

Rigid-Body Torsional Vibrations in Three Typical Members of a Class of Benzene Derivatives*

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Quantitative X-ray crystallographic structure analyses have been carried out on 1,2 dichlorotetramethylbenzene and hexachlorobenzene. In addition, the analysis of Brockway & Robertson's data on hexamethylbenzene has been extended through difference syntheses. The interatomic distances and the interbond angles, the intermolecular distances and the molecular packing are those expected for such molecules.

Dielectric and heat-capacity data of these compounds indicate that a considerable amount of molecular freedom exists in the crystalline solid at room temperatures. The present analyses have clearly established the nature of this freedom. In the three members studied, a pronounced rigid-body torsional vibration has been observed in the plane of the molecule. In addition, 1,2 dichlorotetramethylbenzene possesses an orientational disorder: the chlorine atoms and the methyl groups are distributed randomly among three crystallographically non-equivalent positions. The orientational disorder has been interpreted in terms of discontinuous molecular reorientations of $n\pi/3$, the reorientations being a consequence of the relatively large rigid-body torsional vibrations.

Introduction

For some time, it has been known that certain penta- and hexa-substituted benzene derivatives possess properties that suggest disorder in the crystalline solid at room temperatures. This class of compounds includes the chlorine and/or methyl derivatives. The temperature dependence of the disorder has received extensive heat-capacity, dielectric and dilatometric studies (Huffman, Parks & Daniels, 1930; White, Biggs & Morgan, 1940; Morgan & Yager, 1940; Chihara & Seki, 1948; Seki & Chihara, 1949). The results show pronounced second-order transitions.

Originally, these transitions were interpreted as representing the onset or the termination of rotation. In the rotator state, the molecules were assumed to be rotating freely in their plane about an axis passing through the center of the molecule. However, such transitions do not occur in tetra-substituted derivatives or in higher members if some or all of the substituent positions contain larger atoms or bulkier groups. From this, it was concluded that the molecules had to possess an approximate disc-like symmetry in order for rotation to occur.

With the demonstration of localized atoms by the structure determination of hexamethylbenzene (Brockway & Robertson, 1939), it became clear that some of

the foregoing ideas had to be modified. This was done by Kauzmann (1942) when attempting to describe the observed distribution of dielectric relaxation times of the polar molecules of the rotating class. Essentially, Kauzmann suggested that in the rotator state, discontinuous molecular reorientations of $n\pi/3$ occurred in the plane of the molecule, the integer n permitting higher-order reorientations. In the non-rotator state, such reorientations were assumed to be non-existent.

Now, since the X-ray method is the most direct approach to the understanding of the foregoing phenomena, room-temperature structure analyses of three typical members of the rotating class were undertaken. The general example, 1,2 dichlorotetramethylbenzene, proved to be of the most interest. The others, hexachlorobenzene (Lonsdale, 1931) and hexamethylbenzene, were chosen for convenience. The structure of the former has been completely redetermined; the analysis of the latter has been extended through difference syntheses*.

Experimental

Good single crystals of 1,2 dichlorotetramethylbenzene and hexachlorobenzene were grown either by slow evaporation of benzene or by slow cooling of ethanol. They were elongated along the monoclinic b axis and displayed a pseudo-hexagonal face development. End faces were seldom observed, the crystals usually terminating with irregular fractures. Cleavage occurred easily parallel to b , especially with hexachlorobenzene.

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Nickel-filtered Cu *K* radiation was employed in all the X-ray experiments. The crystal specimens were chosen so as to have a cross-section of about 0.1 mm. \times 0.1 mm. and the length of the needle axis was cut to less than 0.5 mm. Crystallographic data were obtained from oscillation, rotation and Weissenberg photographs. Density measurements were made by flotation in aqueous silver nitrate solutions. Some of the relevant data collected are shown below.

1,2 Dichlorotetramethylbenzene, $C_{10}H_{12}Cl_2$

$$a = 8.16 \pm 0.02, \quad b = 3.98 \pm 0.01, \quad c = 16.95 \pm 0.03 \text{ \AA}, \\ \beta = 116.4 \pm 0.2^\circ.$$

Space group, $P2_1/c$; $d_o = 1.34 \text{ g.cm.}^{-3}$, $d_c = 1.360 \text{ g.cm.}^{-3}$;
2 molecules/unit cell.

Hexachlorobenzene, C_6Cl_6

$$a = 8.08 \pm 0.02, \quad b = 3.87 \pm 0.01, \quad c = 16.65 \pm 0.03 \text{ \AA}, \\ \beta = 117.0 \pm 0.2^\circ.$$

Space group, $P2_1/c$; $d_o = 2.03 \text{ g.cm.}^{-3}$, $d_c = 2.041 \text{ g.cm.}^{-3}$;
2 molecules/unit cell.

Hexamethylbenzene, $C_{12}H_{18}$

(Brockway & Robertson, 1939)

$$a = 8.92 \pm 0.02, \quad b = 8.86 \pm 0.02, \quad c = 5.30 \pm 0.01 \text{ \AA}. \\ \alpha = 44.5^\circ, \quad \beta = 116.7^\circ, \quad \gamma = 119.6^\circ.$$

Space group, $P\bar{1}$; $d_o = 1.042 \text{ g.cm.}^{-3}$, $d_c = 1.061 \text{ g.cm.}^{-3}$;
1 molecule/unit cell.

In collecting intensity data two exposures were taken of each crystal, one being prolonged so that the weaker reflections could be observed. The intensities were estimated visually, employing the multiple-film technique in order to correlate the weak and the strong reflections. The total range of intensities covered was about several thousand to one. The estimations were carried out with the aid of a standard scale prepared from the crystal in question and, in general, two independent estimates were in good agreement. The intensities were modified with Lorentz and polarization factors and placed on an approximate absolute scale by Wilson's method. This scale was changed repeatedly throughout the analysis by comparing observed and calculated structure factors.

The present intensity data on hexachlorobenzene (133 observed reflections) are in good agreement with those of Lonsdale (65 observed reflections).

Structure analysis

The structures of 1,2 dichlorotetramethylbenzene and hexachlorobenzene are nearly isomorphous. They were solved by trial-and-error methods and, since similar techniques were employed, only the former will be described in any detail.

At the onset, an unexpected observation was made:

there were only two molecules of 1,2 dichlorotetramethylbenzene in the unit cell. Space-group requirements fix the positions of these molecules at centers of symmetry. However, it is quite apparent that 1,2 dichlorotetramethylbenzene is not centrosymmetrical. Therefore, it was assumed that the chlorine atoms and the methyl groups are distributed at random through the crystal among three crystallographically non-equivalent positions. The justification of such an assumption was the fact that the effective radii of the chlorine atom and the methyl group are approximately the same (about 2 Å). Somewhat similar behaviour has been encountered in the past. Among these examples are *p*-bromiodobenzene (Hendricks, 1933; Klug, 1947) and certain chloromethyl pyrimidine derivatives (Clews & Cochran, 1948).

The possibility of there being a fault structure present was also considered, for some mosaic blocks may have contained molecules oriented in one direction while others may have contained them oriented in other directions. However, prolonged rotation photographs failed to show any additional layer lines so that it was concluded that the distribution was truly random and homogeneous.

The orientation of the molecules was obtained through the consideration of outstandingly strong reflections. An understanding of the three most intense low-order reflections proved to be of the utmost importance. These reflections are (10 $\bar{6}$), (202) and (30 $\bar{4}$), and they make approximate 60° angles with one another. Furthermore, their second orders are outstandingly strong for their region in reciprocal space. Now, it can easily be shown that the signs of the first orders are the same. If this were not so, then the intersections of these planes on (010) would correspond to a severely distorted hexagon. This, however, would imply that the molecules are steeply inclined with respect to (010), a fact that is not consistent with the cell dimensions. Therefore, the signs must be the same and these were fixed as positive from approximate molecular dimensions; only the substituent positions can lie near the intersections of the first positive maxima (after the origin) of these planes. Such an orientation and inclination give the substituent positions a geometrical structure factor approximating unity for all orders so that the signs of the higher orders are also fixed and any decrease in intensity of the higher orders must be due primarily to the fall-off of the atomic scattering factor.

Approximate carbon positions were determined by considering outstandingly strong reflections from small-spacing planes: (2,0, $\bar{1}2$), (404), (60 $\bar{8}$), (3,0, $\bar{1}4$), (406) and (7,0, $\bar{1}0$). Their traces were drawn on the (010) plane and their signs fixed by requiring the orientation of the benzene ring to correspond with that determined by the substituent positions. The final result is shown in Fig. 1 and it will be seen that the atoms group themselves close to these planes.

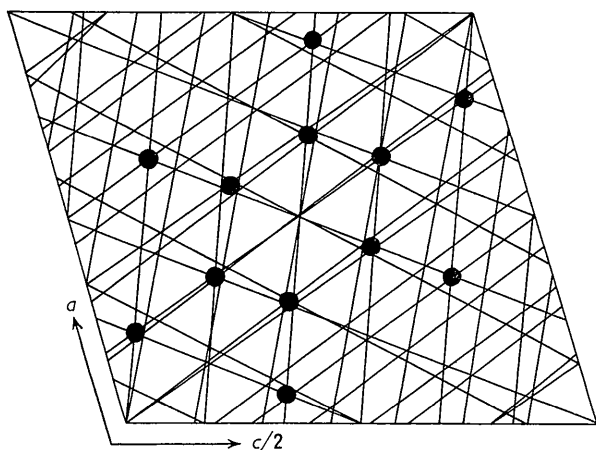


Fig. 1. 1,2 Dichlorotetramethylbenzene. Traces of the outstanding ($h0l$) planes.

Structure analysis proper began with the coordinates thus derived. An approximate substituent-position scattering curve was synthesized as follows. The empirical carbon scattering curve derived from anthracene data was scaled to 9 (the number of electrons in a methyl group) and an isotropic temperature factor, $B = 3.5 \text{ \AA}^2$, was applied to a Hartree chlorine atom at rest. Since the distribution of the chlorine atoms and the methyl groups was assumed to be random, two-thirds of the 'methyl' curve was added to one-third of the resulting chlorine curve and the totals were taken to represent the scattering power of a substituent position. This scattering factor proved to be sufficient in the early stages of analysis. However, as refinement progressed, it was changed considerably.

The work of refining the atomic coordinates proceeded by a straight-forward application of double Fourier series methods. Electron- and difference-density projections were investigated. During refinement, the a and c axes were subdivided into 30 and 60 parts, respectively, and computations were performed with the aid of Robertson strips. Final electron and difference densities were computed with an IBM Type 650 Magnetic Drum Data Processing Machine. At this time, the a and c axes were divided into 50ths and 100ths respectively. A general two-dimensional program was employed. It evaluated a 150-term series over 1326 points in the asymmetric unit in approximately 15 min. The results obtained employing the two grids were practically identical.

After each cycle of refinement, the substituent-position scattering curve was adjusted by calculating an empirical scattering curve. Such a procedure assumed atomic coordinates and the carbon scattering curve. These two were obtained from electron and/or difference densities in the immediate vicinity of atoms. The empirical scattering curve derived always remained within reasonable bounds and the whole procedure proved to be quite satisfactory.

The electron density of 1,2 dichlorotetramethylbenzene refined from $R = 0.55$ to $R = 0.24$ in five cycles; $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$. The large initial value of R was due, in most part, to the uncertainty associated with the substituent-position scattering power. Two additional isotropic difference cycles reduced R to 0.21*. At this stage, it was quite apparent that further refinement would require the consideration of anisotropic thermal vibrations. However, the object of this investigation centered upon, at least, the qualitative demonstration of the type of disorder existing in the crystalline solid and this was already amply borne out by the electron and isotropic difference densities. Therefore, the analysis was terminated at this point.

The refinement of hexachlorobenzene commenced at $R = 0.40$ and proceeded at $R = 0.21$ in three cycles. The smaller initial R and the speedier refinement were due to the more precise nature of the substituent positions and also to their greater scattering power. Two additional isotropic difference cycles reduced R to 0.17.

The structure analysis of hexamethylbenzene was extended in this investigation because: hexamethylbenzene is closely related to the other compounds studied; the solid possesses a discontinuity in heat capacity at low temperatures; the observed electron density vaguely suggests anisotropic thermal motion. In order to verify the latter, the electron density was recomputed on a smaller grid (50ths \times 50ths) employing Brockway & Robertson's signs and structure factors. Contours of constant density were drawn by graphical interpolation of line sections. However, the results proved to be inconclusive although in close agreement with Brockway & Robertson.

In order to facilitate the interpretation of difference densities of hexamethylbenzene, Robertson's empirical scattering curve was replaced by a McWeeny carbon atom that was modified, in the first instance, with a mean molecular isotropic temperature factor \dagger . This temperature factor was obtained along with an approximate absolute scale constant from $\ln (|F_o|/|F_c|)$ versus $(\sin \langle \theta \rangle / \lambda)^2$, $|F_c|$ here representing structure factors calculated for atoms at rest. In subsequent cycles, the carbon atoms and the methyl groups were assigned different isotropic temperature factors. The initial value of R was 0.32. It reduced to 0.23 in three isotropic difference cycles. At this stage, a parameter variation was performed on the temperature factors. Variations of up to $|\Delta B| = 0.5 \text{ \AA}^2$ from the final B values were without appreciable

* The term isotropic difference cycle is used to denote that the calculated atoms were assumed to be undergoing isotropic thermal motions.

\dagger Grenville-Wells (1956) compares the empirical naphthalene scattering curve to a McWeeny carbon atom and shows how the two can be correlated. If, however, such correlations are ignored, the transform of the empirical scattering curve resembles a Gaussian rather than a Hartree or McWeeny atom.

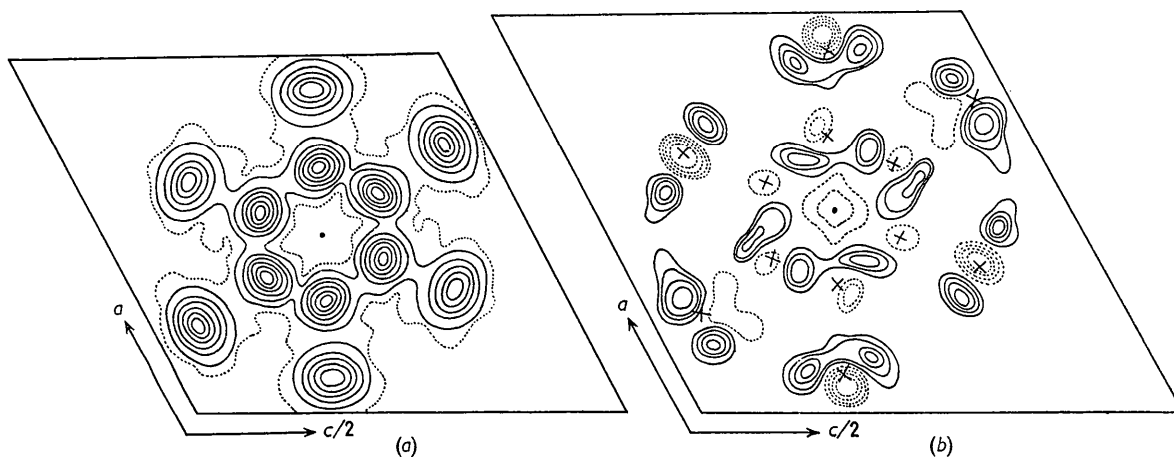


Fig. 2. 1,2 Dichlorotetramethylbenzene. (a) (010) electron density; contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$ for carbon and $2 \text{ e.}\text{\AA}^{-2}$ for the substituent group; one-electron line broken. (b) (010) difference density; contours at intervals of $0.25 \text{ e.}\text{\AA}^{-2}$; negative contours broken; zero contour omitted.

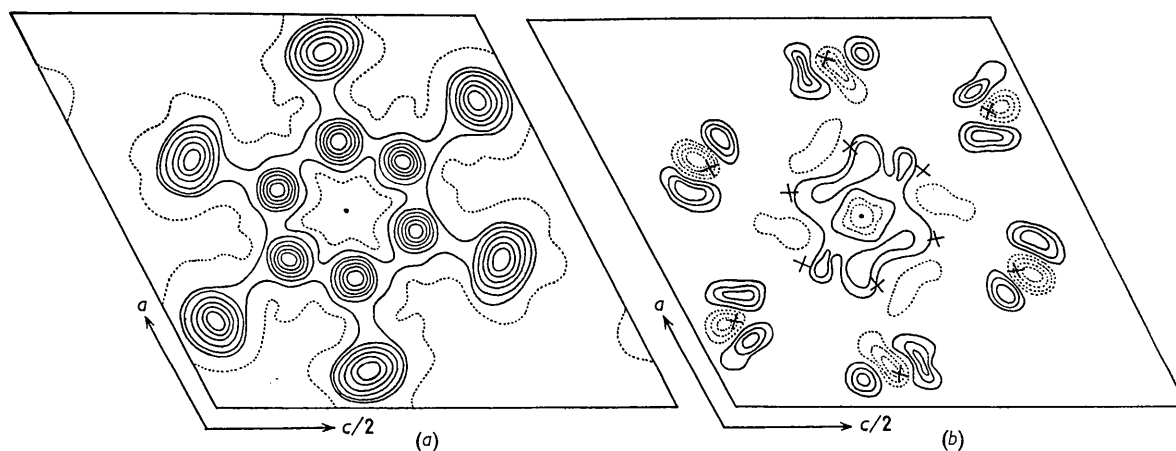


Fig. 3. Hexachlorobenzene. (a) (010) electron density; contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$ for carbon and at $2, 4, 8, 12, \dots, \text{ e.}\text{\AA}^{-2}$ for chlorine; one-electron line broken. (b) (010) difference density; contours at intervals of $0.5 \text{ e.}\text{\AA}^{-2}$; negative contours broken; zero contour omitted.

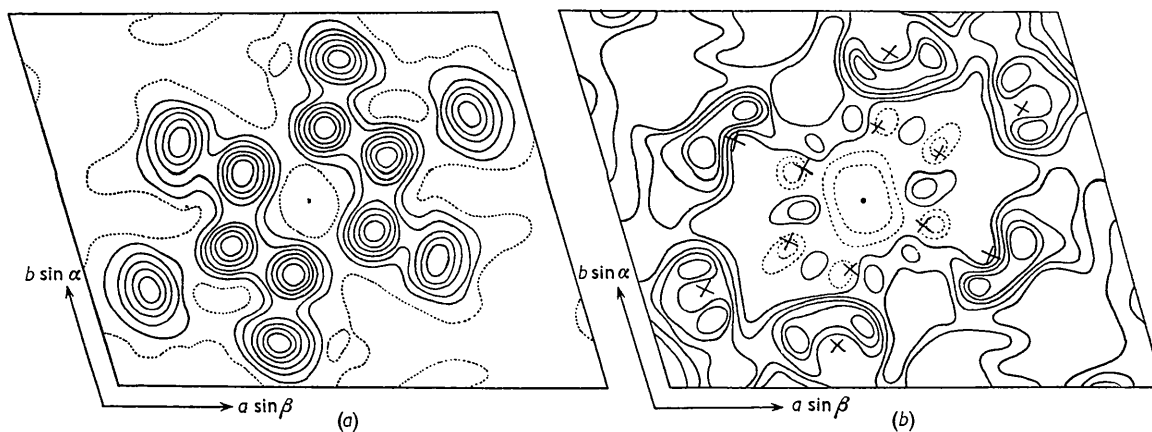


Fig. 4. Hexamethylbenzene. (a) c-axis projection of electron density; contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$; one-electron line broken. (b) c-axis projection of difference density; contours at intervals of $0.25 \text{ e.}\text{\AA}^{-2}$; negative contours broken; zero contour omitted.

effect. Furthermore, placing hydrogen atoms at physically plausible positions (every other methyl group having the same orientation, the first with two hydrogens and the second with one hydrogen above the plane of the benzene ring) improved agreement in some of the very low-order reflections but no significant overall agreement was effected.

Results

The final electron and isotropic difference density projections are shown in Figs. 2-4. All the reflections within the limiting sphere for Cu $K\alpha$ were included in the difference syntheses. As a first approximation, accidentally unobserved reflections were taken to be $\frac{1}{2}I_{\min.}$, where $I_{\min.}$ is the weakest observed intensity. Hamilton (1955) has suggested the use of $\frac{1}{3}I_{\min.}$ in the centrosymmetrical case; however, this value was constantly low when compared to calculated structure factors.

A common and striking characteristic of the electron and difference densities is the ellipticity of the substituent atoms, immediately suggesting that the atoms are undergoing relatively large anisotropic thermal vibrations. In addition, the lines of maximum vibration possess an approximate hexagonal distribution.

Another feature, common to the difference densities, is the large negative minimum at the center of the benzene rings. Such behaviour has been observed before in other benzene derivatives, and also in other aromatic systems. The possibility of it being due to diffraction effects in the calculated structure was considered, but it was found that the first diffraction maximum of the ring carbons occurs approximately 0.3-0.4 Å away from the center of the benzene ring.

From the electron density of 1,2 dichlorotetramethylbenzene, Fig. 2(a), it will be seen that the peak heights of the substituent positions are about the same. The transform of a twelve-electron atom, with appropriate thermal motion, corresponds closely to the electron density of an isolated substituent atom. Since the sum of two-thirds of a methyl group and one-third of a chlorine atom synthesizes approximately a twelve-electron atom, the original assumption of a random distribution over six positions seems amply verified.

The positions of the atoms in the $h0l$ projection of 1,2 dichlorotetramethylbenzene are consistent with a regular planar hexagon of carbon atoms, 1.39 ± 0.01 Å, with a carbon-substituent distance of 1.68 ± 0.03 Å. The uncertainty in the latter distance is due to the disorder which affects the substituent atoms. Actually, the distance is somewhat meaningless in a crystallographic sense, since it is a weighted mean of carbon-methyl and carbon-chlorine distances. The distances of closest approach between neighboring molecules and the lines of maximum and minimum molecular tilt are shown in Fig. 5(a). The molecules are inclined about 21.5° to (010) along $L_{\max.}$. Table 1 lists the final

coordinates of the atoms, the y coordinates being deduced from the inclination of the molecules assuming strict planarity.

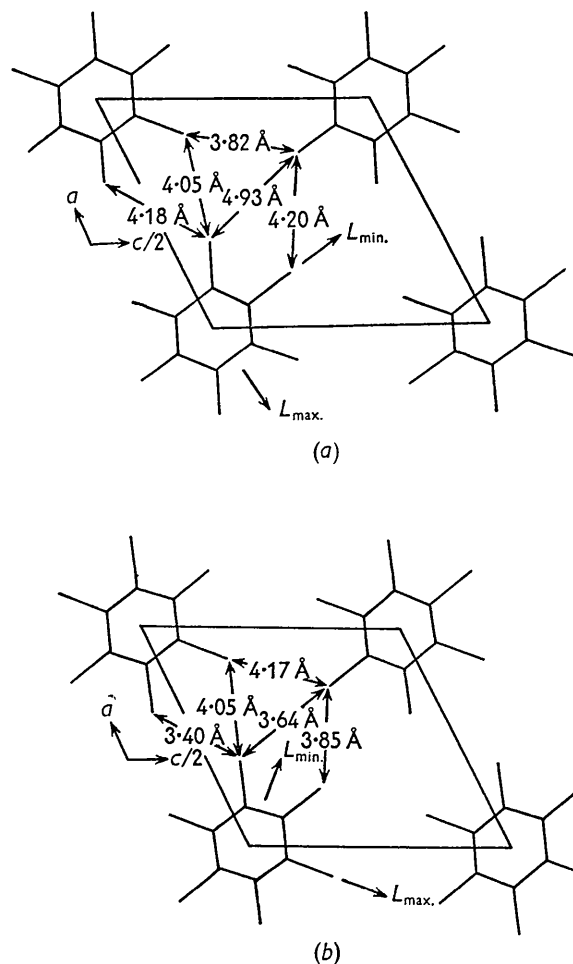


Fig. 5. Distances of closest approach between neighboring molecules. (a) 1,2 Dichlorotetramethylbenzene. (b) Hexachlorobenzene.

Table 1. Final atomic coordinates, 1,2 dichlorotetramethylbenzene

Atom	x/a	y/b	z/c
C ₁	0.192	0.103	0.072
C ₂	0.128	0.000	0.183
C ₃	-0.067	-0.103	0.114
X ₁	0.408	0.258	0.156
X ₂	0.256	0.000	0.397
X ₃	-0.145	-0.258	0.250

Hexachlorobenzene was first described quantitatively in a celebrated paper by Lonsdale (1931). However, Lonsdale's data were limited and, furthermore, the structure was not refined. The present analysis confirms the ellipticity of the chlorine atoms originally observed by Lonsdale but in addition determines the positions and the shapes of the carbon atoms much more precisely. From the $h0l$ projection,

the molecule approximates a regular planar hexagon, 1.39 ± 0.02 Å, with a carbon-chlorine distance of 1.70 ± 0.02 Å. The distances of closest approach between neighboring molecules and the lines of maximum and minimum molecular tilt are shown in Fig. 5(b). The molecules are inclined about 20.0° to (010) along L_{\max} . Table 2 lists the final atomic coordinates of the atoms, the y coordinates being deduced from the molecular inclination as above.

Table 2. Final atomic coordinates, hexachlorobenzene

Atom	x/a	y/b	z/c
C ₁	0.189	0.072	0.061
C ₂	0.128	-0.072	0.189
C ₃	-0.058	-0.128	0.128
Cl ₁	0.403	0.153	0.131
Cl ₂	0.278	-0.153	0.408
Cl ₃	-0.128	-0.275	0.281

The final isotropic difference density of hexamethylbenzene, Fig. 4(b), removes any doubt, Fig. 4(a), as to the ellipticity of the methyl groups. Anomalous regions in the difference density can be easily cor-

Table 3. 1,2 Dichlorotetramethylbenzene

h0l	F _o	F _c	h0l	F _o	F _c	h0l	F _o	F _c
100	37	29	302	5	-3	60E	6	4
200	32	-28	304	19	-10	60A	* 2	-3
300	26	-29	306	11	12	60E	6	5
400	22	-17	308	* 2	1	60E	25	31
500	6	5	30,10	6	8	60,10	* 2	-3
600	10	-11	30,12	4	5	60,12	6	-6
700	4	5	30,14	5	-7	60,14	11	-13
800	4	2	30E	11	-16	60,1E	* 2	-4
900	4	-4	30A	50	62	60,1E	* 2	-4
002	35	31	30E	28	-22	60,2E	5	-6
004	31	-36	30E	3E	-37	60,2E	5	4
006	30	-39	30,10	18	-20	70A	* 2	-7
008	30	-31	30,1E	9	7	70E	* 1	-1
00,10	14	10	30,1A	24	30	70E	* 0	-4
00,12	12	-9	30,1E	* 2	7	70E	11	-13
00,14	4	1	30,1E	4	4	70A	9	-11
00,16	* 2	2	30,20	* 1	0	70E	* 2	-5
00,18	4	-6	40E	14	-10	70E	25	22
102	20	-17	40A	30	36	70,10	18	21
104	4	-9	40E	22	26	70,1E	* 2	1
106	44	-35	40E	2	-2	70,1A	* 2	3
108	20	20	40,10	3	-3	70,1E	4	-7
10,10	5	6	40,12	6	-7	70,1E	4	-6
10,12	12	-17	40,14	* 0	-1	70,20	12	-4
10,14	* 1	-0	40E	40	-35	80E	6	-6
10,16	6	-4	40A	4	3	80A	4	-6
10,18	4	9	40E	* 1	2	80E	* 2	-8
10E	38	32	40E	25	-23	80E	* 2	-4
10A	18	-16	40,10	14	19	80,10	4	6
10E	53	62	40,1E	* 2	-2	80,1E	* 2	-7
10E	10	-2	40,1A	* 2	-4	80,1E	* 2	0
10,10	16	-21	40,1E	* 2	2	80,1E	4	5
10,1E	* 2	-3	40,1E	* 2	2	80,1E	4	5
10,1A	3	0	40,20	4	7	80,1E	5	-5
10,1E	8	8	50E	* 2	-1	80E	4	-4
10,1E	5	-4	50A	16	16	90A	5	-7
10,20	* 0	-3	50E	* 2	-1	90E	5	4
202	56	65	50E	* 2	1	90E	* 1	0
204	* 1	3	50,10	13	-6	90,10	* 2	-1
206	19	-26	50,1E	* 0	-2	90,1E	* 2	5
20E	* 2	-3	50E	16	25	90,1A	* 1	-4
20,10	11	-6	50A	19	-16	90,1E	* 1	-5
20,12	* 2	1	50E	14	-11	90,1E	3	-5
20,14	* 4	-4	50E	15	-14	10,04	* 0	7
20,16	1	3	50,10	7	4	10,0E	4	-6
20E	15	-17	50,1E	9	8	10,0E	4	-6
20A	29	-30	50,1A	9	-10	10,0E	3	-8
20E	10	-11	50,1E	6	4	10,0,10	* 4	6
20E	7	10	50,1E	* 2	0	10,0,14	12	17
20,10	16	-13	50,20	3	-6			
20,1E	30	29	60E	* 2	0			
20,1A	13	16	60A	* 2	-1			
20,1E	* 2	-2	60E	4	6			
20,1E	* 2	-5	60E	3	5			
20,20	5	-7	60,10	3	-8			

Table 4. Hexachlorobenzene

h0l	F _o	F _c	h0l	F _o	F _c	h0l	F _o	F _c
100	21	22	302	8	6	60,10	* 5	-1
200	30	-30	304	35	-30	60E	* 7	11
300	20	-11	306	* 7	-17	60A	10	14
400	37	-38	308	21	-23	60E	8	-12
500	8	-10	30,10	32	38	60E	69	68
600	25	-24	30,1E	* 6	5	60,10	15	6
700	28	33	30,1A	8	-6	60,1E	30	-27
800	* 7	16	30E	36	-33	60,1A	25	-16
900	10	-14	30A	101	109	60,1E	9	-10
002	21	19	30E	17	-20	60,1E	18	-13
004	27	-28	30E	55	-49	70E	8	-6
006	21	-15	30,10	22	-17	70A	* 7	5
008	32	-36	30,1E	8	-13	70E	8	16
00,10	8	-11	30,1A	27	14	70E	15	-19
00,12	22	-24	30,1E	12	-13	70A	25	-26
00,14	27	38	30,1E	27	33	70E	24	-23
00,16	9	11	30,20	12	13	70E	13	13
00,18	17	-11	40E	24	-22	70E	10	30
102	28	-33	40A	67	74	70,10	30	27
104	30	-37	40E	13	8	70,1E	9	-12
106	50	-45	40E	* 7	0	70,1A	33	36
108	55	68	40,10	8	15	70,1E	8	4
10,10	* 7	5	40,1E	17	-17	70,1E	24	-22
10,12	20	-19	40,1A	* 5	-11	70,20	12	-6
10,14	* 7	10	40E	52	-46	80E	17	-17
10,16	17	-15	40A	17	-9	80E	8	-12
10,18	* 4	-7	40E	* 4	6	80A	8	11
10E	22	22	40E	37	-31	80A	6	11
10A	21	-28	40,10	63	71	80E	28	-32
10E	103	113	40,1E	10	5	80E	* 7	-7
10E	* 5	-1	40,1A	28	-25	80,10	13	-19
10,10	25	-20	40,1E	* 7	-4	80,1E	12	-14
10,12	8	10	40,1E	8	-12	80,1A	* 6	0
10,14	8	-14	40,20	8	1	80,1E	15	16
10,16	8	-5	50E	13	14	80,1E	17	-12
10,18	21	-17	50A	24	22	80E	13	-13
202	105	111	50E	10	-18	90A	17	-18
204	17	-13	50E	* 7	-14	90E	* 7	11
206	21	-13	50,10	17	-18	90E	17	16
20E	8	12	50,1E	10	19	90,10	8	-12
20,10	25	-29	50E	55	67	90,1E	25	26
20,12	* 7	-16	50A	20	-20	90,1A	* 4	-2
20,14	18	-18	50E	39	-32	90,1E	21	-20
20,16	20	25	50E	24	-20	90,1E	4	-11
20E	32	-33	50,10	8	-6	10,04	* 7	19
20A	30	-29	50,1E	10	10	10,0E	8	-9
20E	32	-32	50,1A	30	-21	10,0E	17	-15
20E	8	-10	50,1E	33	38	10,0,10	17	-16
20,10	36	-26	50,1E	13	10	10,0,1E	* 4	6
20,1E	67	75	50,20	21	-20	10,0,1A	12	17
20,1A	30	21	60E	8	-14			
20,1E	15	-16	60A	9	-15			
20,1E	* 6	-2	60E	24	28			
20,20	13	-14	60E	* 5	-1			

related with the erratic fluctuation of the one-electron contour in the electron density. From projection, the benzene ring is approximately a planar hexagon 1.39 ± 0.01 Å. The carbon-methyl distance is 1.54 ± 0.01 Å. In all respects, orientation, inclination, and intermolecular distances, the present structure is quite similar to that of Brockway & Robertson.

At this point, it should be pointed out that rigid-body molecular oscillations cause displacements of electron-density peaks and, therefore, systematic errors in bond distances (Cruickshank, 1956a). To correct for this effect, a knowledge of the mean square amplitudes of oscillation in the plane containing the oscillation is required. Since the present refinement was carried out employing isotropic atoms, these quantities have not been determined and, consequently, the aforementioned effect has not been compensated for.

The observed and calculated structure factors of 1,2 dichlorotetramethylbenzene and hexachlorobenzene are given in Tables 3 and 4, respectively. Accidentally unobserved reflections are denoted with asterisks.

Discussion

The important facts which have emerged from this investigation are the anisotropic disorder, observed in all the molecules studied, and the apparent randomness of the chlorine atoms and the methyl groups in 1,2 dichlorotetramethylbenzene. It will now be shown how these two observations can be correlated and also shown to be compatible with known dielectric behaviour.

Dielectric behaviour suggests that the unsymmetrical penta- and hexa-substituted chloro-methyl benzene derivatives possess considerable molecular freedom in the solid. They have relatively large dielectric constants at higher temperatures (i.e. 25° C.) that cannot be accounted for by atomic and electronic polarizations alone. Furthermore, they exhibit dielectric loss in the solid which, with the dielectric constant, is temperature and frequency dependent, the frequency dependence occurring in the kilocycle region.

Now, although dielectric evidence seems to indicate freely rotating molecules in the solid, the present results preclude this possibility in a general way. The atoms of the molecules are localized about mean equilibrium positions. However, they possess large anisotropic thermal vibrations and the directions of maximum vibration form a pseudo-hexagonal array. These observations suggest that, in addition to the normal thermal motions of the atoms, the molecules undergo a rigid-body torsional vibration. Although interesting in itself, such an internal degree of freedom, alone, cannot successfully account for known dielectric behaviour.

However, an additional molecular freedom has been observed in 1,2 dichlorotetramethylbenzene: the random distribution of the chlorine atoms and the methyl groups. On the basis of X-ray results alone, such a behaviour cannot be interpreted unambiguously since the X-ray method gives time-averaged results. Thus, according to the X-ray method, it is quite impossible to distinguish whether the random distribution is due to a static or a dynamic phenomenon. But, the fact that the dielectric properties of this compound are frequency dependent in the kilocycle region immediately suggests that the random distribution is due to a dynamic phenomenon. Since such a natural absorbing frequency is small compared to the frequency of atomic or molecular vibrations, the frequency dependence must be due to an entirely different type of process. One such process has been put forth by Kauzmann (1942): the molecules undergo discontinuous molecular reorientations of $n\pi/3$, when they are free to reorient to any of six equilibrium positions. However, the potential barriers restricting such reorientations are somewhat larger than the average thermal energy of the crystal (about $15kT$ for 1,2 dichlorotetramethylbenzene). Nevertheless, since the molecules have already been shown to possess relatively large rigid-body torsional vibrations, it should

be quite possible for any given molecule to acquire, through thermal fluctuations, a considerable amount of torsional energy in excess of the average and thereby be able to reorient itself.

Now, such a dynamic model, when time-averaged, is found to be quite consistent with the X-ray results. For if the frequency dependence is due to a reorientation process, the frequency of the process must be in the kilocycle range. Since such a period is small compared with the duration of an X-ray experiment, a completely random distribution of chlorine atoms and methyl groups would be expected in chloro-methyl substituted derivatives. In addition, the atoms would be localized about mean equilibrium positions because the time spent in transition is small compared to the average life-time near a given equilibrium position. Such a behaviour is, in fact, satisfied in 1,2 dichlorotetramethylbenzene.

From the foregoing discussions, it is clear that a rigid-body torsional vibration coupled with discontinuous molecular reorientations of $n\pi/3$ is capable of correlating the dielectric and X-ray behaviour of 1,2 dichlorotetramethylbenzene. Although a dynamic model was employed in conjunction with time-averaged X-ray results, the time-averaged dynamic model has been shown to be quite compatible with the latter. However, it is difficult to say whether the fore-mentioned behaviour is a common phenomenon to all members of the class studied. On the basis of dielectric evidence, it would seem to be so, since many more members of the class have been shown to possess similar properties. On the basis of the X-ray method, generalizations would be unwarranted owing to the fact that the class has not received a thorough study.

In closing, it should be pointed out that of late, an increasing body of evidence has been accumulating pointing out that relatively small planar molecules undergo rigid-body torsional vibrations. Benzene, in preliminary communications (Cox & Smith, 1954; Cox, Cruickshank & Smith, 1955), has been reported to do so. In view of the present results, this is not unexpected since benzene can be considered to be the simplest example of the class studied. Other recent examples are acridine (Phillips, 1956) and anthracene (Cruickshank, 1956b); undoubtedly, many other uninvestigated ones exist.

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Crystal Structures of Zr_5Ge_3 , Ta_5Ge_3 and Cr_5Ge_3

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The crystal structures of Zr_5Ge_3 , Ta_5Ge_3 and Cr_5Ge_3 have been examined by means of Debye-Scherrer diagrams and compared with the corresponding silicides. Cr_5Ge_3 crystallizes in the $T1$ type structure with $a = 9.41_3$ Å and $c = 4.78_0$ Å. Ta_5Ge_3 crystallizes in the $T1$ structure also, as previously reported, but transforms to the Nowotny structure ($D8_8$ type) with $a = 7.58_1$ Å and $c = 5.23_5$ Å if 5% of carbon is added. Zr_5Ge_3 crystallizes directly in the Nowotny structure ($D8_8$ type) with $a = 7.99_3$ Å and $c = 5.59_7$ Å. Apparently the residual impurities are sufficient to stabilize this phase in the latter case. The germanide structures are thus the same as the corresponding silicide structures.

Introduction

A comparison of the structures of the silicides and germanides of the transition metals, in so far as the structures have been determined, shows a complete correspondence of structure types, in spite of the fact that the germanium atom is considerably larger than the silicon atom. In the case of the phases with the formula M_5Si_3 it is known that the expected binary phases are frequently replaced by the so-called Nowotny phase having a $D8_8$ type structure, the stabilization of the latter apparently being brought about by the presence of atoms of carbon, boron, oxygen or nitrogen, often in very small amounts (Parthé, 1957). In order to extend the analogy between the silicides and germanides somewhat further, the compounds Zr_5Ge_3 , Ta_5Ge_3 and Cr_5Ge_3 were examined.

Preparation of samples

The specimens were prepared from powders of zirconium hydride, tantalum hydride, chromium, and germanium. The powders were mixed in proper portions in trichlorethylene in a hard-metal ball-mill and the dried powders were hot-pressed in graphite dies. The temperature was 1200° C. and time at temperature about 2 min. Since this temperature was

above the melting point of germanium, the pressure was applied slowly.

Cr_5Ge_3

The powder diagram of Cr_5Ge_3 could be indexed to correspond to a tetragonal unit cell with the lattice constants:

$$a = 9.41_3 \text{ Å}, \quad c = 4.78_0 \text{ Å}, \quad c/a = 0.507.$$

The extinctions lead to the space group D_{4h}^8-I4/mcm . The agreement between observed and calculated values of the intensities (Table 1) was obtained if the Cr atoms were placed in positions 4(b) and 16(k) with the parameter $x = 0.07_4$ and $y = 0.22_3$, while the Ge atoms were in positions 4(a) and 8(h) with the parameter $x = 0.17$. Thus Cr_5Ge_3 has the same structure as Cr_5Si_3 , which is of the $T1$ type. The lines of the phase Cr_3Ge were also observed in the specimen.

A second specimen to which 5 atomic% carbon was added showed the same $T1$ structure of the binary phase Cr_5Ge_3 .

Ta_5Ge_3

The specimen prepared from tantalum hydride and germanium confirmed the $T1$ structure of the binary phase Ta_5Ge_3 reported by Nowotny, Searcy & Orr (1956). With the addition of 5 atomic% carbon, however, the powder pattern was different and recogniz-

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