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Structures of 1:3:5-Trichlorobenzene at 20 °C. and −183 °C., and of 1:3:5-Tribromobenzene at 20 °C.

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$C_6H_3Cl_3$, $C_6H_3Br_3$ are isomorphous, $P2_12_12_1$ with $Z = 4$. The structure is of a layer type, the molecules being planar and inclined at about ±27° to (001). The mean thermal expansion coefficients for $C_6H_3Cl_3$ from −183 °C. to 20 °C. are 58, 46, 109×10^{-6} along *a*, *b*, *c* respectively. The lack of exact triangular symmetry of the molecule is shown both in the lengths of intermolecular bonds and in the anisotropy of the atomic Debye factors. The structure is compared with those of other symmetrically-substituted ring compounds.

Introduction

This work was undertaken for the following reasons:

(1) Derivation of structures at different temperatures is essential for knowledge of the way in which various physical phenomena are related—for example, atomic and molecular vibrations and thermal expansion coefficients.

(2) A study of isomorphous compounds is useful not only for the actual process of structure analysis, but also for giving information about the degree of reliability of determination of light-atom parameters in the presence of heavier atoms.

(3) 1:3:5-triphenylbenzene is a polar structure of a layer type (Farag, 1954). It was interesting to see whether other symmetrically-substituted derivatives $C_6H_3R_3$ would crystallize similarly.

(4) A comparison of the structures of $C_6H_3Cl_3$, of cyanuric trichloride $C_3N_3Cl_3$ and of B-trichloroborazole $B_3N_3H_3Cl_3$, and of their molecular diamagnetic susceptibilities (which can only be deduced from the crystal susceptibilities when the structures are known) would give valuable information concerning the π-electron orbital areas for these three compounds and perhaps throw some light on packing forces.

Experimental details

The X-ray examination was carried out by L. M. Pant, who also deduced the preliminary structures. H. J. Milledge prepared Pegasus computer programmes and refined the structures.

$C_6H_3Cl_3$ and $C_6H_3Br_3$ are isomorphous and there is no discontinuous structure transition between room and liquid-nitrogen temperatures.

The only systematic absences are $\{h00\}$ for h odd, $\{0k0\}$ for k odd, $\{00l\}$ for l odd. The space group $P2_12_12_1$ was confirmed by Patterson and Fourier projections. Unit-cell dimensions are as follows:

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	$C_6H_3Cl_3$			$C_6H_3Br_3$
	−183 °C.	20 °C.	$\alpha . 10^6$	20 °C.
a	13·77 Å	13·93 Å	58 °C^{-1}	14·23 Å
b	13·07	13·19	46	13·55
c	$3{\cdot}82_5$	3·91	109	4·08

$C_6H_3Cl_3 . \varrho_o = 1{\cdot}66$ g.cm.$^{-3}$ at 20 °C.; $Z = 4$ gives $\varrho_c = 1{\cdot}68$ g.cm.$^{-3}$.

$C_6H_3Br_3 . \varrho_o = 2{\cdot}637$ g.cm.$^{-3}$ at 22 °C.; $Z = 4$ gives $\varrho_c = 2{\cdot}659$ g.cm.$^{-3}$.

Trichlorobenzene crystallizes in needles, elongated on c, very soft and easily affected by moisture. In order to prevent the crystals from going whitish and translucent within about half an hour, they had to be sealed into thin-walled glass tubes or (for other axes) in glass bulbs. Of 241 possible $\{hk0\}$ reflexions, using Cu $K\alpha$ radiation, 173 were observed at −183 °C. and 150 at 20 °C.; but of the $\{0kl\}$ and $\{h0l\}$ only about 25 reflexions were observed in each zone out of a possible 65.

The $C_6H_3Br_3$ crystals, also acicular, are not affected by moisture but do appear to sublime slowly and were therefore also enclosed in glass tubes. Corresponding figures for observed reflexions are:

$\{hk0\}$ 175 out of 255 theoretically possible,
$\{0kl\}$ 41 out of 73 possible,
$\{h0l\}$ 47 out of 78 possible.

The low temperature was attained by passing over the crystal nitrogen gas from a Dewar flask filled with boiling liquid nitrogen, kept at a steady level. The photographic exposure was begun after 15 to 20 min. preliminary cooling. The temperature measured by a thermocouple was steady at −183 °C. Only the $\{hk0\}$ reflexions were measured at the low temperature, owing to difficulty of crystal setting and preservation. The values of a and b were determined from 16,0,0; 17,1,0; 17,4,0 and from 0,14,0; 2,16,0; 5,15,0 respectively and c from the layer-line spacing on an oscillation photograph taken on a 5·75 cm.-radius semi-cylindrical film calibrated by means of a room-temperature rotation photograph.

Intensities were measured visually, using intensity scales made with the same crystal, a film pack to correspond with the film pack used for the actual exposures, and a multiple-exposure camera with a range of exposure times. Four reflexions consistently showed extinction effects varying with the crystal used. These were omitted from the refinement process. Absorption corrections were made, including allowance for the non-uniformity of cross-section of the specimen, but these did not improve the overall agreement of the observed and calculated structure factors and it seems probable that the major experimental error is in the estimation of integrated intensities for spots of different shapes.

Wilson's method was used to obtain preliminary values for the scale factor and temperature factor at both temperatures, and a preliminary structure obtained by the usual Patterson technique. The von Eller photosommateur was found to be very useful at this stage. Refinement proceeded by means of Fourier difference synthesis until a reasonable trial structure was achieved, and further refinement was carried out by computer. The programmes available can

(1) process the data;

(2) calculate structure factors with given atomic scattering factors for any space group, using trial values of atomic parameters, scaling factor and anisotropic Debye factors in specified directions, and supply the appropriate R-factor;

(3) refine all these parameters separately or together by least-squares methods; and calculate standard deviations at each stage;

(4) calculate all required molecular geometry.

Most of the refinements were carried out using the James–Brindley atomic scattering factors for Cl and Br, and the Hoerni & Ibers (1954) factors for (spherical) C. Later the effect of using the Thomas & Umeda (1957) values for Br was tested and it was found that the atomic co-ordinates remained unchanged, but that the B-factors for the Br atoms (and the scaling factor required) had to be increased (see Table 7). The results given in Tables 1–6 and all but the last column of Table 7 refer to the James–Brindley factors.

The thermal vibration ellipsoid for each atom was assumed to have its principal axes in directions radial (R) tangential (T) and normal (N) to the benzene ring. Hydrogen atoms were clearly visible on the $\{hk0\}$ low-temperature Fourier difference projection when the Cl only were removed, and the room-temperature $\{hk0\}$ Fourier projection showed a marked tangential spread of the Cl electron contours. The hydrogen atoms were therefore included at an early stage of refinement with an isotropic Debye factor. Carbon was also given an isotropic B, but chlorine was at first assumed to have an anisotropic temperature factor of the form

$$P \cos^2 \varphi + Q \sin^2 \varphi \ ,$$

where φ is the angle between the normal to the reflecting plane and the projection on (001) of the direction (T) of the maximum vibration amplitude. Subsequent refinement by computer distinguished B_R, B_T, B_N.

Structural details

It is clear that the molecular planes must lie in or near to (001). This is shown by

(1) the short c axis, not much larger than the van der Waals' diameter of Cl; and the acicular crystal habit;

(2) the large thermal expansion coefficient along c;

(3) the diamagnetic susceptibilities of $C_6H_3Br_3$, which result in a small anisotropy in (001) and large in (100) and (010);

Table 1. *Fractional co-ordinates for* $C_6H_3X_3$ *at given temperatures*

Atom	Fig. 3	$C_6H_3Cl_3$ (−183 °C.)			$C_6H_3Cl_3$ (20 °C.)			$C_6H_3Br_3$ (20 °C.)		
		x	y	(z) estimated	x	y	z	x	y	z
X_1	(1)	0·3469	0·2316	0·588	0·3490	0·2336	0·584	0·3494	0·2261	0·597
X_3	(2)	0·3608	0·6419	0·680	0·3626	0·6359	0·687	0·3591	0·6403	0·686
X_5	(3)	0·6600	0·4364	0·128	0·6588	0·4339	0·129	0·6568	0·4363	0·074
C_1	(4)	0·4071	0·3446	0·521	0·4086	0·3452	0·521	0·4096	0·3449	0·513
C_2	(5)	0·3640	0·4364	0·618	0·3653	0·4338	0·622	0·3685	0·4335	0·614
C_3	(6)	0·4130	0·5289	0·562	0·4163	0·5248	0·564	0·4138	0·5227	0·553
C_4	(7)	0·5051	0·5286	0·410	0·5058	0·5245	0·416	0·5005	0·5237	0·390
C_5	(8)	0·5486	0·4364	0·312	0·5474	0·4347	0·312	0·5416	0·4351	0·290
C_6	(9)	0·4987	0·3442	0·369	0·4992	0·3441	0·368	0·4963	0·3457	0·351
H_2	(10)	0·292	0·436	0·736	0·295	0·435	0·737	0·301	0·433	0·734
H_4	(11)	0·543	0·600	0·367	0·543	0·596	0·374	0·536	0·593	0·340
H_6	(12)	0·532	0·272	0·294	0·532	0·273	0·290	0·528	0·277	0·271

Note: These values, and those given later for the Debye factors, are those used in the final *tested* refinement, not those recommended for the next cycle by the computer, except where otherwise stated. C_1 is the carbon attached to X_1, C_2 to H_2 etc.

(4) the near ultraviolet absorption spectrum (Schnepp, 1959. This, however, was not known until the structure had been completed).

Taking the co-ordinates of equivalent positions as

$$x, y, z;\ \tfrac{1}{2}+x, \tfrac{1}{2}-y, \bar{z};\ \bar{x}, \tfrac{1}{2}+y, \tfrac{1}{2}-z;\ \tfrac{1}{2}-x, \bar{y}, \tfrac{1}{2}+z$$

(to fix the origin uniquely) the final atomic parameters are as given in Table 1, and the molecular geometry as in Table 2.

Table 2. *Bond lengths* (Å) *within the molecule*

(See Fig. 1 for explanation of bonds concerned)

Bond	$C_6H_3Cl_3$ (−183 °C.)		$C_6H_3Cl_3$ (20 °C.)		$C_6H_3Br_3$ (20 °C.)	
X_1–C_1	1·713	1·701	1·709	1·711	1·855	1·857
X_3–C_3	1·702		1·714		1·855	
X_5–C_5	1·689		1·710		1·861	
X_1–X_3	5·377	5·367	5·325	5·354	5·626	5·635
X_3–X_5	5·351		5·374		5·641	
X_5–X_1	5·372		5·364		5·639	
C_1–C_2	1·389	1·396	1·374	1·387	1·398	1·397
C_2–C_3	1·401		1·413		1·392	
C_3–C_4	1·395		1·376		1·402	
C_4–C_5	1·396		1·378		1·396	
C_5–C_6	1·404		1·387		1·395	
C_6–C_1	1·389		1·395		1·400	
C–H (mean)		1·084		1·083		1·083

The molecular planes, as defined by X_1, X_3, X_5 (X=Cl, Br), the direction cosines of X_1–X_3, X_3–X_5, X_5–X_1, and the maximum and minimum deviations of carbon atoms from these planes are given in Tables 3 and 4.

Table 3. *Equations of molecular planes*

Cl_1 Cl_3 Cl_5 (−180 °C.)	$-0·4159x+0·0741y-0·9064z=3·8016$
Cl_1 Cl_3 Cl_5 (20 °C.)	$-0·4232x+0·0838y-0·9021z=3·8600$
$Br_1Br_3Br_5$ (20 °C.)	$-0·4731x+0·0685y-0·8784z=4·2818$

The standard deviations of the fractional co-ordinates, are less than 0·0004 and 0·0005 in x and y for $C_6H_3Cl_3$ at the two temperatures, and less than 0·0003 for $C_6H_3Br_3$, for the halogen atoms. For the carbon atoms they are less than 0·0014, 0·0015, 0·0023 respectively. We believe these figures give an over-optimistic estimate of the accuracy achieved, partly owing to having $\Delta F=0$ for many unobserved reflexions in the equations. During the course of the refinement various benzene-ring models were tried, including one in which extreme carbon–carbon bond lengths were 1·33, 1·47 Å. This refined to $R=11·2\%$, with standard deviations similar to the above, although two carbon atoms had changed their y co-ordinates by over 0·004 (0·05 Å).

Owing to the poor experimental data for all but $\{hk0\}$ reflexions, the values of z are the least accurate of all. For $C_6H_3Cl_3$ at −183 °C. they could only be estimated on the assumption of a plane, equiangular molecule with reasonable packing conditions, and although they cannot be far wrong, it is not possible to assign a standard deviation to them. The low-temperature

Table 4. *Direction cosines of halogen–halogen directions relative to the crystal axes, with deviations of carbon atoms from planes of halogen atoms*

	$C_6H_3Cl_3$ (−183 °C.)			$C_6H_3Cl_3$ (20 °C.)			$C_6H_3Br_3$ (20 °C.)		
	α	β	γ	α	β	γ	α	β	γ
X_1–X_3	−0·4840	−0·8620	+0·1505	−0·4865	−0·8614	+0·1458	−0·4617	−0·8676	+0·1847
X_3–X_5	−0·4219	+0·8672	+0·2644	−0·4358	+0·8552	+0·2806	−0·4197	+0·8592	+0·2926
X_5–X_1	+0·9086	+0·0002	−0·4176	+0·9079	−0·0058	−0·4193	+0·8808	+0·0087	−0·4735
Deviations of C atoms from planes	0 to −0·0031 Å			−0·0025 to +0·0111 Å			−0·0007 to +0·0060 Å		

Table 5

Residual factors $R = \Sigma||F_c| - |F_o||/\Sigma|F_o|$, omitting the 400, 230 and 600, 340 intensities, which show strong and moderately strong extinction, and including unobserved intensities in $\Sigma|F_o|$ at one-half minimum-observable value; all $\times 10^{-2}$

	$C_6H_3Cl_3$ (−183 °C.)	$C_6H_3Cl_3$ (20 °C.)	$C_6H_3Br_3$ (20 °C.)
$R\{hk0\}$	8·45	10·9	9·5
$R\{0kl\}$	—	8·4	9·6
$R\{h0l\}$	—	—	9·6

x, y co-ordinates were refined *after* this estimation. The standard deviations in z for $C_6H_3Br_3$, for which more data were available, are less than 0·0025 for Br (0·018 for carbon). It is not believed, therefore, that the change in mean C–C length, or the individual variations, have real significance, and it is doubtful whether the variations of C–Cl (C–Br) bond length with position or with temperature are significant either.

What is certainly real, however, is the tilt of the Cl_1–Cl_3, (Br_1–Br_3) bond away from parallelism with [010], and the consequent asymmetry of the intermolecular bonds. These are shown in Table 6, which must be interpreted in relation to Figs. 1, 2, 3.

Table 6. *Intermolecular bond lengths*

(See Fig. 3)

	$C_6H_3Cl_3$ (−183 °C.)	$C_6H_3Cl_3$ (20 °C.)	$C_6H_3Br_3$ (20 °C.)
X–X			
(3)–(13) or (14)	3·544	3·650	3·765 Å
(3)–(16)	3·552	3·628	3·762
(3)–(17)	3·944	4·042	3·989
(3)–(19)	4·036	4·132	4·155
(1)–(22)	3·655	3·749	3·858
(1)–(21)	4·004	4·149	4·225
H–X			
(11)–(17)	2·878	2·963	3·016
(12)–(19)	2·897	2·984	3·078
(10)–(21)	2·894	2·969	3·096
(10)–(22)	3·163	3·214	3·344

Note. If Cl_1, Cl_3, Cl_5 have coordinates x_1, y_1, z_1; x_2, y_2, z_2; x_3, y_3, z_3; then the numbers correspond to the following:

(1) x_1, y_1, z_1; (3) x_3, y_3, z_3; (13) $\frac{3}{2}-x_3, 1-y_3, \frac{1}{2}+z_3$;
(14) $\frac{3}{2}-x_3, 1-y_3, -\frac{1}{2}+z_3$; (16) $\frac{1}{2}+x_1, \frac{1}{2}-y_1, 1-z_1$;
(17) $1-x_1, \frac{1}{2}+y_1, \frac{1}{2}-z_1$; (19) $1-x_2, -\frac{1}{2}+y_2, \frac{1}{2}-z_2$;
(21) $\frac{1}{2}-x_2, 1-y_2, \frac{1}{2}+z_2$; (22) $\frac{1}{2}-x_2, 1-y_2, -\frac{1}{2}+z_2$.
(10), (11), (12) are H_2, H_4, H_6 respectively.

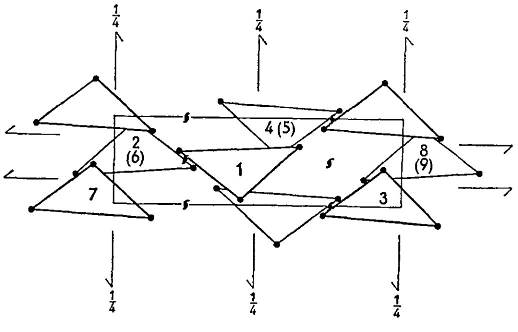

Fig. 1. Tribromobenzene (0*kl*).

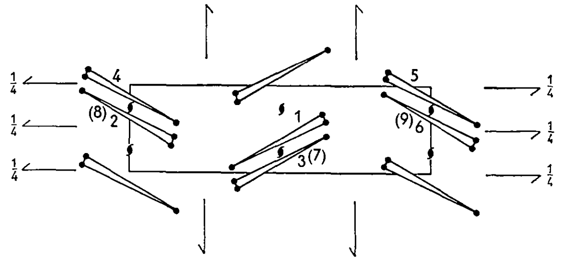

Fig. 2. Tribromobenzene (*h*0*l*)

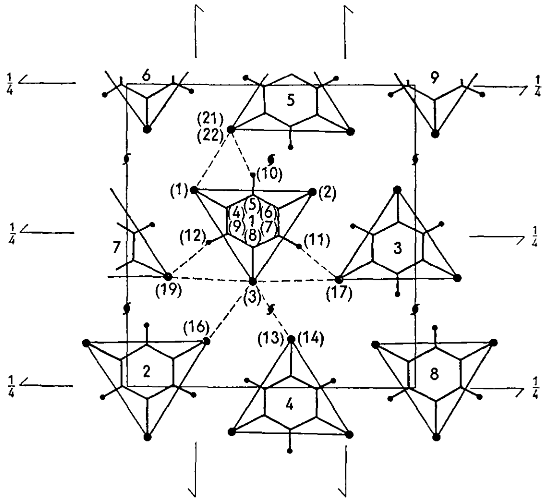

Fig. 3. Tribromobenzene (*hk*0)

Thermal vibrations

Table 7 shows the various atomic Debye-factors corresponding to the radial, tangential and normal directions.

In order to understand how far these have meaning, a brief account of the refining process is necessary and $C_6H_3Cl_3$ (20 °C.) will be taken as an example. Wilson's statistical method gave $B = 3{\cdot}5$ for $\{hk0\}$. The carbon atoms were given this isotropic value for the first refinement and all three Cl atoms were, on the basis of the first Fourier map, given the value

$$B = P\cos^2\varphi + Q\sin^2\varphi$$

where $P = 7{\cdot}1$, $Q = 3{\cdot}5$ and φ is the angle between the normal to the reflecting plane (hkl) and the projection on (001) of the tangential direction for the atom in question. It soon became clear that P and Q were too high, and values of 5·1, 3·0 were substituted.

When the refinement had apparently reached its limit, H atoms having been included with isotropic $B = 4$, a new refinement was attempted, putting in

Table 7. *Atomic Debye factors with standard deviations and corresponding mean-square and root-mean-square vibration amplitudes in directions radial, tangential and normal to the molecule*

	$C_6H_3Cl_3$ (−183 °C.)				$C_6H_3Cl_3$ (20 °C.)				$C_6H_3Br_3$ (20 °C.) (I)				$C_6H_3Br_3$ (II)			$C_6H_3Br_3$ (III)		
	B (Å²)	σ	$\overline{u_x^2}$ (Å²)	$(\overline{u_x^2})^{\frac{1}{2}}$ (Å)	B (Å²)	σ	$\overline{u_x^2}$ (Å²)	$(\overline{u_x^2})^{\frac{1}{2}}$ (Å)	B (Å²)	σ	$\overline{u_x^2}$ (Å²)	$(\overline{u_x^2})^{\frac{1}{2}}$ (Å)	B (Å²)	$\overline{u_x^2}$	$(\overline{u_x^2})^{\frac{1}{2}}$ (Å)	B (Å²)	$\overline{u_x^2}$	$(\overline{u_x^2})^{\frac{1}{2}}$ (Å)
X_1 (*R*)	0·89	0·12	0·0113	0·106	2·80	0·16	0·0354	0·188	1·80	0·11	0·0228	0·151	1·71	0·0217	0·147	1·97	0·0249	0·158
X_3 (*R*)	0·83	0·13	0·0105	0·102	2·84	0·17	0·0359	0·189	1·76	0·11	0·0223	0·149	1·75	0·0221	1·149	2·01	0·0254	0·159
X_5 (*R*)	0·42	0·13	0·0053	0·073	2·08	0·19	0·0263	0·162	1·45	0·14	0·0184	0·136	1·21	0·0153	0·124	1·51	0·0191	0·139
C_1 (*R*)	1·36	0·50	0·0172	0·131	4·2	0·79	0·053	0·23	2·0	0·96	0·0253	0·159	1·54	—	—	1·71	—	—
C_3 (*R*)	1·88	0·52	0·0238	0·154	3·6	0·74	0·046	0·21	2·0	0·99	0·0253	0·159	2·06	—	—	2·08	—	—
C_5 (*R*)	1·00	0·49	0·0127	0·113	3·0	0·76	0·038	0·20	2·0	0·97	0·0253	0·159	0·71	—	—	0·84	—	—
X_1 (*T*)	1·30	0·14	0·0175	0·132	5·67	0·27	0·0718	0·268	4·20	0·18	0·0532	0·231	4·02	0·0509	0·226	4·51	0·0571	0·239
X_3 (*T*)	1·24	0·14	0·0157	0·125	4·60	0·22	0·0582	0·241	3·80	0·17	0·0481	0·219	3·68	0·0466	0·216	4·07	0·0515	0·227
X_5 (*T*)	1·90	0·14	0·0240	0·155	7·16	0·29	0·0906	0·301	4·20	0·15	0·0532	0·231	4·14	0·0524	0·229	4·47	0·0566	0·238
C_1 (*T*)	1·33	0·60	0·0168	0·130	4·0	0·89	0·051	0·22	2·0	1·39	0·0253	0·159	1·19	—	—	1·28	—	—
C_3 (*T*)	1·62	0·56	0·0205	0·143	2·7	0·69	0·034	0·18	2·0	1·31	0·0253	0·159	1·61	—	—	1·66	—	—
C_5 (*T*)	1·00	0·62	0·0127	0·113	3·7	0·69	0·047	0·22	2·0	1·36	0·0253	0·159	(2·62)	—	—	(2·77)	—	—
X_1 (*N*)	1·60	0·64	0·0203	0·142	4·49		0·0568	0·238	4·6	0·4	0·0582	0·241	4·63	0·0586	0·242	4·84	0·0613	0·248
X_3 (*N*)	1·10	0·65	0·0139	0·118	3·51		0·0444	0·211	3·6	0·4	0·0456	0·214	4·00	0·0506	0·225	4·09	0·0518	0·228
X_5 (*N*)	0·50	0·61	0·0063	0·080	4·88		0·0618	0·249	3·6	0·4	0·0456	0·214	3·83	0·0485	0·220	3·99	0·0505	0·225
C_1 (*N*)	1·3	2·7	0·0165	0·128	2·4		0·031	0·18	2·0	2·4	0·0253	0·159	1·23	—	—	—	—	—
C_3 (*N*)	1·3	2·7	0·0165	0·128	3·7		0·047	0·22	2·0	2·5	0·0253	0·159	2·68	—	—	—	—	—
C_5 (*N*)	1·3	2·7	0·0165	0·128	3·4		0·043	0·21	2·0	2·6	0·0253	0·159	(6·28)	—	—	—	—	—

Note: The three sets of data given for $C_6H_3Br_3$ correspond to the following: (I) Debye factors actually tested in the last refinements. (II) Debye factors *recommended* by computing process when James–Brindley atomic scattering factors were used for Br. (III) Debye factors *recommended* by computing machine when Thomas & Umeda (1957) scattering factors for Br were used. The latter led to slightly increased R-values, but did not change the atomic co-ordinates from those given in Table 1.

more symmetrical carbon positions and averaged *B*-factors as follows:

B (radial)	Cl 2·55	C 3·2	H 4·0
B (tangential)	Cl 5·5	C 3·3	H 4·0
B (normal)	Cl 4·1	C 3·0	H 4·0

these being the *mean* values from previous refinements for the three symmetrical atoms in each case. The *R*-factor went up by about 2·5% and the recommendations were for the new co-ordinates to be retained and *B* values near to the former ones to be re-introduced. Acceptance of this recommendation brought down the *R*-factor by 3%. It seems clear therefore that the three Cl atoms do not have identical anisotropic Debye-factors but that in particular $Cl_1(T)$, $Cl_3(T)$, $Cl_5(T)$ differ by more than their probable errors. If this is so, then these anisotropic and asymmetric Debye factors cannot be interpreted solely in terms of rigid-body vibrations of the molecule.

The standard deviations for the carbon atom *B*-factors are so large that the details are unimportant, although it seemed clear from the analysis that the *B*-factors for C_1, C_3, C_5 (attached to Cl atoms) are different from those for C_2, C_4, C_6. It is difficult to know how much of apparent *B*-factors for the carbon atoms would in fact be due to bond anisotropy.

The values of $X(N)$, which correspond to vibrations nearly along the *z* direction, are subject to a much larger experimental error than those of $X(R)$ or $X(T)$ because of the paucity of experimental data other than in the $\{hk0\}$ zone. Nevertheless it is these movements which lead to the large thermal expansion coefficient along the crystal axis [001].

Comparison of structure with those of other symmetrically-substituted ring compounds

Symm. $C_6H_3Cl_3$ and $C_6H_3Br_3$ are unlike symm. $C_6H_3(C_6H_5)_3$ in that they do not form polar structures. They are similar in having layer structures, and in that the *M* directions in all molecules (*M* joins X_5 to the mid-point of X_1-X_3) lie very nearly in one crystallographic axial plane.

The structure of $C_3N_3Cl_3$ has not been fully determined, but early X-ray and optical measurements show it to be a layer structure of plane molecules (Lonsdale, 1936, referring to unpublished work of Miss I. E. Knaggs).

A comparison with B-trichlorborazole $B_3N_3H_3Cl_3$ is particularly interesting. This will be dealt with in more detail in a separate publication (Lonsdale & Milledge, in preparation). The trichloroborazole structure has been determined by Coursen & Hoard (1952). The space group is *Pnma* and the molecule has mirror-image symmetry. The *L* axis is along [010] and *N* is at 27·6° to [001]. In $C_6H_3Cl_3$ the *L* axis is 4·8° from [010] and *N* is 25·6° from [001]; the (010) projections of the two compounds are closely similar, although the arrangements in the layer plane (001) are different.

The diamagnetic susceptibility measurements, which will be described elsewhere (Lonsdale & Toor, 1959) indicate that the anisotropy of the benzene nucleus in $C_6H_3Br_3$ is about $47\cdot10^{-6}$ c.g.s.e.m.u./g.mol. as compared with $60\cdot10^{-6}$ for benzene.

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