

The Crystal Structure of Benzene Iododichloride

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The crystal of benzene iododichloride, $C_6H_5ICl_2$, is monoclinic. The unit cell, containing 8 molecules, has the dimensions $a = 15.6$, $b = 5.45$, $c = 19.6$ Å, $\beta = 90^\circ 30'$ and the space group is $B2_1/a$. An alternative space group is $P2_1/a$, with unit cell dimensions $a = 15.6$, $b = 5.45$, $c = 12.3$ Å, $\beta = 128^\circ 30'$. The method of double Fourier synthesis was applied, using first $Cu K\alpha$ and later $Mo K\alpha$ radiation, and the projections of the electron density on the ac and bc planes were made. The ICl_2 group is linear and symmetrical, and its direction is approximately at right angles to the plane of the benzene ring. The line joining the I, C_1 and C_4 atoms is approximately parallel to the ac plane. The I-Cl distance is 2.45 Å, the C-I distance is 2.00 Å. The angle Cl_2-I-C_1 is 86° . The closest approach between I and Cl in adjacent molecules is 3.40 Å, between I and I 4.70 Å, between Cl and Cl 4.44 Å, between I and CH 4.08 Å, between Cl and CH 3.77 Å and between CH and CH 3.55 Å. The main binding forces in the crystal are evidently between neighbouring iododichloride groups.

Physical and X-ray data

Crystals of benzene iododichloride were grown by slowly cooling a solution in carbon tetrachloride. They take the form of yellow needles and belong to the monoclinic system. The elongation of the needles is along the symmetry axis, here taken as the b axis. The most commonly developed faces are $\{001\}$ (cleavage plane), $\{100\}$, $\{101\}$, $\{011\}$ and $\{01\bar{1}\}$.

The crystals decompose fairly rapidly when exposed to air and ultra-violet light, and it was necessary to grow fresh ones for each set of photographs taken.

Work on the crystal was started some years ago by one of us (E.M.A.) using filtered $Cu K\alpha$ radiation, and the following data were obtained from oscillation and Weissenberg photographs:

$$a = 15.6, b = 5.45, c = 19.6 \text{ \AA}, \beta = 90^\circ 30'.$$

The unit cell contains 8 molecules of $C_6H_5ICl_2$ and the calculated density is 2.19 g.cm.^{-3} , in agreement with an observed density of 2.2 g.cm.^{-3} .

Spectra of general type hkl occur only with $h+l = 2n$. Spectra of type $h0l$ have $h = 2n$ and $l = 2n$, and spectra of type $0k0$ have $k = 2n$. The cell is therefore centred on the B face, and the space group is $B2_1/a$ (or $B2_1/c$).

An alternative unit cell is primitive with $a = 15.6$, $b = 5.45$, $c = 12.3$ Å, $\beta = 128^\circ 30'$ and the corresponding space group is $P2_1/a$, but the nearly orthogonal b -centred cell has certain advantages in practice and has therefore been used.

The optimum thickness for these crystals with $Cu K\alpha$ radiation, the only radiation at first available, is about 0.005 cm. and it was necessary to use crystals about 0.025 cm. in thickness. With these, Weissen-

berg photographs were obtained with exposures of the order of 20 hr., and the intensities were compared visually with a set of spots produced by graded exposures. The intensities were corrected for polarization and the usual geometrical factors, but not for absorption, for scaling factor or for temperature effect. From these preliminary measurements it was possible to determine the nature of the structure with some degree of accuracy.

At this point the first author (E.M.A.) left Cape Town and the work was completed by the second author, who took a new set of Weissenberg photographs with $Mo K\alpha$ radiation, for which the optimum crystal thickness is about 0.043 cm. The crystals used had thicknesses of about 0.04 cm. and exposures up to 40 hr. were made. Intensities were measured on the micro-photometer of the Royal Observatory of the Cape of Good Hope, using the method described by Klug (1950). In addition to the geometrical and polarisation corrections, a temperature correction, $\exp\{-B(\sin^2 \theta)/\lambda^2\}$, was applied with $B = 3.0 \text{ \AA}^2$. No allowance for absorption was made. The 84 $h0l$ spectra were scaled by Wilson's method of comparing the average observed and calculated intensities. Only the measurements obtained with molybdenum ra-

Table 1. Atomic coordinates

(Values in fractions of the unit cell)

Atom	x	y	z
I	0.175	0.335	0.077
Cl_1	0.134	0.011	-0.004
Cl_2	0.215	0.658	0.160
C_1	0.058	0.335	0.120
C_2	0.038	0.171	0.173
C_3	-0.043	0.171	0.203
C_4	-0.107	0.335	0.182
C_5	-0.088	0.498	0.130
C_6	-0.007	0.498	0.100

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Table 2. *Observed and calculated values of the $h0l$ structure factors*

(Corrected for temperature effect)								
$h0l$	$ F_o $	F_c	$h0l$	$ F_o $	F_c	$h0l$	$ F_o $	F_c
200	24	-25	40 $\bar{2}$	58	-65	10,0,8	19	-21
400	19	-16	404	43	-41	10,0,10	20	-20
600	35	34	40 $\bar{6}$	9	-4			
800	23	-21	408	13	15	10,0, $\bar{2}$	21	-21
12,0,0	11	8	4,0, $\bar{10}$	22	20	10,0, $\bar{4}$	36	-34
14,0,0	13	9	4,0, $\bar{14}$	20	-22	10,0, $\bar{6}$	10	-8
			4,0, $\bar{16}$	22	-25	10,0, $\bar{8}$	16	16
002	33	32				10,0, $\bar{10}$	15	10
004	24	-24	604	10	-7	10,0, $\bar{16}$	17	-17
006	9	-13	606	31	-32			
008	22	-21	608	27	-25	12,0,4	19	-21
0,0,10	4	9	6,0,10	13	19	12,0,6	30	-29
0,0,12	31	37	6,0,12	21	24			
0,0,14	21	23				12,0, $\bar{02}$	18	14
			60 $\bar{2}$	52	55	12,0, $\bar{6}$	22	-20
202	55	-50	60 $\bar{6}$	34	-33	12,0, $\bar{8}$	21	-20
204	28	-26	60 $\bar{8}$	16	-14	12,0, $\bar{14}$	11	10
206	12	12	6,0, $\bar{12}$	17	18			
208	31	33	6,0, $\bar{14}$	26	26	14,0,2	10	-8
2,0,10	32	36				14,0,6	11	13
2,0,14	20	-24	802	20	-17	14,0,8	13	16
			806	24	22			
20 $\bar{2}$	14	16	808	31	33	14,0, $\bar{6}$	23	21
20 $\bar{4}$	35	36	8,0,10	14	16	14,0, $\bar{8}$	13	12
20 $\bar{6}$	17	16						
2,0, $\bar{10}$	21	-22	80 $\bar{2}$	9	6	16,0,2	14	15
2,0, $\bar{12}$	33	-35	80 $\bar{4}$	39	37	16,0,4	15	15
			80 $\bar{6}$	30	31			
402	22	20	8,0, $\bar{12}$	14	-11	16,0, $\bar{4}$	15	-11
404	13	16	8,0, $\bar{18}$	15	17	16,0, $\bar{10}$	11	11
406	16	14						
408	15	-18	10,0,2	15	12	18,0,4	12	-12
4,0,10	35	-40	10,0,4	25	21	18,0, $\bar{8}$	13	-12
4,0,12	20	-22	10,0,6	11	8			

Table 3. *Observed and calculated values of the $0kl$ structure factors*

(No correction for temperature)								
$0kl$	$ F_o $	F_c	$0kl$	$ F_o $	F_c	$0kl$	$ F_o $	F_c
002	41	32	018	30	32	040	8	-15
004	30	-25	0,1,10	29	26	044	9	15
006	12	-15	0,1,12	5	14	048	11	24
008	28	-23	0,1,16	17	-30			
			0,1,18	13	-18	052	17	20
0,0,10	6	11				054	16	26
0,0,12	41	50	020	25	-14	058	9	-22
0,0,14	28	34	024	20	17	0,5,10	8	-27
			026	25	20			
012	42	-35	0,2,10	9	10	060	23	47
014	39	-36				062	7	16
016	15	-9	032	4	2			

diation, and the projections obtained from them, are published in this paper.

Determination of the structure

With 8 molecules in the unit cell nothing is fixed by symmetry. In the preliminary work of determining the structure it was assumed that any high-order spectrum with large F had been formed almost entirely by contributions from the iodine atoms, and in this way the signs of the structure factors $F(h0l)$ and $F(0kl)$ were provisionally determined. A projection on

the ac plane was made; this gave the approximate positions of both I and Cl and showed the ICl_2 group to be symmetrical and linear. The I and Cl atoms determine the signs of the structure factors $F(h0l)$ and $F(0kl)$ uniquely, and from the first approximate projection a set of signs was calculated for the second projection, which gave good resolution for I and Cl but no accurate positions for the C atoms of the benzene ring. A diffraction ring surrounded the I atom. It disappeared when a temperature factor with $B = 4 \text{ \AA}^2$ was applied, but this did not improve the resolution.

The projection on the bc plane gave very poor resolution on account of the overlapping of atoms, and only approximate coordinates could be assigned to the Cl atoms and the benzene ring.

With the atomic coordinates determined in the preliminary work as a basis, three refinements of the $h0l$ projection were carried out, using the intensities obtained with Mo $K\alpha$ radiation. The benzene ring now appeared plainly, and fairly accurate x and z coordinates could be assigned to the carbon atoms. These refinements reduced the value of

$$R = \frac{\sum\{|F_o| - |F_c|\}}{\sum|F_o|}$$

for the $h0l$ intensities from 0.20 to 0.11.

A difference projection,

$$\rho_o - \rho_c = \frac{1}{A} \sum_h \sum_l \{F_o(h0l) - F_c(h0l)\} \times \exp\{-2\pi i(hx/a + lz/c)\},$$

showed no peaks comparable with that of a carbon atom, but no information about the positions of the hydrogen atoms could be obtained.

The best projection on the bc plane was obtained when no temperature factor was applied to the 30 scaled $0kl$ spectra ($R = 0.30$). A temperature factor changed R to 0.20, causing general flattening of the peaks, and reduced the resolution. An allowance was made for the overlap of the iodine atoms (Booth, 1948, p. 43) which gave a correction of 0.045 Å to the y coordinate. An ab projection would have given no better resolution than the bc projection, and was not made.

Discussion

The ICl_2 group is linear and symmetrical, a result which is in agreement with the configuration of trihalogen groups in compounds investigated by Mooney, namely NH_4I_3 (1935), NH_4BrICl (1938), $\text{N}(\text{CH}_3)_4\text{ICl}_2$ (1939). Helmholtz & Rogers (1940) have found that the anion of potassium fluoriodate ($\text{K}[\text{IO}_2\text{F}_2]$), containing a six-valent iodine atom, has a configuration that may be regarded as a trigonal bipyramid, with the F atoms at the two apexes and one equatorial position unoccupied (see Fig. 3(a)).

It seems that in the case of divalent iodine in ionic compounds investigated by Mooney and of trivalent iodine in benzene iododichloride two valencies of iodine are oppositely directed, which agrees with the orientation of the two valencies directed towards the F atoms in KIO_2F_2 . The third valency in trivalent iodine (Fig. 3(b)) is directed approximately at right angles to the other two (see below).

The ICl_2 group and the plane of the benzene ring are approximately at right angles to one another. The direction of downward tilt of the benzene ring is indicated by means of an arrow in Fig. 2. The ICl_2 group makes an angle of $45^\circ (\pm 2^\circ)$ with the ac plane and the benzene ring an angle of $50^\circ (\pm 2^\circ)$.

The projection of the $\text{I}-\text{C}_1$ distance on the ac plane is $2.00 (\pm 0.05)$ Å, which may be compared with the sum of the covalent radii of 2.12 Å and with the $\text{I}-\text{C}_1$ distance found by Archer (1948) in para-chlor-iodoxy benzene, 1.93 Å. Also, the projection of the C_1-C_4 distance on the ac plane is $2.80 (\pm 0.05)$ Å, which agrees well with the C_1-C_4 distance in the normal benzene ring. Hence, the atoms I, C_1 and C_4 have been taken to lie in a straight line parallel to the ac plane. Owing to the bad resolution of the benzene ring in the

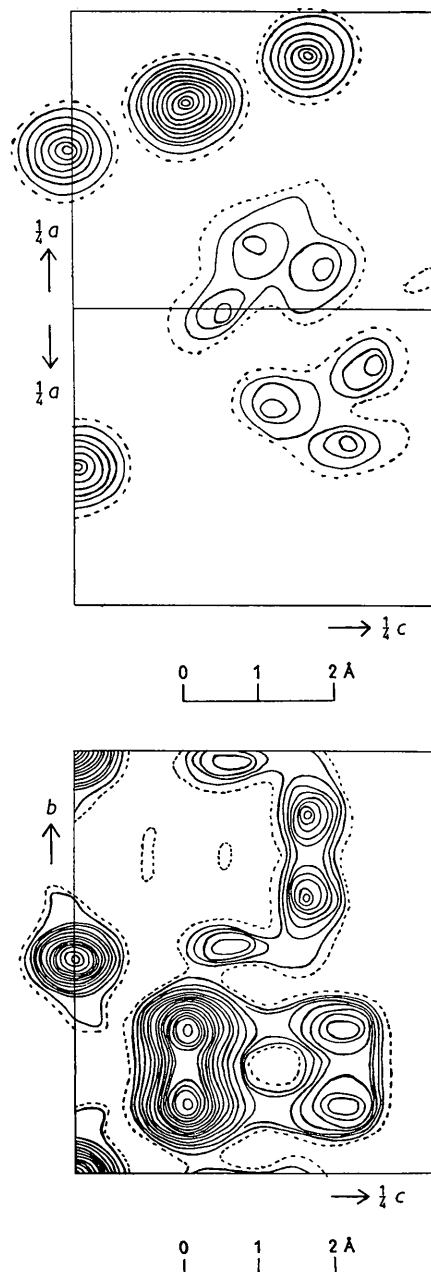


Fig. 1. Electron-density projected on the (010) (above) and (100) (below) planes. Contour intervals are approximately $1 \text{ e.}\text{\AA}^{-2}$ for carbon, $2 \text{ e.}\text{\AA}^{-2}$ for chlorine, $4 \text{ e.}\text{\AA}^{-2}$ for iodine atoms, the $2 \text{ e.}\text{\AA}^{-2}$ contour being broken.

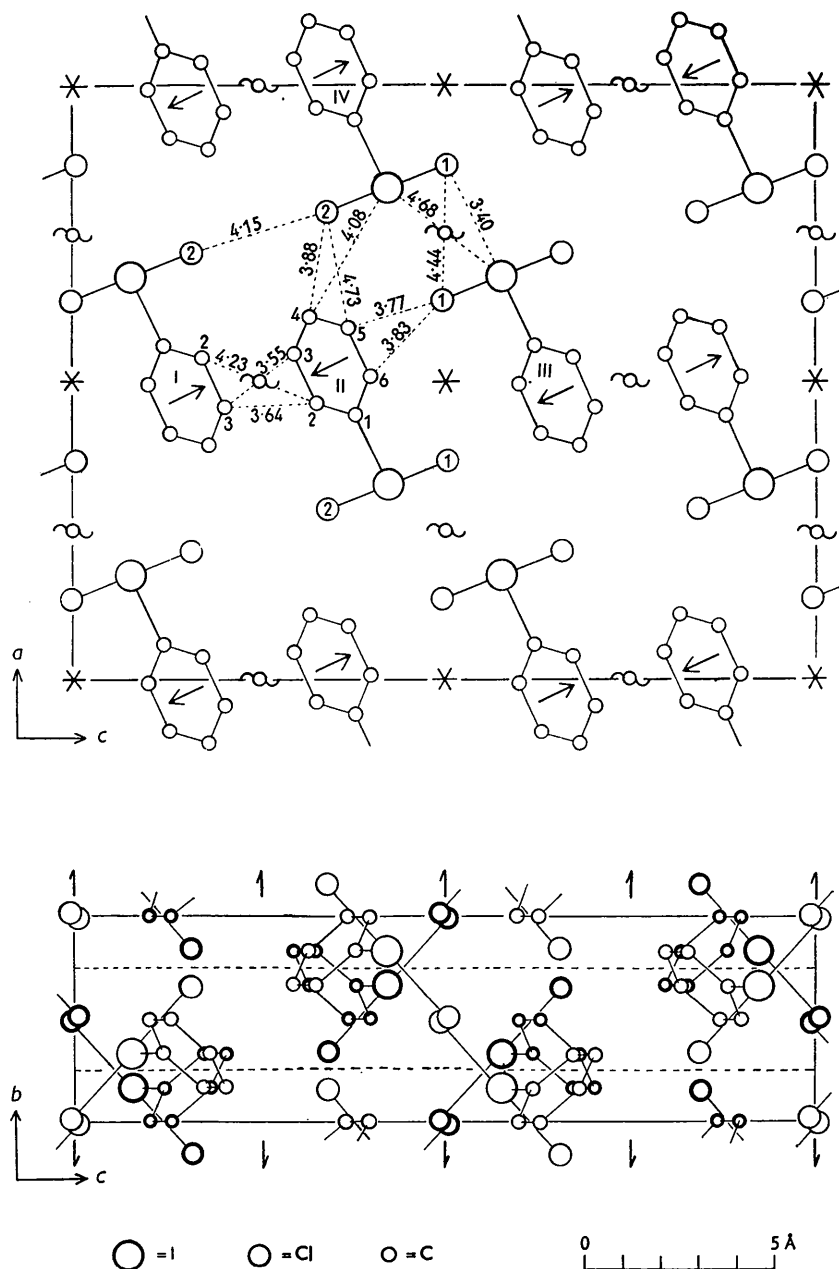


Fig. 2. Structure of benzene iododichloride projected on the (010) (above) and (100) (below) planes. Symmetry operations and intermolecular distances in Å are shown. The direction of downward tilt of the benzene ring to the (010) plane is indicated by arrows. The molecules denoted by the heavier circles are $\frac{1}{2}a$ above or below the others.

b c projection, the *y* coordinates of the C atoms were mainly determined by assuming the benzene ring to be a regular hexagon of side 1.40 Å, the plane of which makes an angle of 50° with the *a c* plane.

The I-Cl distance is 2.45(±0.015) Å, which is rather longer than those obtained by Mooney for NH₄BrICl (1938) and N(CH₃)₄ICl₂ (1939), namely 2.38 and 2.34 Å respectively.

The closest approach between the different molecules occurs between the I and Cl₁ atoms of molecules III and IV, derived from one another by means of the

screw axis. This distance, 3.40 Å, is very much smaller than the sum of the ionic radii of iodine and chlorine, 4.0 Å. A similar close approach, although between different atoms, was found by Archer (1948) between the I and O₁ atoms in the crystal of para-chlor-iodoxy benzene, which was 2.72 Å instead of at least the sum of the ionic radii, 3.3 Å. This close approach of the I and Cl₁ atoms probably indicates the main binding force in the crystal.

The distances I-I and Cl₁-Cl₁ between molecules III and IV are 4.68 and 4.44 Å respectively, which

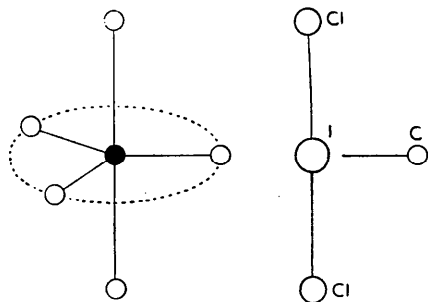


Fig. 3. (a) Trigonal bipyramid. (b) CCl_2 structure.

are considerably greater than their distances of closest approach, 4.30 and 3.60 Å. The I-C distance of 4.08 Å between molecules II and IV compares well with the distance of closest approach, 4.05 Å.

The $\text{C}_5\text{-Cl}_1$ distance of 3.77 Å between molecules II and III and the $\text{C}_3\text{-C}_3$ distance of 3.55 Å between molecules I and II agree well with the distances of closest approach, 3.65 and 3.7 Å respectively. In fact, a CH-CH distance between different molecules as low as 3.4 Å has been recorded by Iball (1934) in chrysene. From the *ac* projection the angle $\text{Cl}_2\text{-I-C}_1$ appears

to be $86^\circ(\pm 1^\circ)$ and not 90° . The latter angle would have given a $\text{C}_5\text{-Cl}_1$ distance of 3.51 Å, which is rather short.

The packing of the molecules accounts for the existence of the cleavage plane parallel to (001).

In conclusion the authors wish to thank Prof. R. W. James for his constant interest and help throughout the course of this work. We also wish to thank Dr W. S. Rapson and Dr M. Lamchen for preparing the material, and Dr R. H. Stoy, H. M. Astronomer at the Cape of Good Hope, for the use of the micro-photometer.

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Short Communications

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Acta Cryst. (1953). **6**, 92

Space-group of *Andrographis*. By B. S. BASAK and D. R. DASGUPTA, *Indian Association for the Cultivation of Science, Calcutta 32, India*

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Andrographis, a crystalline bitter principle extracted from *Andrographis paniculata* (kalmegh), has the molecular formula $\text{C}_{20}\text{H}_{30}\text{O}_5$. The crystal is found to be monoclinic on morphological study. Goniometric study, together with rotation photographs, gave

$$a = 6.530, b = 8.036, c = 19.530 \text{ \AA}; \beta = 97^\circ 10'.$$

The density of the crystal was measured to be $1.21 \pm 0.01 \text{ g.cm.}^{-3}$ by the flotation method, whence *Z*, the number of molecules per unit cell, is 2.

Weissenberg photographs about the three crystallographic axes showed that the absence of the odd orders of (0*k*0) were the only extinctions observed. The space group was therefore either $C_2^2\text{-P}2_1$ or $C_{2h}^2\text{-P}2_1/m$. Since there are only two molecules in the unit cell, the latter space group requires that there should be either a molecular centre of symmetry or a molecular plane of symmetry.

The complete structural formula of this substance is not yet known but certain features have been discovered

by Sarkar & Moktadar (1935). They found the presence of only one double bond, together with one methylenedioxy group, so the molecule cannot have a centre of symmetry. If it has to possess a plane of symmetry, all the atoms of the molecules have to lie on that plane. This is quite improbable for such a complex molecule. Thus the possibility of the space group $C_{2h}^2\text{-P}2_1/m$ is excluded and the crystal is found to belong to the space group $C_2^2\text{-P}2_1$. A more detailed paper on the subject will be published shortly.

Thanks are due to Prof. K. Banerjee for his interest in the work and to Dr H. G. Biswas for kindly presenting us with the substance.

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