

Table 4. Bond lengths and angles and their standard deviations

	Bond length	σ		Bond angle	σ
B—F(1)	1.41 Å	0.03 Å	F(1)—B—F(2)	108.5°	1.5°
B—F(2)	1.37	0.02	F(1)—B—F(3)	112.2	1.8
B—F(3)	1.30	0.03	F(1)—B—F(4)	110.6	1.7
B—F(4)	1.38	0.03	F(2)—B—F(3)	110.2	1.8
Cu—N(1)	2.02	0.01	F(2)—B—F(4)	108.2	1.7
Cu—N(2)	2.03	0.01	F(3)—B—F(4)	107.1	1.5
Cu—F(4)	2.56	0.01 (5)	N(1)—Cu—N(2)	86.4	0.5
C(1)—N(1)	1.48	0.02	N(1)—Cu—F(4)	94.6	0.5
C(2)—N(2)	1.49	0.02	N(2)—Cu—F(4)	93.1	0.5
C(1)—C(2)	1.56	0.03	Cu—N(1)—C(1)	106.7	1.1
			Cu—N(2)—C(2)	108.4	1.1
			N(1)—C(1)—C(2)	108.3	1.1
			N(2)—C(2)—C(1)	106.9	1.4
			Cu—F(4)—B	116.3	1.5

and the semi-coordinated bond result in the distortion of the BF_4^- ion.

References

- BILLY, C. & HAENDLER, H. M. (1957). *J. Amer. Chem. Soc.* **79**, 1049.
 BROWN, B. W. & LINGAFELTER, E. C. (1964). *Acta Cryst.* **17**, 254.
 BROWN, D. S., LEE, J. D., MELSOM, B. G. A., HATHAWAY, B. J., PROCTER, I. M. & TOMLINSON, A. A. G. (1967). *Chem. Comm.* p. 369.
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1041.
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
 KOMIYAMA, Y. & LINGAFELTER, E. C. (1964). *Acta Cryst.* **17**, 1145.
 PAJUNEN, A. (1967). *Suom. Kem.* **B40**, 32.

Acta Cryst. (1968). **B24**, 734

The Rigid-Body Vibrations of Molecules in Crystals II. Application of the Schomaker-Trueblood Analysis

BY DESMOND M. BURNS, WILLIAM G. FERRIER AND JOHN T. McMULLAN
Physics Department, University of Dundee, Dundee, Scotland

(Received 10 July 1967)

The rigid-body motions of nine non-centrosymmetric molecules, examined in a previous paper with use of the Cruickshank analysis, have been re-analysed by the Schomaker-Trueblood technique, which takes account of correlation between translation and libration. Detailed results are given for 1-methylthymine and phenylcyclobutenedione to illustrate the improvement that results, and it is concluded that the rigid-body model is widely applicable. It is also pointed out how the full Schomaker-Trueblood analysis permits the rigidity of parts of molecules to be examined, and the advantages of such an approach are stressed.

Introduction

In an earlier paper (Burns, Ferrier & McMullan, 1967*a*) hereinafter referred to as I, the anisotropic temperature parameters of seventeen molecular crystals were analysed in terms of rigid-body motions as suggested by Cruickshank (1956). Criteria were proposed on the basis of which it could be decided whether or not the rigid-body model adequately accounted for the atomic thermal parameters obtained from the usual least-squares refinement. An atom-by-atom comparison was then used to classify the seventeen molecules roughly in order of their rigidity. Since then it has been shown (Schomaker & Trueblood, 1968) that the Cruickshank analysis is incomplete for molecules that do not possess a centre of symmetry, since in such cases correlation between translation and libration cannot be neglected.

Of the seventeen structures analysed in I, eight (numbered consecutively 2 through 9 in Table 1 of I*) have centrosymmetric molecules and are therefore unaffected. The remaining nine molecules have been re-analysed by the Schomaker-Trueblood (briefly, S-T) technique. It is a striking confirmation of the need for the full S-T analysis that of the molecules classified as unequivocally rigid in I, only *N*-acetylglycine was non-centrosymmetric.

Procedure

The S-T analysis gives values of the comparison parameters that are independent of the origin and orien-

* In the case of *cis,cis*-1,2,3,4-tetraphenylbutadiene only half of the molecule was shown by mistake, although the analysis was carried through referred to the centre of the whole molecule as origin.

tation of the coordinate axes used, and this was fully verified in the present work by using two different rectangular Cartesian coordinate frames: the first defined by the principal axes of inertia of the molecule at its centre of mass; the second defined by unit vectors $\mathbf{b} \times \hat{\mathbf{c}}^*$, \mathbf{b} , $\hat{\mathbf{c}}^*$. In addition, for some of the molecules, the analysis was carried out with reference to the direct-cell axes $\mathbf{a}, \mathbf{b}, \mathbf{c}$ as suggested by Burns, Ferrier & McMullan (1967*b*) without using an orthonormal frame at all. In this case the eigenvalues and eigenvectors of the U^{ij} tensors were determined directly as suggested by Waser (1955). These eigenvalues and eigenvectors can be used to obtain the comparison parameters exactly as in I, except that now the matrices Λ^o and Λ^c which diagonalize the U^o and U^c matrices are no longer orthogonal, so that the rotation matrix \mathbf{R} whose trace gives the orientation parameter has to be determined from the relation $\mathbf{R} = (\Lambda^o)^{-1} \Lambda^c$ instead of simply $\hat{\Lambda}^o \Lambda^c$. This analysis also led to precisely the same results as before.

In the course of the work, the magnitude of the round-off error in the program (JMTRAC) was directly assessed by using as input a set of b_{ij} values for chrysene that had been calculated from a rigid-body model. These data were rounded off to the form 0.0xxxx which is the precision quoted in the literature for many well-determined structures. The r.m.s. values of the resulting comparison parameters were 0.0004 Å² for the size, zero for the shape, and 0.7° for the orientation. The inversion procedure for the 22 × 22 matrix in the full S-T analysis was checked in all cases by forming the product of the matrix with its calculated inverse. In no case was an off-diagonal term greater than 10⁻⁷, a more usual figure being 10⁻¹⁰.

Results

The overall effect of the S-T analysis is summarized in Table 1, where all seventeen molecules are listed in

a revised order of decreasing rigidity. For the non-centrosymmetric molecules, the improvement in fit is roughly indicated by the ratios of the averaged S-T comparison parameters to the averaged Cruickshank comparison parameters, the averages being taken over all the atoms of a molecule. This averaging has been done, despite our belief that only an atom-by-atom comparison is meaningful, merely to indicate a trend, since it is not proposed to present full comparison data for all nine molecules. Also shown in Table 1 is the revised status of each molecule, and, in brackets, the previous status and the previous order of listing.

The re-classification has been done strictly on the basis of the criteria established in I, the published e.s.d.'s of the b_{ij} being used to compute the e.s.d. of U^o and so determine the acceptability or otherwise of the size parameter. However, examination of the results for 1-methylthymine (Table 2) shows an effect that is rather disturbing. All the shape and orientation parameters are perfectly satisfactory, yet four of the atoms are classified as doubtful and one as non-rigid on the basis of their size parameters alone. Thus, for atom C(7), the size parameter of 67 is taken as doubtful because it is 2.4 times the computed standard deviation of 28, although it amounts to only 2.9% of the value of U^o . Since the least-squares process of fitting the best rigid-body minimizes the differences between U^{ij} and U_c^{ij} , one would expect the size parameter to be less sensitive to deviations from rigidity than the shape and orientation parameters. The detailed results for 1-methylthymine make nonsense of this expectation. A suspicion that the published e.s.d.'s might perhaps be too low led to a careful scrutiny of the published papers. In only six of the seventeen papers had a value of the standard deviation of an observation of unit weight been quoted, these ranging from 'near 1.0' to 2.0, and even in these six cases it was not always clear whether or not the e.s.d.'s quoted included this factor. No value was quoted for 1-methylthymine, and no details were

Table 1. *Seventeen molecular structures in an amended order of decreasing rigidity*

		$\bar{\Delta}U_{ST}/\bar{\Delta}U_C$	\bar{S}_{ST}/\bar{S}_C	$\bar{\theta}_{ST}/\bar{\theta}_C^*$	
1 (1)	<i>N</i> -Acetylglycine	0.36	0.55	0.90	R (R)
2 (2)	Chrysene	—	—	—	R (R)
3 (10)	Phenylcyclobutenedione	0.76	0.20	0.50	R (?)
4 (3)	<i>cis, cis</i> -1,2,3,4-Tetraphenylbutadiene	—	—	—	R (R)
5 (4)	Bicyclohexylidene	—	—	—	R (R)
	Quinhydrone:				
6 (5)	(1) Hydroquinone	—	—	—	R (R)
7 (6)	(2) Quinone	—	—	—	R (R)
8 (7)	1,8-Bisdehydro[14]annulene	—	—	—	R (R)
9 (11)	Cytosine-5-acetic acid	0.43	0.61	0.77	R (?)
10 (8)	3-3-Bi-2-isoxazoline	—	—	—	? (?)
11 (9)	[2.2]Paracyclophane	—	—	—	? (?)
12 (15)	1-Methylthymine	0.31	0.21	0.26	? (NR)
13 (13)	Isocytosine (A)	0.34	0.30	0.94	? (NR)
14 (14)	Isocytosine (B)	0.56	0.29	0.56	? (NR)
15 (12)	Cytosine	0.48	0.33	1.10	? (NR)
16 (16)	Cytidine	0.78	0.89	0.94	NR (NR)
17 (17)	1-Cyclohexenyl-1-cyclobutenedione	0.73	1.58	0.93	NR (NR)

* $\bar{\Delta}U$, \bar{S} and $\bar{\theta}$ are the averaged comparison parameters for the whole molecule, the subscripts ST and C referring to results for the full Schomaker-Trueblood and Cruickshank analyses respectively.

given of the expression used for calculating the e.s.d.'s. However, the weighting scheme was derived from a study of the random errors in the experimental data, and Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) have emphasized the need in such cases for having the standard deviation of an observation of unit weight close to unity. How close to unity, unfortunately, seems to be very much a matter of personal opinion. Thus Sharma & McConnell (1965) were quite happy with a value of 1.5, while Marsh, Bierstedt & Eichhorn (1962) interpreted a value of 1.6 as indicating the presence of systematic error and suggested that the e.s.d.'s quoted for their b_{ij} might be appreciably underestimated. Where such uncertainty exists the strict application of the criterion on size would be unrealistic, and one might plausibly suggest an alternative criterion based on the absolute value of $(U^o - U^c)/U^o$. For example, if a value of 3% in this quantity is chosen as the e.s.d. in U^o , then 1-methylthymine is reclassified as unequivocally rigid, with every atom rigid, while cytosine and the two tautomeric forms of isocytosine are all three materially improved. We still feel, however, that the most satisfactory criterion is that described in I, and would make a plea for greater rigour in the presentation of e.s.d.'s in published structures.

Examination of Table 1 shows how the inclusion of the correlation matrix S tightens up the agreement with the rigid-body model in all cases except molecules 16 and 17 where the model is simply not appropriate. The detailed results for phenylcyclobutenedione, where the improvement is very striking, are shown in Table 2. Four atoms which were previously questionable and two which were previously non-rigid are now completely satisfactory, and only one (previously rigid) is

now questionable because of a size parameter 2.8 times the e.s.d. of U^o .

Three different sets of rigid-body tensors for phenylcyclobutenedione are displayed in Table 3, with the e.s.d.'s shown in brackets. The first and second columns show the results for inertial axes with origin at the centre of mass, the first column being for the simple Cruickshank analysis and the second column for the S-T analysis. It will be seen that the T and ω tensors agree very well indeed, and the same kind of agreement was found for other molecules when the S-T analysis was performed in the inertial frame. The marked improvement in fit with the rigid-body model effected by the inclusion of the correlation matrix S is shown by the e.s.d.'s of T and ω in the two columns: those in column 2 are roughly half of those in column 1. When considering the magnitude of the components of S , it must be borne in mind that the analysis does not determine the diagonal elements directly, but only the differences $S_{22} - S_{33}$, $S_{33} - S_{11}$, and $S_{11} - S_{22}$. The actual diagonal elements shown in Table 3 were obtained by imposing the subsidiary condition $\text{Trace}(S) = 0$. Schomaker & Trueblood (1968) have pointed out that the Schwartz inequality imposes on the trace the limitation $\text{Tr}(S) \leq \{\text{Tr}(T)\text{Tr}(\omega)\}^{\frac{1}{2}}$, but apart from this the trace is indeterminate. If any other value had been chosen then each of the diagonal elements listed would have been increased by one-third of that value. The only way of obtaining the diagonal elements explicitly is by a lattice-dynamical calculation (Pawley, 1968).

The third column contains the rigid-body tensors as determined by the S-T analysis in the orthogonal frame defined by $\hat{b} \times \hat{c}^*$, \hat{b} , \hat{c}^* . The origin of this frame is 7.3 Å from the centre of mass, and the effect of this is shown by the greatly increased values of the elements of T

Table 2. *Size, shape, and orientation parameters for 1-methylthymine and phenylcyclobutenedione calculated on the basis of the S-T analysis*

	Atom	U^o (Å ² × 10 ⁴)	$U^o - U^c$ (Å ² × 10 ⁴)	(σ)	S	θ (°)	
1-Methylthymine	N(1)	1776	-6	(31)	25	7	R
	C(2)	1808	-84	(31)	38	4	?
	C(3)	1754	-25	(29)	10	5	R
	C(4)	1572	-1	(31)	29	5	R
	C(5)	1678	88	(37)	17	15	?
	C(6)	1784	75	(40)	16	13	R
	C(7)	2316	-67	(28)	5	4	?
	O(8)	2635	85	(27)	3	0	NR
	O(9)	1826	-53	(21)	26	12	?
	C(10)	2110	-12	(33)	3	9	R
Phenylcyclobutenedione	C(1)	1679	19	(29)	15	24	R
	C(2)	2041	-23	(34)	1	8	R
	C(3)	2082	-57	(38)	15	9	R
	C(4)	2190	48	(43)	21	8	R
	C(5)	1840	21	(30)	16	18	R
	C(6)	1460	52	(27)	29	51*	R
	C(7)	1460	50	(27)	6	11	R
	C(8)	1824	0	(33)	17	3	R
	C(9)	1793	-84	(30)	20	21	?
	C(10)	2593	-52	(30)	19	10	R
	O(1)	2421	11	(28)	28	6	R
	O(2)	2202	14	(25)	1	9	R

* This large value of the orientation parameter is acceptable because of a nearly circular section of the thermal ellipsoid.

and S. It is noticeable that the relative precision of the off-diagonal elements of S has increased, while there has been a compensating decrease in the relative precision of T. Clearly the overall reliability of the rigid-body model cannot depend on the choice of co-ordinate system. Schomaker & Trueblood also show that ω is invariant to a shift of origin. This is not directly apparent from Table 3, since a rotation is also involved in the change of reference frame. However, we have checked that the two ω tensors are related by the rotation alone, as is evidenced by the invariance of their trace. This affords an additional confirmation of the correctness of the program.

It would be possible on the basis of the detailed results in Table 2 to classify phenylcyclobutenedione as a rigid molecule, in the sense that it would certainly refine satisfactorily by the Pawley (1964) method. However, Lonsdale, Walley & El Sayed (1966) have stressed the importance of examining, not only the whole molecule, but also limited parts of it, in order to investigate the possibility of independent, non-rigid-body vibrations of particular atoms. In this way they demonstrated unequivocally that the ketonic oxygen atoms in anthraquinone display large out-of-plane vibrations which are not accounted for on a rigid-body model. The S-T treatment permits this type of analysis to be extended to non-centrosymmetric units, and since Wong, Marsh & Schomaker (1964) suggest that the out-of-plane vibrations of the two oxygen atoms in phenylcyclobutenedione are not rigid-body motions, it was decided to investigate this point. Accordingly, the rigid-body analysis was repeated omitting the two oxygen atoms. The result was a slight tightening up of the ten carbon atoms, C(9) in particular going rigid, and a clear indication that O(1) did in fact have a substantial non-rigid-body vibration perpendicular to the molecular plane. There was no such clear indication in the case of O(2). Although the results here are hardly as conclusive as was the case in anthraquinone, they seem to us to demonstrate the value of such a procedure.

Conclusions

The present work has confirmed the need for the full S-T analysis in investigating the validity of the rigid-body model, and has shown the wide applicability of

that model. Since the results are independent of the choice of origin, the rigidity of any part of a molecule can now be separately investigated, and this should certainly be done where an atom-by-atom scrutiny of the results for the whole molecule gives reason for suspecting some atoms of non-rigid-body motions. Another, and perhaps better, method of examining non-rigid-body vibrations in a quasi-rigid molecule would be to follow the suggestion of Pawley (1964) that structure refinement be done using the rigid-body model from the start. His actual equations, of course, need to be amended to include the correlation matrix S, but this actually simplifies his suggested procedure, since the abortive attempt to determine a unique origin, which is necessarily non-linear, is avoided. We are confident that at least eleven of the present seventeen structures would refine to a satisfactory level on this basis. Completion of the refinement with the b_{ij} allowed to vary independently would then yield definite information about deviations from rigidity of any particular atom.

The authors wish to thank Dr A. Nechvatal for helpful discussions of various points.

References

- BURNS, D. M., FERRIER, W. G. & MCMULLAN, J. T. (1967a). *Acta Cryst.* **22**, 623.
 BURNS, D. M., FERRIER, W. G. & MCMULLAN, J. T. (1967b). *Acta Cryst.* **23**, 1098.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754.
 CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Edited by PEPINSKY, R., ROBERTSON, J. M. & SPEAKMAN, J. C. p.47. Oxford: Pergamon Press.
 LONSDALE, K., WALLEY, D. & EL SAYED, K. (1966). *Acta Cryst.* **20**, 13.
 MARSH, R. E., BIERSTEDT, R. & EICHORN, E. L. (1962). *Acta Cryst.* **15**, 310.
 PAWLEY, G. S. (1964). *Acta Cryst.* **17**, 457.
 PAWLEY, G. S. (1968). *Acta Cryst.* **B24**, 485.
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968) *Acta Cryst.* **B24**, 63.
 SHARMA, B. D. & MCCONNELL, J. F. (1965). *Acta Cryst.* **19**, 797.
 WASER, J. (1955). *Acta Cryst.* **8**, 731.
 WONG, CHI-HSIANG, MARSH, R. E. & SCHOMAKER, V. (1964). *Acta Cryst.* **17**, 131.

Table 3. *Rigid-body tensors for phenylcyclobutenedione*

	Cruickshank analysis			S-T analysis			S-T analysis		
	Centre of mass coordinates			Centre of mass coordinates			Orthogonal crystal coordinates		
T (\AA^2) $\times 10^4$	506 (19)	-13 (18)	-21 (20)	507 (10)	-13 (10)	-21 (11)	7181 (526)	134 (181)	-912 (144)
		427 (27)	19 (27)		428 (14)	17 (14)		1865 (78)	-852 (60)
			431 (38)			425 (20)			1020 (41)
ω (rad^2) $\times 10^4$	137 (20)	5 (5)	0 (8)	136 (11)	-1 (3)	0 (4)	34 (2)	-6 (4)	4 (3)
		26 (4)	1 (4)		28 (2)	-2 (2)		120 (11)	-38 (4)
			35 (3)			34 (2)			44 (3)
S ($\text{\AA} \cdot \text{rad}$) $\times 10^4$				-13 (9)	-45 (9)	9 (5)	64 (43)	216 (12)	-135 (9)
				9 (4)	8 (6)	-21 (2)	-852 (75)	-20 (30)	118 (19)
				6 (3)	-11 (2)	6 (6)	417 (29)	2 (16)	-43 (31)