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RIGID BODY ANALYSIS OF THE THERMAL MOTION IN A 2-BENZOYL-1, 3, 4-TRIPHENYL-1-CYCLOPENTANOL CRYSTAL*

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On the basis of the anisotropic temperature factors, obtained from X-ray crystal structure analysis, thermal vibrations of a 2-Benzoyl-1,3,4-Triphenyl-1-Cyclopentanol crystal were investigated in terms of rigid body motion by the metod of Schomaker and Trueblood. Libration of the molecule as a whole is small. Phenyl moieties librate independently around bonds linking them to the cyclopentanol ring; translational components of their vibrations are similar to those of the whole molecule; correlation of translation and rotation is insignificant.

1. *Introduction*

The crystal and molecular structure of 2-Benzoyl-1,3,4-Triphenyl-1-Cyclopentanol was recently solved by the single crystal X-ray method [1]. The analysis of the packing of molecules showed that there are no significant intermolecular interactions. The molecular structure with atom numbering and some distances is shown in Fig. 1. In the structure refinement, carried out by the full-matrix leasts quares method, all atoms were assumed to vibrate independently in anisotropic, harmonic approximation. The temperature factors u_{ij} are listed in Table I, as they were not given in the previous paper.

The point of interest of this study was to verify whether a rigid body model can be successfully used to describe the thermal vibration of the molecule. This molecule seemed to be interesting for this type of study since it is well balanced in shape and consists of several rigid fragments.

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* Dedicated to Professor Kazimierz Gumiński on the occasion of his 70-th birthday.

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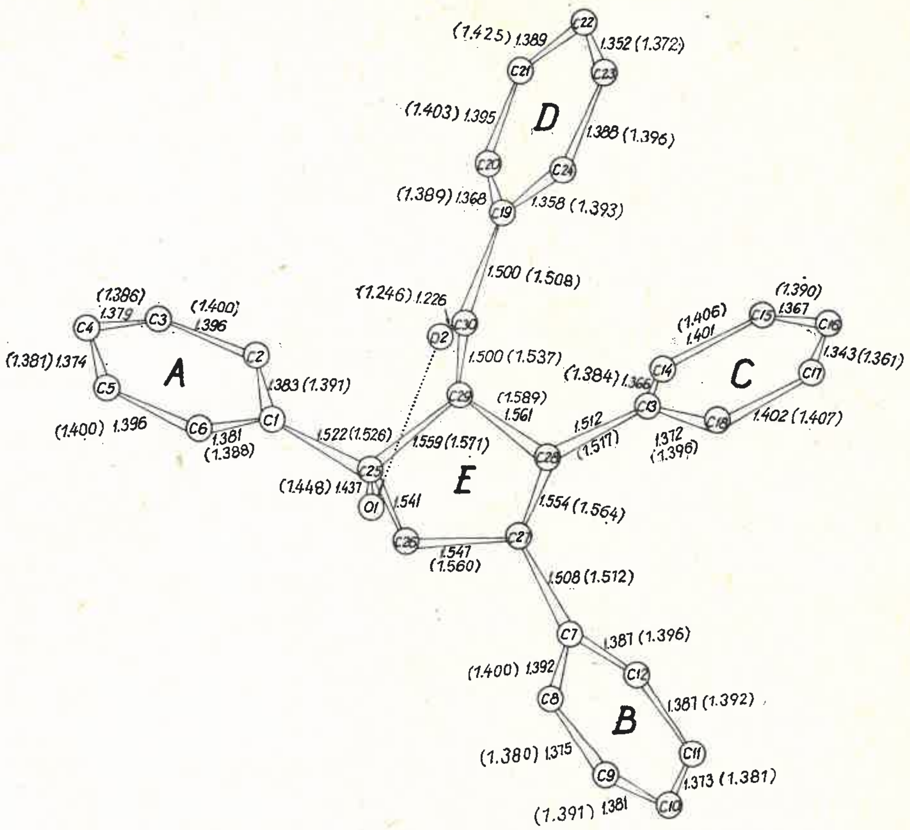

Fig. 1. View of the molecule of 2-benzoyl-1,3,4-triphenyl-1-cyclopentanol with marked bond lengths in Å; values in brackets correspond to bonds length corrected for thermal motion.

TABLE I

Thermal parameters ($\times 10^4$) with their standard deviations in the form:

$$\exp\left[-2\pi^2(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+u_{33}l^2c^{*2}+2u_{23}klb^*c^*+2u_{13}hla^*c^*+2u_{12}hka^*b^*)\right]$$

	u_{11}	u_{22}	u_{33}	u_{23}	u_{13}	u_{12}
C1	334(13)	260(11)	359(12)	−8(9)	110(10)	−54(9)
C2	395(15)	410(13)	341(12)	−1(10)	77(11)	3(11)
C3	516(18)	519(15)	412(14)	7(12)	11(13)	−65(14)
C4	671(20)	499(15)	367(14)	−75(12)	109(14)	−82(15)
C5	621(19)	498(16)	459(15)	−131(12)	228(14)	− 11(14)
C6	465(16)	415(13)	418(14)	−67(11)	144(12)	−7(12)
C7	403(14)	289(11)	368(12)	−37(9)	131(11)	−44(10)
C8	461(16)	504(15)	333(13)	−13(11)	151(12)	87(12)
C9	530(18)	617(18)	490(16)	81(13)	143(14)	131(15)
C10	621(20)	678(18)	357(14)	29(13)	123(14)	36(16)
C11	745(23)	627(17)	328(14)	−7(12)	227(15)	91(16)
C12	497(17)	428(14)	457(14)	−40(11)	208(13)	54(13)

TABLE I (continued)

	u_{11}	u_{22}	u_{33}	u_{23}	u_{13}	u_{12}
C13	375(14)	283(11)	339(11)	18(9)	128(10)	3(10)
C14	386(17)	470(16)	785(21)	246(15)	50(15)	−46(13)
C15	606(21)	419(16)	975(25)	173(17)	244(19)	−148(16)
C16	808(26)	394(16)	774(21)	179(15)	243(20)	−57(17)
C17	667(24)	569(20)	920(24)	344(18)	3(20)	49(18)
C18	497(19)	446(16)	717(20)	229(14)	27(16)	12(14)
C19	421(15)	366(12)	399(12)	−32(10)	177(11)	10(11)
C20	522(19)	481(16)	758(20)	−192(15)	108(16)	−75(15)
C21	795(28)	551(20)	1007(27)	−247(18)	322(23)	−161(20)
C22	1124(43)	438(20)	1561(44)	−374(25)	603(36)	−220(24)
C23	1011(43)	528(25)	2334(79)	−424(35)	356(44)	205(28)
C24	686(24)	442(17)	1305(34)	−233(20)	160(24)	167(18)
C25	267(12)	293(11)	364(12)	−34(9)	86(10)	10(9)
C26	438(16)	284(12)	361(12)	4(10)	115(12)	−52(11)
C27	321(14)	321(11)	343(12)	−6(9)	108(11)	−2(10)
C28	274(12)	302(11)	304(11)	34(9)	66(9)	−3(10)
C29	288(13)	278(11)	298(11)	13(8)	88(10)	3(9)
C30	330(14)	360(12)	283(11)	34(9)	70(10)	33(10)
O1	310(10)	385(9)	455(10)	−61(8)	46(8)	47(8)
O2	340(10)	469(10)	614(11)	−50(8)	183(9)	−23(8)

2. *Methods and results*

The u_{ij} values obtained in the structure refinement were treated as observed ones for the calculation of the possible rigid body motion of the molecule by the method of Schomaker and Trueblood [2].

Most of the calculations were done with XANADU program written by Roberts and Sheldrick adapted for CYBER 72.

The orthogonal coordinate system defined so that XO parallel to a^*, YO to b, and ZO to z was used throughout the calculations.

Two models were used: one treating the whole molecule as a rigid body, the second consisting of the rigid fragments of a molecule vibrating independently. The molecule was divided into phenyl rings taken together with adjacent atoms in order to avoid the singularity mentioned by Cruickshank [3] for circular planar molecules. The obtained tensors of vibration are given in Table II together with the discrepancy factors R_g. The discrepancy factor is defined

$$R_g = \frac{\sum\limits_{ij} (u_{ij}^{o} - u_{ij}^{c})^2}{\sum\limits_{ij} u_{ij}^{o2}},$$

where u_{ij}^{o} are observed values and u_{ij}^{c} are values calculated by the least squares fit to the rigid body motion. The Hamilton significance test was applied to the discrepancy factors

[4]. The ratio, $\mathcal{R}_{\text{obs}}$, of the R_g factors of the two models, with the value 0.07 taken as the average R_g for the second model, was 3.9. Since $\mathcal{R}_{\text{obs}}-1 = 2.9 \gg \mathcal{R}_{60,160,0.005}-1 = 0.31$ the model of the whole molecule vibrating as a rigid body can easily be rejected at the 0.005 significance level. However, a comparison of the translational tensors T calculated for the whole molecule and for its fragments showed that the corresponding elements of the tensors, except three, are equal within a range of 2σ, and all are equal within the 3σ range. All elements of screw motion tensors S, except two, were equal to zero, within the 2σ range. Hence, as far as translational motion is concerned the whole molecule behaves as a rigid body.

TABLE II

Vibrational tensor (× 10^4) with e.s.d.'s in parentheses

Atom used in rigid body model	Librational tensor L (radians)^2			Correlation of translation and rotation tensor S (radians × Å)			Translational tensor T (Å^2)		
C1–C6, C25	36(8)	3(5)	26(8)	−10(9)	−13(11)	6(7)	272(14)	−14(14)	21(11)
$R_g = 0.0528$		32(7)	24(9)	−13(9)	20(9)	−7(6)		271(16)	3(13)
			88(16)	6(17)	−7(14)	−11(9)			321(12)
C7–C12, C27	58(12)	−18(9)	29(10)	3(14)	15(13)	18(11)	323(21)	−28(20)	32(17)
$R_g = 0.0709$		39(9)	−45(11)	15(10)	11(12)	12(9)		279(23)	−34(19)
			86(24)	18(23)	12(22)	−14(16)			317(16)
C13–C18, C28	47(10)	−62(11)	−28(8)	2(14)	1(12)	−3(17)	272(24)	2(20)	4(25)
$R_g = 0.0596$		304(25)	110(15)	1(32)	−11(15)	4(25)		313(21)	−11(21)
			73(12)	−3(17)	4(11)	9(17)			273(26)
C19–C24, C30	198(14)	−202(12)	62(10)	25(21)	−19(14)	−17(23)	313(31)	−59(25)	−3(32)
$R_g = 0.0463$		302(27)	−117(16)	−19(38)	−19(22)	40(32)		384(23)	−1(29)
			86(11)	−17(18)	40(12)	−16(20)			227(34)
C25–C29, O1	12(10)	5(7)	−2(9)	−3(7)	−1(7)	−10(7)	238(15)	2(11)	2(13)
$R_g = 0.0567$		12(12)	20(6)	−1(9)	5(7)	−10(10)		278(12)	−13(11)
			47(12)	−10(8)	−10(9)	−2(9)			288(12)
All	20(2)	−5(2)	2(2)	3(13)	1(3)	21(5)	248(35)	−32(28)	23(24)
$R_g = 0.2667$		11(3)	1(1)	1(4)	1(13)	−5(6)		254(25)	−4(21)
			25(4)	21(10)	−5(7)	−4(14)			329(24)

To analyse the librational components of vibrations we used a model which could be called a "riding rigid body". It was assumed that the libration of molecule fragments is composed of their own libration and of the libration of the molecule as a whole; hence the corresponding tensors were subtracted. Eigenvalues and eigenvectors for the difference tensors are given in Table III. This table also gives the corresponding angles of the main libration vector with the axis of the orthogonal coordinate system to compare with the angles formed by the bond linking phenyl moieties to the cyclopentan. From this data it follows that the principal axis of libration of the phenyl ring is approximately parallel to the bond linking the phenyl to the cyclopropanol. Librational amplitudes in the other directions are comparatively small, similarly as those obtained for the whole molecule.

TABLE III

Analysis of libration for riding rigid body model

Atom used in the model	Eigenvalues of tensor L (Å)^2	Eigenvectors			Angles with the orthogonal system of axis (Å)					
					Main libration vector			Bond		
C1−C6, C25	27	0.354	0.367	0.860	111	112	150	110	109	151
A	4	−0.357	0.903	−0.238						
	2	−0.864	−0.223	0.451						
C7−C12, C27	35	0.399	−0.513	0.760	66	121	40	68	106	29
B	9	0.906	0.349	−0.240						
	−2	−0.142	0.784	0.604						
C13−C18, C28	114	0.196	−0.915	−0.353	102	23	69	98	25	67
C	6	0.835	0.344	−0.429						
	1	0.514	−0.211	0.831						
C19−C24, C30	158	0.562	−0.772	0.298	125	39	108	110	27	106
D	15	0.739	0.307	−0.600						
	1	0.372	0.557	0.742						
All	9	0.378	−0.657	0.923						
	7	−0.827	0.423	0.369						
	3	−0.415	−0.904	0.106						

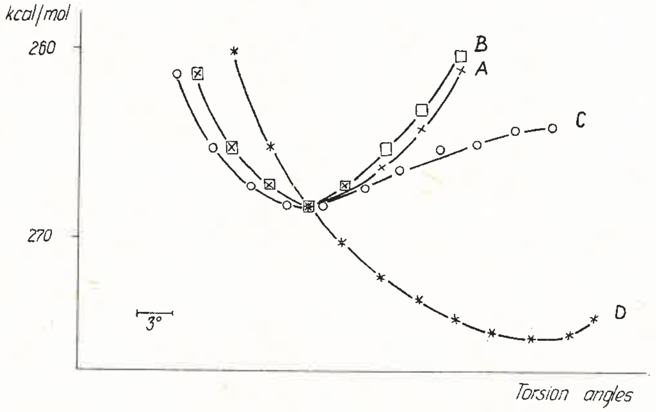

Fig. 2. Potential energy as a function of torsion angles for phenyls *A*, *B*, *C* and *D*

We tried to correlate the thermal motion with van der Waals interactions in the crystal structure using potential energy calculation in the atom-atom approximation. Calculations were done with program EENY written by Motherwell using potential constants given by Giglio [5]. The results are illustrated in Fig. 2 showing potential energy of intra- and intermolecular interactions calculated for all neighbouring molecules as a function of torsional parameters. For three phenyl rings minimum energy corresponds well to the torsional angles observed in the crystal structure. For phenyl ring *D* discrepancy is probably due to the neglecting of the interaction of the π-electrons of phenyl and the carbonyl group. Potential energy curves (Fig. 2) calculated for each torsional angle varying independently are similar for phenyl *A*, *B* and *C* and therefore do not reflect the difference between the maximal mean square displacement of phenyls *A*, *B* and phenyl *C*. This is probably connected with the cooperativity of the librational motion of the phenyl rings in this crystal structure.

3. Conclusions

There are no significant differences between the translational vibration of the whole molecule and its fragments. The libration of the whole molecule is small, whereas the librations of phenyl moieties are much greater and are around bonds linking the moieties to the cyclopentan ring. The coupling of translational and librational vibrations is insignificant.

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