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The Thermal Anisotropy of 1.3.5-Trichlorobenzene and of 1.3.5-Tribromobenzene

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The anisotropic Debye factors for symm. $C_6H_3Cl_3$ (at 293 °K. and 90 °K.) and for symm. $C_6H_3Br_3$ (at 293 °K.) are analysed in respect of rigid-body and internal vibrations. The accuracy of the data are insufficient to give reliable information about the carbon or bromine non-rigid-body movements, but the three chlorine atoms are not equivalent either in respect of thermal vibrations or of intermolecular bonding.

Introduction

Elsewhere we discuss (Lonsdale, Milledge & Rao, 1960) a simple method of determining the amplitudes of rigid-body translational and librational vibrations of molecules in crystals and of distortional vibrations of the individual atoms. This can be done by an analysis of the anisotropic Debye factors in different directions in the molecule, the simplifying assumption being made that the vibrations are phase-independent. The results will be misleading unless the experimental data are free from systematic errors and are reliable to better than 10%. Indeed it is true that the errors will nearly all be concentrated in the deduced intramolecular amplitudes; yet the results so far obtained (Lonsdale & Milledge, 1959) seem to be well outside the limits of experimental error and to be supported both by the reasonableness of the proper molecular vibrations indicated and by the parallelism of the results found at room temperatures and (scaled down, of course) at liquid–nitrogen temperatures.

In the course of a comparative study of the C–C and B–N bonds we have investigated the structures of 1.3.5-trichlorobenzene (at 293 °K. and 90 °K.), (m.p. 63 °C.); 1.3.5-tribromobenzene (m.p. 120 °C.) (Milledge & Pant, 1960), and BBB-trichloroborazole (m.p. 84 °C.) (Coursen & Hoard, 1952; Lonsdale & Milledge, 1959). The latter, although not isomorphous with the benzene compounds, is very similar in structure. The charge distribution in the borazole molecule appears, however, to be different (Lonsdale, 1959) and the diamagnetic anisotropy is much less than that of the benzene compounds (Lonsdale & Toor, 1959). A comparison of their molecular thermal vibrations is likely to be of great interest. In the case of symm. $C_6H_3Cl_3$ and $C_6H_3Br_3$, however, accuracy of the experimental F values is only about 8%, and there are not many reflexions observed other than in the $\{hk0\}$ zone. On the other hand, data are available at two temperatures for the Cl derivative and the further possibility of comparison with the Br derivative makes an analysis worth while.

Analysis of the Debye factors

In Table VII of Milledge & Pant (1960) values of the Debye factors are given for each atom for the radial (**R**), tangential (**T**) and normal (**N**) directions relative to the molecular plane. The standard deviations for the carbon atom B-values are so large for the N-direction in $C_6H_3Cl_3$ and for all directions in $C_6H_3Br_3$ that they are not worth further consideration. We are left with the values given here in Tables 1 and 2.

In these structures X_1–X_3 (X = Cl, Br) is nearly parallel to the b-axis, and the molecule is tilted by about 27° out of the (001) plane. If p is the average C–C distance and q the average C–X distance, we shall take p as 1·40, q as 1·70 for C–Cl, 1·86 for C–Br (Milledge & Pant, 1960). Hence $p^2 = 1{\cdot}96$ Å^2, $(p+q)^2 = 9{\cdot}61$, $10{\cdot}63$ Å^2 respectively.

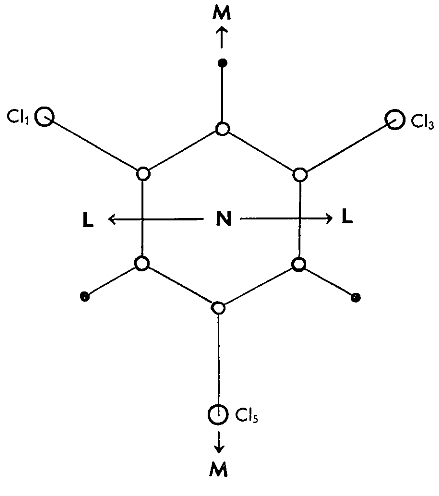

Fig. 1. Directions of **L**, **M**, **N** relative to the molecule.

Assuming phase-independence of the various molecular vibrations, we use Higgs' (1955) formula

$$\overline{u_x^2} = \Sigma u_x^2(\text{rigid-body}) + \Sigma u_x^2(\text{internal})$$

Table 1

B_x-values and corresponding $\overline{u_x^2} \sim B_x/8\pi^2$ for symm. $C_6H_3Cl_3$ at 90 °K. and 293 °K., with standard deviations (using James–Brindley *f*-curves for Cl) for the last round of refinement. (All in Å²)

Atom and direction	1.3.5 $C_6H_3Cl_3$ (90 °K.)				(293 °K.)			
	B_x	σ_x	$\overline{u_x^2}$	$\sigma(\overline{u_x^2})$	B_x	σ_x	$\overline{u_x^2}$	$\sigma(\overline{u_x^2})$
$Cl_1(R)$	0·89	0·12	0·0113	0·0015	2·80	0·16	0·0354	0·0020
$Cl_3(R)$	0·83	0·13	0·0105	0·0016	2·84	0·17	0·0359	0·0021
$Cl_5(R)$	0·42	0·13	0·0053	0·0016	2·08	0·19	0·0263	0·0024
$C_1(R)$	1·36	0·50	0·0172	0·0063	4·2	0·79	0·053	0·010
$C_3(R)$	1·88	0·52	0·0238	0·0065	3·6	0·74	0·046	0·009
$C_5(R)$	1·00	0·42	0·0127	0·0053	3·0	0·76	0·038	0·009
$Cl_1(T)$	1·30	0·14	0·0164	0·0018	5·67	0·27	0·0718	0·0034
$Cl_3(T)$	1·24	0·14	0·0157	0·0018	4·60	0·22	0·0582	0·0028
$Cl_5(T)$	1·90	0·14	0·0240	0·0018	7·16	0·29	0·0906	0·0036
$C_1(T)$	1·32	0·60	0·0168	0·0075	4·0	0·89	0·051	0·011
$C_3(T)$	1·62	0·56	0·0205	0·0070	2·7	0·69	0·034	0·009
$C_5(T)$	1·00	0·60	0·0127	0·0075	3·7	0·69	0·047	0·006
$Cl_1(N)$	1·60	0·64	0·0203	0·0080	4·49	0·76	0·0568	0·0096
$Cl_3(N)$	1·10	0·65	0·0139	0·0081	3·51	0·56	0·0444	0·0071
$Cl_5(N)$	0·50	0·61	0·0063	0·0076	4·88	0·71	0·0618	0·0090

Table 2

B_x values and corresponding $\overline{u_x^2} \sim B_x/8\pi^2$, for 1.3.5 $C_6H_3Br_3$ at 293 °K. for (I) the last tested refinement, using James–Brindley *f*-curves: II recommended (full shift) but not tested for next round: (III) recommended when Thomas–Umeda (1957) *f*-curves are used for Br; with standard deviations for I, which will not vary much for II or III

Atom and direction	$B_{x\text{I}}$	σ_x	$\overline{u_{x\text{I}}^2}$	$\sigma(\overline{u_{x\text{I}}^2})$	$B_{x\text{II}}$	$\overline{u_{x\text{II}}^2}$	$B_{x\text{III}}$	$\overline{u_{x\text{III}}^2}$
$Br_1(R)$	1·80	0·11	0·0228	0·0014	1·71	0·0217	1·97	0·0249
$Br_3(R)$	1·76	0·11	0·0223	0·0014	1·75	0·0221	2·01	0·0254
$Br_5(R)$	1·45	0·14	0·0184	0·0018	1·21	0·0153	1·51	0·0191
$Br_1(T)$	4·20	0·18	0·0532	0·0023	4·02	0·0509	4·51	0·0571
$Br_3(T)$	3·80	0·17	0·0481	0·0021	3·68	0·0466	4·07	0·0515
$Br_5(T)$	4·20	0·15	0·0532	0·0019	4·14	0·0524	4·47	0·0566
$Br_1(N)$	4·60	0·49	0·0582	0·0062	4·63	0·0586	4·84	0·0613
$Br_3(N)$	3·60	0·42	0·0456	0·0053	4·00	0·0506	4·09	0·0518
$Br_5(N)$	3·60	0·42	0·0456	0·0053	3·83	0·0485	3·99	0·0505

to obtain a series of equations which express the observed mean-square amplitudes as a sum of rigid-body translational vibrations along **L**, **M**, **N**; rigid-body librational vibrations about these axes; and independent atomic vibrations Cl_{1R}, Cl_{2R}, …, Cl_{1T}, … etc., the latter implying distortions of the molecule. **L**, **N** are parallel to X_1–X_3, and normal to the molecular plane respectively; **M** is normal to **L**, **N**. The librational movements being small, the corresponding atomic vibration amplitudes $p\varphi$ or $(p+q)\varphi$ Å (φ in radians) are assumed to be tangential to the perpendicular from the atom on to the libration axis.

The appropriate set of equations, putting $\cos^2 30 = 0{\cdot}75$, $\sin^2\theta = 0{\cdot}25$, are

$$\overline{u^2}(X_1, R) = 0{\cdot}75t_L^2 + 0{\cdot}25t_M^2 + X_{1R}^2 \tag{1}$$

$$\overline{u^2}(X_3, R) = 0{\cdot}75t_L^2 + 0{\cdot}25t_M^2 + X_{3R}^2 \tag{2}$$

$$\overline{u^2}(X_5, R) = t_M^2 + X_{5R}^2 \tag{3}$$

$$\overline{u^2}(\mathrm{C}_1, R) = 0{\cdot}75t_L^2 + 0{\cdot}25t_M^2 + \mathrm{C}_{1R}^2 \tag{4}$$

$$\overline{u_2}(\mathrm{C}_3, R) = 0{\cdot}75t_L^2 + 0{\cdot}25t_M^2 + \mathrm{C}_{3R}^2 \tag{5}$$

$$\overline{u^2}(\mathrm{C}_5, R) = t_M^2 + \mathrm{C}_{5R}^2 \tag{6}$$

$$\overline{u^2}(X_1, T) = 0{\cdot}25t_L^2 + 0{\cdot}75t_M^2 + (p+q)^2\varphi_N^2 + X_{1T}^2 \tag{7}$$

$$\overline{u^2}(X_3, T) = 0{\cdot}25t_L^2 + 0{\cdot}75t_M^2 + (p+q)^2\varphi_N^2 + X_{3T}^2 \tag{8}$$

$$\overline{u^2}(X_5, T) = t_L^2 + (p+q)^2\varphi_N^2 + X_{5T}^2 \tag{9}$$

$$\overline{u^2}(\mathrm{C}_1, T) = 0{\cdot}25t_L^2 + 0{\cdot}75t_M^2 + p^2\varphi_N^2 + \mathrm{C}_{1T}^2 \tag{10}$$

$$\overline{u^2}(\mathrm{C}_3, T) = 0{\cdot}25t_L^2 + 0{\cdot}75t_M^2 + p^2\varphi_N^2 + \mathrm{C}_{3T}^2 \tag{11}$$

$$\overline{u^2}(\mathrm{C}_5, T) = t_L^2 + p^2\varphi_N^2 + \mathrm{C}_{5T}^2 \tag{12}$$

$$\overline{u^2}(\mathrm{Cl}_1, T) = t_N^2 + (p+q)^2(0{\cdot}25\varphi_L^2 + 0{\cdot}75\varphi_M^2) + X_{1N}^2 \tag{13}$$

$$\overline{u^2}(\mathrm{Cl}_3, N) = t_N^2 + (p+q)^2(0{\cdot}25\varphi_L^2 + 0{\cdot}75\varphi_M^2) + X_{3N}^2 \tag{14}$$

$$\overline{u^2}(\mathrm{Cl}_5, N) = t_N^2 + (p+q)^2\varphi_L^2 + X_{5N}^2 \tag{15}$$

In these equations there are 15 observed mean-square amplitudes and 21 unknowns: t_L, t_M, t_N, φ_L, φ_M, φ_N, and X_{1R}, …, X_{5N}. All the unknown (amplitude)² are zero or positive; and within the standard deviations given it would not be possible to distinguish between C_1, C_3, C_5, at either temperature, nor between X_{1R} and X_{3R} for either Cl or Br. We may, in fact, (failing evidence to the contrary) assume that Cl_{1R}, Cl_{3R}, Br_{1R} and Br_{3R} are negligible. It is reasonable to assume that Cl_{5R}, Br_{5R} are also negligible. In that case we can determine t_L and t_M from equations (1), (2) and (3), and we obtain

	t_L^2	t_M^2	t_L	t_M
$C_6H_3Cl_3$				
90 °K.	0·0128	0·0053	$0{\cdot}11_5$ Å	0·07 Å
(σ)	(0·0016)	(0·0016)	—	—
$C_6H_3Cl_3$				
293 °K.	0·0387	0·0263	$0{\cdot}19_5$	0·16
(σ)	(0·0022)	(0·0024)	—	—
$C_6H_3Br_3$ (290 °K.)				
I	0·0240	0·0184	$0{\cdot}15_5$	0·13
(σ)	(0·0016)	(0·0018)	—	—
II	0·0241	0·0153	$0{\cdot}15_5$	$0{\cdot}12_5$
III	0·0272	0·0191	$0{\cdot}16_5$	0·14

According to Table 1, $\overline{u^2}$ for C(R) are consistently higher than for $X(R)$, by amounts that are just outside the standard deviations. These differences imply that at 90 °K., $C_R^2=0{\cdot}0089$ and at 293 °K. $C_R^2=0{\cdot}0130$. They would be consistent with a 'breathing vibration' in the benzene ring of about 0·1 Å amplitude. They might alternatively be accounted for by a permanent distortion of the carbon-atom electron distribution due to the bonding with Cl. Or they may be due to an accumulation of experimental errors not taken account of in the standard deviations given. But in the latter case it is noteworthy that they occur at both temperatures.

Substituting the deduced values of t_L^2, t_M^2 in equations (7), (8), (9) we obtain

	$(p+q)^2\varphi_N^2+X_{1T}^2$	$(p+q)^2\varphi_N^2+X_{3T}^2$	$(p+q)^2\varphi_N^2+X_{5T}^2$
$C_6H_3Cl_3$ 90 °K.	0·0092	0·0085	0·0112
$C_6H_3Cl_3$ 293 °K.	0·0424	0·0288	0·0612
$C_6H_3Br_3$ (293 °K.)			
I	0·0334	0·0283	0·0292
II	0·0334	0·0291	0·0349
III	0·0360	0·0304	0·0294

The differences are within the limits of standard deviation at 90 °K., but are quite outside them for $C_6H_3Cl_3$ at room temperature. For $C_6H_3Br_3$ they are doubtful, but they agree with $C_6H_3Cl_3$ in implying that any independent tangential movement of X_3 must be small. If we assume $X_{3T}=0$ then we have

	φ_N^2	φ_N
$C_6H_3Cl_3$		
(90 °K.)	0·0009	0·030 (1·7°)
(293 °K.)	0·0030	0·085 (3·1°)
$C_6H_3Br_3$		
I	0·0027	0·052 (3·0°)
II	0·0027	0·052 (3·0°)
III	0·0029	0·054 (3·1°)

This gives

$$Cl_{1T}^2=0{\cdot}0136;\quad C_{1T}=0{\cdot}11_7\ \text{Å}\,,$$

and

$$Cl_{5T}^2=0{\cdot}0324;\quad C_{5T}=0{\cdot}18\ \text{Å}$$

both at 293 °K.

It does not seem possible to explain away these figures, which imply that the Cl_1 and Cl_5 atoms are vibrating tangentially *relative to* Cl_3 and the benzene ring, in addition to their rigid-body librations *with* Cl_3 and the benzene ring. Milledge & Pant (1960) give intermolecular distances which show that Cl_1 has nearest neighbours at 3·63, 3·75, 4·04 Å, . . ., Cl_3 at 3·75, 4·13, 4·15 Å, . . ., Cl_5 at 3·63, 3·65, 3·65, 4·04 Å, ... It seems, therefore, that the Cl atom most strongly linked to its neighbours (Cl_5) is vibrating most strongly and that one (Cl_3) most weakly bound is vibrating only weakly or not at all, independently of its rigid-body movements.

The differences between the $Cl_3(T)$ and $C(T)$ values of $\overline{u^2}$ are not large enough to have any significance in terms of independent tangential movements of the carbon atoms.

Nor would it be wise, in view of the large standard deviations, to draw any conclusions from the Cl(N) data except to deduce tentative values of t_N, φ_L, φ_M. They obviously have upper limits, given by the minimum values of $\overline{u^2}(N)$. In fact since from equation (14) we have $(p+q)^2\ (0{\cdot}25\varphi_L^2+0{\cdot}75\varphi_M^2)<0{\cdot}0444$ it follows that the upper limits of φ_L, φ_M are $<0{\cdot}007$ for $t_N=0$. Since the expansion coefficient of $C_6H_3Cl_3$ is very large along [001] (Milledge & Pant (1960) give $\alpha(a)=58$, $\alpha(b)=46$, $\alpha(c)=109$, all $\times 10^{-6}$/°K. over the range 90–293 °K.) it seems likely that φ_L, φ_M are of the same order as the values found for anthracene (Lonsdale, Mason & Milledge, in preparation) where much more precise experimental data permit a more exact determination. That is, they must be about 0·04–0·06 radians at 293 °K. Only φ_L, φ_M librations (which are the ones to produce *out-of-plane* movements) can be responsible for the large anisotropy of expansion, since t_N is limited to values of the same order as t_L and t_M, and translational vibrations will in any case mainly be acoustic vibrations from which, since neighbouring molecules move together, only small expansion effects result.

Acceptance of the lower limit of φ_L, $\varphi_M=0{\cdot}04$ radians would give $t_N^2\le(0{\cdot}0444-0{\cdot}0154)$ for $C_6H_3Cl_3$ at 293 °K. Hence $t_N\le 0{\cdot}17$ Å, a value comparable with t_L, t_M. There is no marked difference in this N direction between $C_6H_3Cl_3$ and $C_6H_3Br_3$. We can definitely say, therefore, that φ_L, φ_M, φ_N are of similar orders of magnitude, 0·05 radians, and produce atomic movements $(p+q)\varphi=0{\cdot}18$ Å, which are about equal to the translational amplitudes t_L, t_M, t_N.

The calculations of atomic co-ordinates and B-factors basic to this paper were carried out with the help of a grant for computing made from the Wellcome Trust, and with the use of tape-editing equipment purchased by means of a grant from the London

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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The crystal structure of Rb_2ThF_6.

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A preliminary survey of the system RbF–ThF_4 (Thoma, 1957) revealed the existence of a compound with the formula Rb_2ThF_6. Examination of the compound by means of the polarizing microscope showed it to be uniaxial positive with indices of refraction

$$N_E = 1{\cdot}494 \pm 0{\cdot}003 \quad \text{and} \quad N_O = 1{\cdot}472 \pm 0{\cdot}003$$

(Landau, 1957). Optical investigations of materials of the above composition quenched from the temperature range 800 °C. to 400 °C. exhibited no phase changes and constant optical properties.

Debye–Scherrer diffraction films were taken of powdered samples using a 114·6 mm.diag. cylindrical camera and Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) radiation. The data thus obtained were indexed and found to best fit a hexagonal cell whose lattice parameters are $a_0 = 6{\cdot}85 \pm 0{\cdot}020$ Å and $c_0 = 3{\cdot}83 \pm 0{\cdot}020$ Å. The density was pycnometrically measured as 5·45 g.cm.$^{-3}$ which may be compared with an X-ray density of 5·56 g.cm.$^{-3}$ calculated with one molecule of Rb_2ThF_6 per unit cell. No systematic absences of reflections were observed from the powder X-ray diffraction data.

The lattice dimensions, crystal symmetry, and diffracted X-ray intensity distribution of Rb_2ThF_6 indicate a close structural relationship with β_1-K_2ThF_6 (Zachariasen, 1948). Presuming these two compounds to be isostructural, the atoms were placed in those positions deduced by Zachariasen in accordance with the space group $C\bar{6}2m$, namely,

2 Rb in $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$; $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$.
1 Th in (0, 0, 0).
3 F in $(x, 0, 0)$; $(0, x, 0)$; $(\bar{x}, \bar{x}, 0)$ where $x = 0{\cdot}640$.
3 F in $(x, 0, \frac{1}{2})$; $(\bar{x}, \bar{x}, \frac{1}{2})$; $(0, x, \frac{1}{2})$ where $x = 0{\cdot}220$.

Table 1. *Comparison of observed and calculated intensities for* Rb_2ThF_6

$hk{\cdot}l$	d (Å)	I (obs.)*	I (calc.) $\times 10^{-5}$
10·0	5·92	16	18
00·1	3·82	0	0·3
11·0	3·43	33	36
10·1	3·23	30	37
20·0	2·97	4	3
11·1	2·79	3	2
20·1	2·35	21	23
21·0	2·25	5	3
30·0	1·98	13	12
21·1	1·94	25	26
00·2	1·92	0	4
10·2	1·83	5	3
30·1	1·756	2	0·9
22·0	1·710	6	5
11·2	1·676	10	9
31·0	1·644	0	1
20·2	1·615	0	1
31·1	1·511	10	9
40·0	1·489	0	0·6
21·2	1·460	0	1·7
40·1	1·344	8	3

* Peak intensities observed from an X-ray diffractometer tracing of a sample prepared by the method of McCreery (1949).

Table 1 shows the satisfactory agreement of observed and calculated intensities, the latter calculated from the formula

$$I \propto |F|^2 . p . (1 + \cos^2 \theta) / \sin^2 \theta \cos \theta ,$$

where F is the structure amplitude, and p is the multiplicity factor.

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