51)	17	19	?
C(1')	975	-24	(40)	716	52 (1,3)	NR
C(4')	917	-132	(38)	115	48*	?
C(3')	863	-170	(38)	371	22 (1,2,3)	NR
C(2')	906	-157	(38)	227	36 (2,3)	NR
C(5')	1177	48	(47)	4	48*	R
O(2)	1139	36	(28)	180	30	?
O(1')	1052	5	(29)	360	47 (1,2)	NR
O(5')	1353	185	(38)	1036	31 (2,3)	NR
O(3')	1292	69	(36)	193	43	NR
O(2')	1218	-106	(34)	22	18	NR
N(1)	1041	-45	(40)	197	29	?
N(3)	1001	52	(37)	23	51	NR
N(6)	1470	-3	(48)	28	15	R
17. 1-Cyclohexenyl-1-cyclobutenedione (Karle, Britts & Brenner, 1964)						
O(1)	1510	-114	(89)	425	11	NR
O(2)	1967	106	(89)	50	43	NR
C(3)	1232	51	(116)	304	56 (1,2)	NR
C(4)	965	-318	(116)	1304	30	NR
C(5)	1097	-266	(116)	1241	37 (1,2)	NR
C(6)	765	-204	(116)	2521	39 (1,3,2)	NR
C(7)	983	-4	(116)	365	44 (1,2)	NR
C(8)	1301	63	(116)	596	26 (2,3)	NR
C(9)	1689	95	(116)	166	25 (1,2)	?
C(10)	2048	423	(116)	664	30 (1,2)	NR
C(11)	1859	162	(116)	62	54	NR
C(12)	1520	6	(116)	458	47	NR

mulae. Even the moderately good fit of the molecules in the second section of Table 1 would seem to indicate that refinement of molecular structures using the rigid-body model from the beginning, as suggested by Pawley (1964), might be worth while as a general procedure. It would certainly ensure that temperature parameters were never inadvertently used as fudge factors to compensate for other effects of possible structural importance.

It must, of course, be appreciated that agreement between the  $U_{ij}^o$  and the  $U_{ij}^c$  does not of itself guarantee that the molecule is actually vibrating as a rigid body, since such non-rigid-body motions as the twisting of the two halves of a molecule about a central bond (e.g. in molecule 4) would be indistinguishable from true rigid-body vibrations. However, even in such a case, the Pawley method would still be applicable.

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