Acta Cryst. (1951). **4**, 172

The Structure of Octachlorocyclobutane, C_4Cl_8[*]

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(*Received* 6 *August* 1950)

Octachlorocyclobutane crystallizes in a two-molecule monoclinic unit with $a = 8{\cdot}00$, $b = 10{\cdot}64$, $c = 6{\cdot}28$ A., $\beta = 107° \, 45'$, space group $P2_1/m$. Atomic co-ordinates have been determined from Fourier syntheses including two sections with corrections for finite termination of series. The cyclobutane ring is considerably puckered and the molecule closely approximates to the symmetry $\bar{4}m$. Averaged C–C and C–Cl distances (1·59 and 1·74 A. respectively) are indicative of longer C–C and shorter C–Cl bonds than the 'normal' values (1·54 and 1·76 A., respectively), although the experimental accuracy attained conceivably would permit of shifts in carbon positions so as to have both C–C and C–Cl bonds of essentially normal lengths. The Cl–C–Cl bond angles are approximately tetrahedral, whereas the average C–C–C angle is 88°.

Introduction

During the past few years several investigators have studied the configuration of the carbon ring in cyclobutane and its derivatives. Wilson (1943) interpreted spectroscopic data from cyclobutane in terms of a planar ring and the molecular symmetry D_{4h}. More recently the fluorinated analogue, C_4F_8, has received considerable attention. On the basis of spectroscopic studies Edgell (1947) first reported that the ring was planar, but later work with better equipment by Edgell & Weiblen (1950) led them to conclude that the molecule had the symmetry D_{2d} with a puckered ring. Lemaire & Livingston (1950), in electron-diffraction studies of the same compound, report preliminary results as indicating a non-planar ring and the molecular symmetry D_{2d}. They note indications of an abnormally long carbon–carbon distance as well. However, Claassen (1950) reports that infra-red and Raman spectra are consistent with a planar ring for C_4F_8. In an X-ray investigation of one form of tetraphenyl cyclobutane, Dunitz (1949) found a planar carbon ring (symmetry center required by the space group) but he states that an isomer of this compound may have a fourfold alternating axis of symmetry.

Recently octachlorocyclobutane, C_4Cl_8, was made available to us for X-ray study by Prof. W. T. Miller of this Department. We have found the molecule to have a non-planar ring and to conform approximately to the molecular symmetry D_{2d}–$\bar{4}m$ although only a single mirror plane is required by the space group.

Experimental procedure

Octachlorocyclobutane, already purified by recrystallization from methyl alcohol, was dissolved in benzene in a small test tube and allowed to crystallize slowly. Clear lath-shaped crystals were obtained which, when examined microscopically between crossed nicol prisms, showed continuous extinction parallel to the needle axis irrespective of any angular rotation about this axis. Nevertheless, it later appeared that the needle axis was not the unique symmetry axis of the monoclinic crystal.

A needle approximately 0·3 mm. in diameter was mounted vertically on the goniometer head so that the needle axis coincided with the rotation axis. As the compound has an appreciable vapor pressure it was necessary to coat the crystal with Canada balsam to prevent too rapid loss by sublimation.

Oscillation photographs were taken and the method of Hendershot (1936) was employed to align the crystal for use on the Weissenberg instrument. The oscillation pictures indicated a spacing of 6·3 A. along the needle axis which was tentatively designated as the c axis.

The zero and four higher layer equi-inclination Weissenberg photographs of this crystal were obtained using Cu $K\alpha$ radiation. The observed symmetry of the X-ray diffraction effects was C_{2h}–$2/m$ with the monoclinic axis lying in a plane normal to the needle axis. Only $(0k0)$ reflections for k odd were missing, as required by the space groups C_2^2–$P2_1$ and C_{2h}^2–$P2_1/m$.

Sections perpendicular to the needle axis of a crystal were cut with a sharp razor blade and specimens were mounted so that the unique symmetry axis of the crystal coincided with the axis of rotation. The zero and six upper-layer equi-inclination Weissenberg photographs were obtained for rotation about the monoclinic axis, b. The triple-film technique was used throughout.

The lattice constants were determined from the two zero-layer Weissenberg photographs (i.e. around b and c) upon which reflections from NaCl had been superimposed. The monoclinic angle was determined by the

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[*] This paper was presented at the April, 1950, meeting of the American Crystallographic Association at Pennsylvania State College, State College, Pennsylvania.

method of angular lag as described by Buerger (1942) and also by direct measurement on the zero-layer b-axis film. Final values are:

$$a = 8{\cdot}00, \quad b = 10{\cdot}64, \quad c = 6{\cdot}28\ \text{A.}; \quad \beta = 107^\circ\ 45'.$$

For 2 molecules within the unit cell the calculated X-ray density is 2·16 g.cm.$^{-3}$. The later analysis is consistent with the assumption of a 2-molecule unit.

The reflections were indexed and the value of $\sin\theta$ for each spot was determined graphically from construction of the reciprocal lattice according to the method of Bunn (1945). Relative intensities were estimated by visual comparison with a calibrated intensity scale having spots comparable in size to those appearing on the films and with the following range of intensities: 2 : 3 : 5 : 6 : 9 : 11 : 13 : 15 : 19 : 22 : 26 : 30 : 35 : 40 : 42 : 43 : 50 : 57 : 64 : 76 : 79 : 82 : 88 : 100 : 118 : 130 : 139 : 145 : 147. The value of 2 indicated a spot that was just visible, whereas that of 147 indicated near-saturation. Intensities thus determined were corrected for the Lorentz and polarization factors and the Tunell (1939) factor to obtain relative $|F_{hkl}|^2$ values. The zero-layer Weissenberg photograph about c was taken as the standard film and by careful cross calibration all relative $|F_{hkl}|^2$ were reduced to the common level. Variations in absorption were small enough to be neglected.

Determination of atomic positions

It was found that the Patterson synthesis, $P(X, Y)$, constructed immediately after obtaining the required ($hk0$) data, was consistent with the centrosymmetric space group, $P2_1/m$. The projection clearly indicated that the molecular symmetry could not be D_{4h} but rather that it was compatible with a puckered model having the symmetry D_{2d}. The orientation of the molecule which accounts in detail for the Patterson synthesis has a diagonal of the carbon ring lying in the symmetry plane in which lie also four twofold chlorine atoms forming an isosceles trapezoid around the two carbon atoms. The perpendicular bisector of the bases of this trapezoid lies almost along the trace of the plane $x = \frac{1}{4}$ in the symmetry plane $y = \frac{1}{4}$. The four fourfold chlorine atoms also form a trapezoid the plane of which is almost coincident with $x = \frac{1}{4}$. Fig. 1 is a sketch of the molecule which should clarify the description. The marked puckering of the carbon ring is apparent. Approximate x and y parameters were obtained for chlorine atoms from this projection and positions were assigned to the carbon atoms using normal bond lengths.

Phases for ($hk0$) reflections were calculated using the trial parameters in order to make the Fourier projection, $\rho(x, y)$, on (001). Chlorine maxima were sufficiently resolved to confirm the postulated model. Again carbon co-ordinates were chosen consistent with known C–C and C–Cl bond lengths.

The next problem was to find approximate values of parameters along c. In effect there are two strings of molecules, one centered at $x = \frac{1}{4}$, $y = \frac{1}{4}$ and the other at $x = \frac{3}{4}$, $y = \frac{3}{4}$, but the separation along z of one string with respect to the other was not yet fixed. There was also the question as to the orientation of the trapezoid of the chlorine atoms in the symmetry plane as the projection did not reveal whether the long or short base was more advanced along z.

In order to resolve these ambiguities we calculated the Patterson section, $P(X, \frac{1}{2}, Z)$, using $|F_{hkl}|^2$ values divided by an arbitrary temperature factor to improve resolution of maxima. It then became possible to establish that the short base of the trapezoid was more advanced in the $+z$ direction and to determine approximate values of z parameters.

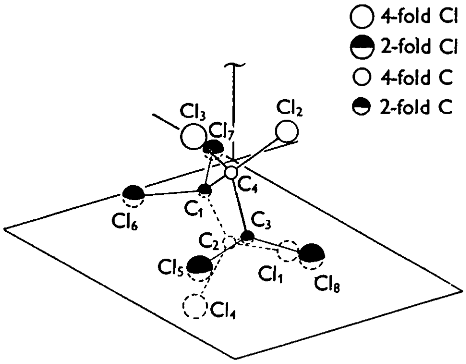

Fig. 1. Sketch of molecule centered in plane $y = \frac{1}{4}$.

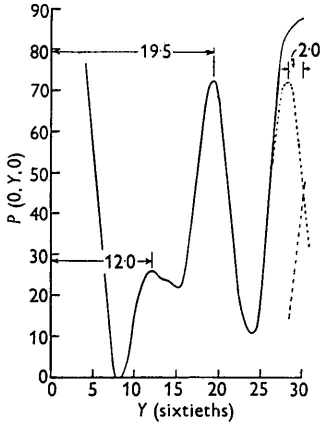

Fig. 2. Patterson line section, $P(0, Y, 0)$.

The Patterson line section, $P(0, Y, 0)$, was computed to give us good values of y co-ordinates for fourfold atoms. This synthesis (Fig. 2) is of interest since not only does it give Cl–Cl separations parallel to b but also a peak corresponding to the expected C–C separation.

We then calculated phases for ($h0l$) reflections and evaluated the Fourier projection, $\rho(x, z)$, on (010). There was some superposition of peaks corresponding to twofold chlorine atoms and carbon maxima were rather poor. The fourfold chlorines were well defined. Atomic positions were obtained, phases were redetermined and the Fourier synthesis was re-evaluated until no further sign changes occurred. Fig. 3 shows the corresponding projection of the structure along the unique axis.

As half of the atoms of the molecule lie in the symmetry plane $y=\frac{1}{4}$ and the other half lie almost exactly in the plane $x=\frac{1}{4}$, we next evaluated the two Fourier sections $\rho(x, \frac{1}{4}, z)$ and $\rho(\frac{1}{4}, y, z)$ using observed amplitudes. Co-ordinates were determined, phases recalculated, and the syntheses reconstructed until all phases remained fixed. These sections gave final atomic positions apart from corrections for finite termination of series.

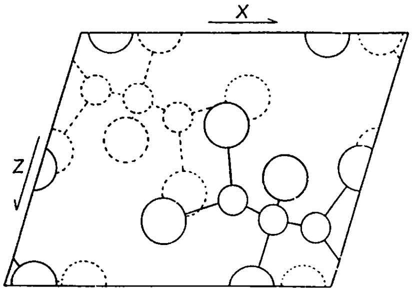

Fig. 3. Schematic projection of unit cell along unique axis (solid lines indicate molecule in $y=\frac{3}{4}$, broken lines that in $y=\frac{1}{4}$).

The X-ray photographs show several reflections of considerable intensity near the limit of observation with Cu $K\alpha$ radiation. Hence it is quite probable that a fair number of unobserved reflections having appreciable amplitudes are not included in the Fourier syntheses of observed amplitudes. We have followed the well known procedure of computing the two sections using calculated amplitudes and applying the resulting small shifts in atomic co-ordinates as corrections (with reversed sign) to the positions obtained above from observed data. Final parameter values are listed in Table 1. The values in parentheses are those given by the Fourier syntheses using only observed amplitudes, i.e. without correction for finite series termination.

Table 1. *Parameters in* C_4Cl_8

	x	y	z
C_1	+0·097 (+0·100)	$\frac{1}{4}$	+0·243 (+0·246)
C_2	+0·239 (+0·242)	+0·146 (+0·146)	+0·252 (+0·264)
C_3	+0·384 (+0·378)	$\frac{1}{4}$	+0·341 (+0·334)
Cl_1	+0·242 (+0·243)	+0·090 (+0·091)	− 0·007 (− 0·005)
Cl_4	+0·237 (+0·237)	+0·018 (+0·019)	+0·420 (+0·425)
Cl_5	+0·462 (+0·462)	$\frac{1}{4}$	+0·638 (+0·638)
Cl_6	+0·022 (+0·022)	$\frac{1}{4}$	+0·466 (+0·465)
Cl_7	− 0·083 (− 0·084)	$\frac{1}{4}$	− 0·005 (− 0·006)
Cl_8	+0·563 (+0·564)	$\frac{1}{4}$	+0·242 (+0·242)

Corrections to chlorine atomic positions were generally small and the parameters listed for them are considered to fix chlorine positions with a probable error of about 0·01 A. The carbon peaks in all syntheses were not too well defined probably because of rippling due to incomplete series. As was expected, larger corrections to carbon parameters had to be made. It is difficult to assign limits of error to the carbon positions.

An isotropic temperature factor of the form $\exp[-B(\sin\theta/\lambda)^2]$ (where B must be determined) was applied to calculated amplitudes for the comparison of calculated and observed values. In addition to determining B, a factor must be obtained which will correct observed amplitudes to an absolute scale. Mathematically,

$$K\,|F_{\text{obs.}}| = |F_{\text{calc.}}|\exp[-B(\sin\theta/\lambda)^2],$$

which may be rewritten in logarithmic form as

$$\ln\frac{|F_{\text{calc.}}|}{|F_{\text{obs.}}|} = \ln K + B(\sin\theta/\lambda)^2.$$

This is of the form $y=mx+b$, the equation of a straight line where $b=\ln K$ and $m=B$. The method of least squares was used to determine best values of the slope and intercept of the straight line. We found $K=2{\cdot}87$ and $B=2{\cdot}97$ A^2.

A detailed comparison between the final approximately absolute values of calculated and observed amplitudes was carried out for all reflections theoretically observable with Cu $K\alpha$ radiation. Reflections representing about 600 forms of the theoretical total of approximately 1100 were actually observed. (The extensive tables of comparison are not reproduced here, but are available in the Doctoral Thesis of Thomas B. Owen, Cornell University, Ithaca, N.Y., 1950.)

The value of the reliability index,

$$\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|,$$

is 0·17 if only planes giving observed reflections are considered, and is 0·21 when only those reflections having amplitudes calculated as unobservably weak are omitted. Inspection of the comparison tables indicates that a significantly lower value of the reliability index would be obtained by using a materially larger value of the thermal parameter, B (with an accompanying small change in K), than that quoted above. Later experience with the structure of B-trichloroborazole (Coursen & Hoard, to be published) suggests that a larger B and a better value of the reliability index probably would result were the methods of Wilson (1949) and of Howells, Phillips & Rogers (1950) employed to put observed and calculated amplitudes on the same approximately absolute basis. This point will be described in greater detail in the forthcoming publication.

Discussion of the structure

As has been stated, there are two strings of molecules parallel to c, one in the plane $y=\frac{1}{4}$ and the other in $y=\frac{3}{4}$, so oriented with respect to each other as to satisfy best packing relations.

To simplify the discussion of the molecular structure the atoms of a molecule have been labelled in Fig. 1. The twofold chlorine atoms form an isosceles trapezoid lying in the symmetry plane; the chlorine atoms occupying fourfold positions form a similar trapezoid essentially of the same dimensions which lies almost in the plane $x=\frac{1}{4}$. The two trapezoids are so oriented as to give the idealized molecule the symmetry $\bar{4}m$. Chlorine atoms on each side of the carbon ring have moved, apparently to minimize the repulsions of adjacent chlorines attached to different carbon atoms. The Cl–C–Cl bond angle, however, remains at about 109° even though an increase would appear to be both feasible and desirable from the steric point of view.

Fig. 4 shows distances and angles between atoms lying in the symmetry plane. A similar sketch for atoms occupying fourfold positions is shown in Fig. 5. Table 2 lists pertinent intramolecular distances and angles. Values in parentheses are those obtained with no correction for rippling.

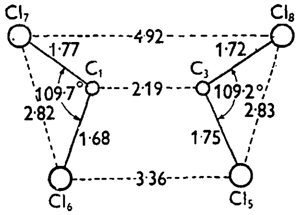

Fig. 4. Distances in plane $y=\frac{1}{4}$.

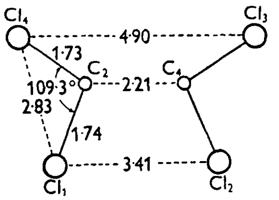

Fig. 5. Distances in plane $x=\frac{1}{4}$.

Table 2. *Interatomic distances in* C_4Cl_8

(All distances in Ångström units and angles in degrees)

C_1–Cl_7	1·77	(1·80)	C_1–C_2	1·60	(1·59)
C_1–Cl_6	1·68	(1·67)	C_2–C_3	1·58	(1·55)
C_3–Cl_8	1·72	(1·75)	Average	1·59	(1·57)
C_3–Cl_5	1·75	(1·82)			
C_2–Cl_1	1·74	(1·75)	Cl_4–Cl_6	3·09	(3·06)
C_2–Cl_4	1·73	(1·71)	Cl_4–Cl_5	3·12	(3·10)
Average	1·74*	($1·74_5$)	Cl_1–Cl_7	3·11	(3·11)
			Cl_1–Cl_8	3·08	(3·07)
Cl_1–Cl_4	2·83	(2·81)	Average	3·10	(3·08)
Cl_5–Cl_8	2·83	(2·84)			
Cl_6–Cl_7	2·82	(2·82)	Cl_4–Cl_7	3·94	(3·96)
Average	2·83	(2·82)	Cl_4–Cl_8	3·99	(4·00)
			Average	3·96	(3·98)
Cl_7–Cl_8	4·92	(4·93)			
Cl_3–Cl_4	4·90	(4·92)	∠ Cl_1–C_2–C_4	109·3	(108·3)
Average	4·91	(4·92)	∠ Cl_6–C_1–Cl_7	109·7	(108·3)
			∠ Cl_5–C_3–Cl_8	109·2	(106)
Cl_5–Cl_6	3·36	(3·36)	Average	109·4	(107·5)
Cl_1–Cl_2	3·41	(3·38)			
Average	3·38	(3·37)	∠ C_1–C_2–C_3	87·1	(85)
			∠ C_2–C_1–C_4	87·4	(88)
C_1–C_3	2·19	(2·12)	∠ C_2–C_3–C_4	88·7	
C_2–C_4	2·21	(2·21)	Average	87·7	(86·5)
Average	2·20	(2·16)			

* Averaged for seven bonds with C_1–Cl_6 omitted.

The puckering of the carbon ring is considerable, the dihedral angle calculated from average carbon–carbon distances being about 22°. This agrees with the preliminary results of Lemaire & Livingston in their study of C_4F_8 in which they find the corresponding angle to be somewhere between 17 and 23°.

Individual C–Cl distances are erratic because of poorly defined carbon maxima in the Fourier sections. They average out to 1·74 A., which is very close to the distance of 1·76 A. observed by Pauling & Brockway (1935) in electron-diffraction studies of CCl_4. In liquid carbon tetrachloride Bray & Gingrich (1943) have observed the corresponding value as 1·74 A. For chlorine atoms bonded to the same carbon atom an average separation of 2·83 A. is found in C_4Cl_8. A value of 2·86 A. is reported by Pauling & Brockway as well as by Cosslett & de Laszlo (1934) in independent investigations of gaseous CCl_4. Eisenstein (1943) found the separation to be 2·95 A. at 27° C. from X-ray studies on the liquid.

Carbon–carbon bond lengths do not agree too well, but the average value is indicative of a departure from the 'normal' value of 1·54 A. Table 3 summarizes C–C spacings in some compounds containing cyclobutane rings.

Preliminary X-ray analysis of dinaphthylene cyclobutane by Dunitz & Weissman (1949) indicates that C–C distances in the central ring may also be longer than 1·54 A.

Using the chlorine positions found in our investigation to construct the idealized chlorine shell for a molecule with symmetry $\bar{4}m$ we calculate C–C distances for various assumed values of the C–Cl bond as follows:

		Resulting C–C	
	Assumed C–Cl	Bonded	Non-bonded
I	1·76 A.	1·533 A.	2·15 A.
II	1·75	1·559	2·18
III	1·74	1·584	2·22

A significantly smaller shell of chlorine atoms than that found experimentally certainly would not permit the co-existence of normal C–C and C–Cl bond lengths since then a C–Cl separation of 1·76 A. would lead to a C–C bond less than 1·54 A. Although the chlorine shell, as we report it, could accommodate normal C–C and C–Cl bonds as in (I), our data are consistent with (III) and lead us to believe that the C–C bond distance is significantly larger than the normal value.

The optical behavior of the compound is of interest because the crystals show extinction parallel to the needle axis which the study has shown not to be the unique axis. We thus conclude that one of the two indicatrix axes in the *ac* plane lies parallel to *c*. This might be expected since the strings of molecules also lie parallel to *c*, as does the fourfold inversion axis of the

Table 3. C–C *spacings in compounds containing cyclobutane rings*

Investigator	Compound	C–C (A.)
Dunitz (1949)	Tetraphenylcyclobutane	1·585 ± 0·02 1·555 ± 0·02 } Av. 1·57
Bauer & Beach (1942)	Methylene cyclobutane	1·56 ± 0·03
Shand, Schomaker & Fischer (1934)	Methylene cyclobutane	1·55 ± 0·02
Lipscomb & Schomaker (1946)	Dimethyl ketene dimer	1·56 ± 0·02
Lemaire & Livingston (1950)	Perfluorocyclobutane	1·60
This investigation	Octachlorocyclobutane	1·60 1·58 } Av. 1·59

idealized molecule. The optical behavior would seem to support the conclusion that the molecular symmetry approximates closely to $\bar{4}m$.

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The Crystal Structure of *p*-Di-tertiary-butylbenzene[*]

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(*Received* 27 *July* 1950)

The structure of *p*-di-tertiary-butylbenzene was investigated by X-ray diffraction methods, using Weissenberg techniques. The principal refractive indices are $\alpha = 1{\cdot}570 \pm 0{\cdot}002$, $\beta = 1{\cdot}585 \pm 0{\cdot}002$ and $\gamma = 1{\cdot}588 \pm 0{\cdot}002$. The density is $(0{\cdot}985 \pm 0{\cdot}010)$ g.cm.$^{-3}$ and the calculated number of molecules per unit cell is $1{\cdot}98 \pm 0{\cdot}05$. Layer-line photographs were taken about [010], [001] and [$1\bar{1}0$]. The cell dimensions are $a = 9{\cdot}89 \pm 0{\cdot}06$, $b = 10{\cdot}13 \pm 0{\cdot}05$, $c = 6{\cdot}35 \pm 0{\cdot}03$ A., and $\alpha = \gamma = 90°$, $\beta = (94{\cdot}8 \pm 0{\cdot}2)°$. The cell is monoclinic and the most probable space group is $P2_1/n$. Patterson and Harker sections were plotted, but could not be used for direct structure determination. Harker–Kasper inequalities were applied to find the signs of 31 ($hk0$) planes. Trial-and-error methods were used to obtain the structure. On the two electron-density projections only two atoms are sufficiently resolved to locate their positions in space. A proposed orientation of the molecules in the cell was used as a solution, and the structure factors were calculated from it.

Introduction

The principal interest in the structure of *p*-di-tertiary-butylbenzene lies in the length of the bonds joining the benzene ring and the tertiary-butyl groups. The high chemical reactivities obtained from experiments on toluene and tertiary-butylbenzene indicate that hyperconjugation may exist between the benzene ring and the substituent groups (Berliner & Bondhus, 1948). If hyperconjugation between these groups and the ring does in fact exist, then the accepted single-bond lengths would be shortened to display a partial double-bond character.

In simpler cases of conjugation, the adjacent hydrogen electrons are delocalized and partake in the C–C bonding. The resultant shortening from single to partial double-bond length has been confirmed by electron diffraction work on butadiene-1, 3 and cyclopentadiene, where the bond linking two CH units is 1·46 A. (Schomaker & Pauling, 1939). With X-ray diffraction, Robertson (1935), working on stilbene, found a distance of 1·44 A. between a benzene ring and a CH; and Jeffrey (1945) a value of 1·44 or 1·45 A. for the bond linking two isoprene units in geranylamine hydrochloride. The structure of *p*-di-tertiary-butylbenzene, although incomplete, is presented here because it does not indicate that a change of the order predicted above exists.

Morphology and optical properties

p-Di-tertiary-butylbenzene was obtained 98·5% pure from Standard Oil Corporation of Indiana. It was

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