

The Crystal Structure of Para-chlor-iodoxy Benzene

BY ELIZABETH M. ARCHER*

The University, Cape Town, South Africa

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Para-chlor-iodoxy benzene ($\text{ClC}_6\text{H}_4\text{IO}_2$) is monoclinic. The cell, containing four molecules, has the dimensions $a = 14.4$ A., $b = 6.50$ A., $c = 8.11$ A. and $\beta = 98\frac{1}{2}^\circ$. The space group is $P2_1/c$. The method of triple Fourier series has been applied to determine the electron density in a series of planes parallel to the ab plane. The plane containing the iodoxy group is very nearly perpendicular to the plane of the benzene ring. The I-O distances are nearly equal, being 1.60 and 1.65 A., with the angle $\text{O-I-O} = 103^\circ$. The I-C distance is 1.93 A., the C-Cl distance is 1.80 A., and the benzene ring is a regular hexagon of side 1.41 A. The closest approach between I and O in adjacent molecules is 2.72 A., that between I and I is 3.60 A., that between Cl and Cl is 3.75 A., and that between CH and CH is 3.9 A. The main binding forces in the crystal are evidently between neighbouring iodoxy groups.

Preparation

The para-chlor-iodoxy benzene used in the experiments was prepared by Dr W. S. Rapson of the University Chemistry Department by the following method.

Para-chlor-iodoxy benzene gradually separated when a solution of para-chlor-iodo benzene in ether was shaken with an excess of Caro's acid for several days (cf. Bamberger & Hill, 1900). It was filtered off from the reaction mixture, and well washed with water. Pure crystals, having the same properties as the material described by Willgerodt (1893), were subsequently grown from this product by crystallization from distilled water.

Fairly good crystals were grown from water and also from glacial acetic acid. They have the habit of colourless, thin flat plates with the a faces predominant and a cleavage plane (001). Those grown from water are in the habit of rectangular plates with an elongation in the c direction, and those grown from acetic acid are diamond shaped with the c axis in the direction of the long diagonal.

All the photographs were taken with crystals grown from acetic acid, as they were slightly thicker than those grown from water.

The unit cell and space group

The unit cell, as determined from rotation and Weissenberg photographs with Cu $K\alpha$ radiation, has the dimensions $a = 14.4$ A., $b = 6.50$ A., $c = 8.11$ A. and $\beta = 98\frac{1}{2}^\circ$. The density of the crystal is 2.4 g.cm.⁻³, so this cell contains four molecules of $\text{ClC}_6\text{H}_4\text{IO}_2$. The space group is $P2_1/c$.

X-ray measurements

All the observations were photographic, and were made with a cylindrical oscillation camera with Cu $K\alpha$

radiation filtered through nickel foil. Complete sets of rotation photographs were taken about the a , b and c axes in order to get all possible hkl spectra. The intensities of the spectra were measured by comparing them visually with a calibrated scale of spots of different exposures. No correction was made for the variation of absorption in different reflexions as the crystals were very small, 0.1 to 0.05 mm. thick, and were cut to approximately uniform cross-section about the axis of rotation. These intensities are, of course, on an arbitrary scale, but they can be expressed on an approximately absolute scale by the use of a suitable multiplication factor.

Patterson-Harker projections

The distances of atoms from a glide plane parallel to the b axis and with translation $\frac{1}{2}c$ may be determined by Harker's method, by evaluating the Patterson series

$$P(u, v, w) = \frac{1}{V} \sum_h \sum_k \sum_l^+ |F(hkl)|^2 \cos 2\pi \left(\frac{hu}{a} + \frac{kv}{b} + \frac{lw}{c} \right)$$

for the line $u = 0$, $w = \frac{1}{2}c$. This gives

$$P(0, v, \frac{1}{2}c) = \sum_k^+ B(k) \cos 2\pi kv/b,$$

where

$$B(k) = \sum_h \sum_k^+ (-1)^l |F(hkl)|^2.$$

The distance of the maxima in P along this line from the origin gives twice the distance of the corresponding atom from the glide plane. This distribution is shown in Fig. 1, where the maxima are determined almost entirely by the iodine atom.

* Porter Scholar of the University of Cape Town.

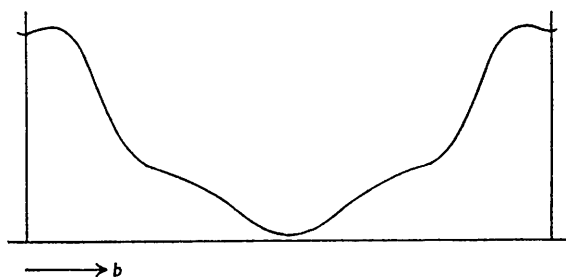


Fig. 1. The Patterson-Harker distribution corresponding to vectors parallel to b across the glide plane.

To obtain the distances of the atoms from a two-fold screw axis parallel to b , $P(u, v, w)$ is evaluated for the plane $v = \frac{1}{2}b$. This gives

$$P(u, \frac{1}{2}b, w) = \sum_h \sum_l C(hl) \cos 2\pi(hu/a + lw/c),$$

where
$$C(hl) = \sum_k (-1)^k |F(hkl)|^2.$$

This distribution is shown in Fig. 2, together with a key diagram, Fig. 3.

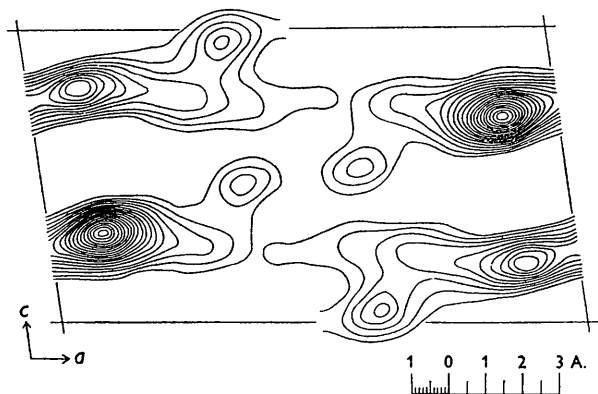


Fig. 2. The Patterson-Harker distribution about the two-fold screw axis, giving the vector distances, parallel to the ac plane, of atoms with a vector separation parallel to b of $\frac{1}{2}b$.

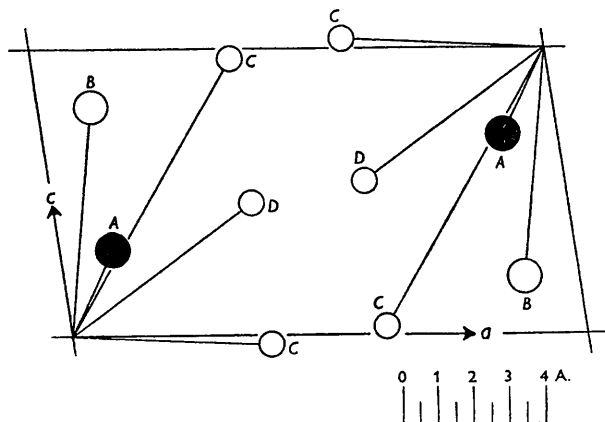


Fig. 3. Key diagram to Fig. 2.

The largest peak, labelled A in Fig. 3, is the only 'space group' peak, its vector distance from the origin being *twice* the vector distance of the iodine atom from the screw axis. The peak B appears because the iodine atoms of molecules (2) and (3) in Figs. 5, 6 and 7, although not derived from one another by the operation of the two-fold screw axis, have a vector separation parallel to b near enough to $\frac{1}{2}b$ for a peak to appear in the Patterson-Harker distribution $P(u, \frac{1}{2}b, w)$. The peak C appears because the iodine and chlorine atoms in the same molecule have a vector separation parallel to b of very nearly $\frac{1}{2}b$, and peak D appears because the iodine atom of molecule (1) and the chlorine atom of molecule (2) have a vector separation parallel to b near enough to $\frac{1}{2}b$ for a peak to appear in the Patterson-Harker distribution $P(u, \frac{1}{2}b, w)$.

The Patterson-Harker projections have thus fixed not only the positions of the iodine atoms, but have given approximate positions to the chlorine atoms also. These co-ordinates were then used to calculate structure factors for the two-dimensional Fourier projections on the planes (100) and (010).

Calculation of structure factors

The structure factors were calculated for the I and Cl atoms only, using the standard expressions for the space group $P2_1/c$. The atomic scattering factors used were those given in *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Vol. II, without the application of any temperature factor. Consequently all the high-order calculated F values are much too large, but this was immaterial, as the only reason for calculating F values was to give appropriate *signs* to the observed F values, since the crystal has a centre of symmetry at the origin.

After completing the analysis of the structure, the structure factors for some of the spectra were calculated using all the atoms in the molecule (co-ordinates in Table 1) and applying a suitable temperature factor to the scattering factors mentioned above. The agreement between the observed and calculated F 's is shown in Table 3.

Two-dimensional Fourier syntheses

In order to check the co-ordinates of the iodine and chlorine atoms obtained from the Patterson-Harker distributions, and to get some idea of the positions of the oxygen atoms and the benzene ring, two-dimensional Fourier projections of the structure were made on the planes (100) and (010) using spectra of the type $0kl$ and $h0l$ respectively. These projections were made using the method of Lipson & Beevers (1936).

It was found that the y co-ordinate of the iodine atom was not quite that given by the Patterson-Harker distribution shown in Fig. 1, in which the distance of the maximum from the origin was taken to represent twice the distance, parallel to b , of the iodine

atom from the glide plane. As this distribution is symmetrical about the origin, the peaks are unresolved from each other, resulting in a displacement of the maxima in the distribution. The two-dimensional projections also gave more accurate co-ordinates for the chlorine atom and showed the region of the benzene ring, but it was impossible to locate the oxygen atoms in the region of the iodine atom.

It was decided, therefore, to determine the structure by means of three-dimensional Fourier sections parallel to the ab plane. For this, all the structure factors

Summations were made for a sufficient number of sections to give the co-ordinates of all the atoms in the molecule without any ambiguity. Fig. 4 shows, superimposed and projected along the c axis on to the ab plane, several sections which pass through two of the four molecules in the unit cell. It can be seen that the peaks due to the oxygen atoms are well resolved from the nearby iodine peak. The benzene ring is not quite so clear. Diagrams showing the structure projected on to the ab , bc and ac planes are given in Figs. 5, 6 and 7 respectively.

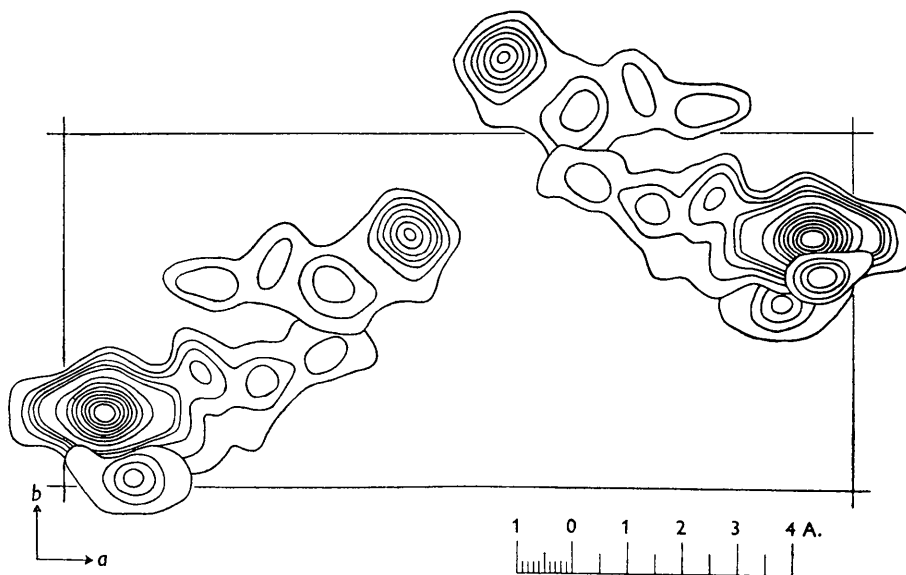


Fig. 4. A projection along the c axis on to the ab plane of several three-dimensional Fourier sections passing through two of the four molecules in the unit cell. Contours are drawn at arbitrary levels of 200, 400, 600, etc. For the iodine atom contours above 1000 are drawn at intervals of 1000.

$F(hkl)$ were required. The signs were obtained by calculating the structure factors for the iodine and chlorine atoms only. In this way not more than 10 or 15 spectra out of nearly 800 used would have the wrong sign, and these, having very small F values, would have a negligible effect on the positions of the centres of the peaks.

Three-dimensional Fourier sections

The electron density in a plane of crystal at $z=z_1$ is given by

$$\rho(xy z_1) = \frac{1}{V(abc)} \times \sum_{h=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} \pm |F(hkl)| \cos 2\pi \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz_1}{c} \right),$$

since the crystal has a centre of symmetry at the origin.

Using an argument similar to that used by Lipson & Beavers (1936) the above expression can be put into a form suitable for the use of Lipson and Beavers strips (see Goodwin & Hardy, 1938).

Estimation of parameters

The co-ordinates of the iodine and chlorine atoms were obtained with considerable accuracy from the three-dimensional Fourier sections and agreed very well with the co-ordinates obtained from the Fourier projections on the planes (010) and (100).

The values of $(\sin \theta)/\lambda$ for the highest order spectra observed in the directions of the a , b and c axes are, respectively, 0.52, 0.62 and 0.62. If the positions of the spectra are plotted on a reciprocal lattice net, the equivalent optical aperture obtained is not circular and results in an elongation of the image of the iodine atom in the direction of the a axis.

As there was no evidence of diffraction rings about the iodine atom, it can be assumed that there was no displacement of the centres of the peaks of the oxygen atoms. The peaks for the carbon atoms in the benzene ring are not very clear and their co-ordinates were calculated on the assumption that the benzene ring is a regular hexagon of side 1.41 Å.

The co-ordinates of the atoms expressed as fractions

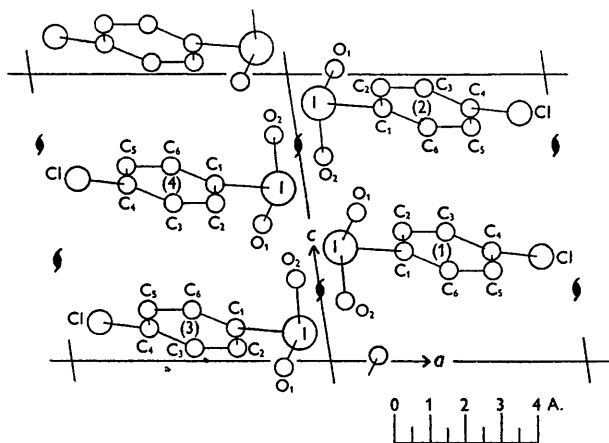


Fig. 5. A projection of the structure in the b direction on to the ac plane.

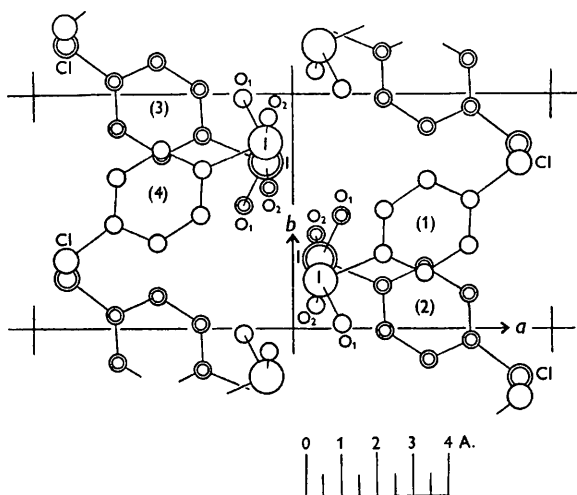


Fig. 6. A projection of the structure in the c direction on to the ab plane. The molecules with double circles are $\frac{1}{2}c$ above or below those with single circles.

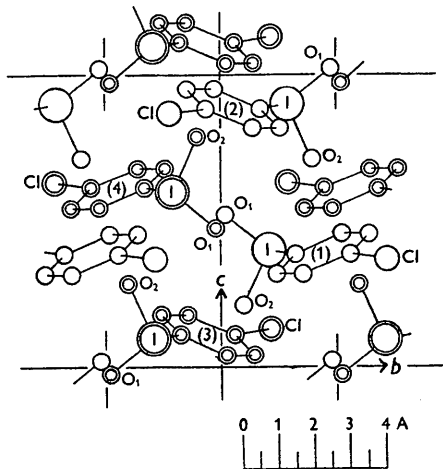


Fig. 7. A projection of the structure in the a direction on to the bc plane. The molecules with double circles are approximately $\frac{1}{2}a$ above or below those with single circles.

of the corresponding lattice translations are given in Table 1.

Table 1. The co-ordinates of the atoms expressed as fractions of the corresponding lattice translations

	x/a	y/b	z/c
I	0.052	0.208	0.400
Cl	0.439	0.710	0.368
O ₁	0.092	0.023	0.520
O ₂	0.042	0.098	0.213
C ₁	0.174	0.322	0.388
C ₂	0.178	0.522	0.455
C ₃	0.260	0.637	0.451
C ₄	0.337	0.552	0.383
C ₅	0.333	0.352	0.316
C ₆	0.251	0.237	0.320

Description of the molecule

The size and shape of the molecule is given in Fig. 8. It can be seen that the plane containing the iodoxy group is very nearly perpendicular to the plane of the benzene ring, which in turn approximately bisects the angle O-I-O.

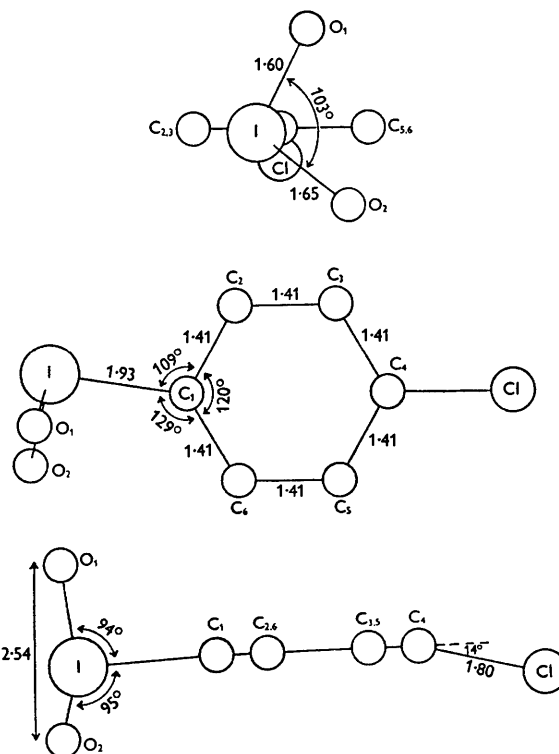


Fig. 8. Three aspects of a single molecule of para-chloroiodoxy benzene, with the interatomic distances marked in Ångström units.

The I-O distances 1.60 and 1.65 Å. (± 0.05 Å.) in para-chloroiodoxy benzene are rather shorter than those obtained in other compounds containing iodine and oxygen, which suggests the existence of double bonding between the iodine and oxygen atoms in the iodoxy group. Table 2 compares the dimensions of the iodoxy group in para-chloroiodoxy benzene with the

dimensions found in iodine-oxygen groups in potassium fluoriodate (KIO_2F_2) and iodic acid (HIO_3) by Rogers & Helmholtz (1940, 1941) and ammonium paraperiodate ($(NH_4)H_3IO_6$) by Helmholtz (1937).

Table 2. *Interatomic distances in compounds containing both iodine and oxygen*

	I-O in the same molecule	$\angle O-I-O$	Closest	Closest
			I to O between different molecules	O to O between different molecules
	A.		A.	A.
Para-chlor-iodoxy benzene	1.60 1.65	103°	2.72 2.87	2.62
Iodic acid	1.80 1.81 1.89	96° 98° 101°	2.45 2.70 2.95	2.76 2.78
Potassium fluoriodate	1.92 1.93	100°	2.82 2.88	—
Ammonium paraperiodate	1.93	Approx. 90°	—	2.60

Table 3. *Table showing the agreement between $F_{obs.}$ and $F_{calc.}$ for the spectra hkl , $Ok\bar{l}$ and $h0l$*

hkl	$F_{obs.}$	$F_{calc.}$	hkl	$F_{obs.}$	$F_{calc.}$	hkl	$F_{obs.}$	$F_{calc.}$
100	52	47.2	40 $\bar{2}$	21	-25.5	10 $\bar{8}$	4	4.5
200	41	39.4	50 $\bar{2}$	41	-41.3	20 $\bar{8}$	4	15.7
300	25	25.2	60 $\bar{2}$	20	-29.1	30 $\bar{8}$	6	9.9
400	6	11.6	70 $\bar{2}$	20	-36.8	40 $\bar{8}$	8	13.5
500	3	-1.9	80 $\bar{2}$	8	-17.2	50 $\bar{8}$	8	8.5
600	11	-19.0	90 $\bar{2}$	6	-13.0	60 $\bar{8}$	9	7.8
700	12	-18.6	10.0 $\bar{2}$	abs.	-1.7	70 $\bar{8}$	11	5.8
800	16	-36.1	11.0 $\bar{2}$	6	17.1	80 $\bar{8}$	3	-2.1
900	11	-20.3	12.0 $\bar{2}$	abs.	5.1	1.0 $\bar{10}$	3	9.1
10.0.0	15	-32.5	13.0 $\bar{2}$	5	13.0	2.0 $\bar{10}$	3	6.6
11.0.0	6	-13.6	14.0 $\bar{2}$	4	10.4	3.0 $\bar{10}$	3	5.0
12.0.0	4	-8.5	15.0 $\bar{2}$	5	12.9	4.0 $\bar{10}$	3	3.8
13.0.0	4	-10.7						
			104	9	-6.6	110	34	-18.7
020	28	-40.3	204	abs.	-4.7	210	61	-40.9
040	9	17.4	304	3	1.5	310	28	-26.5
060	abs.	0.4	404	6	10.6	410	43	-51.9
			504	7	11.2	510	17	-30.7
002	31	14.2	604	9	23.1	610	28	-41.2
004	43	-36.3	704	8	17.8	710	9	-22.9
006	13	-12.5	804	6	28.4	810	7	-15.5
008	4	5.6	904	6	12.0	910	3	-7.1
0.0.10	3	6.5	10.0.4	5	13.0	10.1.0	3	5.4
						11.1.0	4	5.6
102	74	49.6	10 $\bar{4}$	23	-17.6	12.1.0	6	16.2
202	18	17.3	20 $\bar{4}$	45	-38.9	13.1.0	4	7.8
302	24	32.3	30 $\bar{4}$	27	-24.8	14.1.0	5	15.3
402	14	20.7	40 $\bar{4}$	23	-23.6	15.1.0	4	10.2
502	18	31.8	50 $\bar{4}$	18	-19.0			
602	9	15.1	60 $\bar{4}$	13	-13.0	120	36	-19.2
702	9	18.9	70 $\bar{4}$	6	-6.7	220	50	-29.1
802	abs.	5.0	80 $\bar{4}$	5	9.8	320	15	-13.1
902	4	-4.4	90 $\bar{4}$	6	7.1	420	15	-15.6
10.0.2	4	-2.2	10.0. $\bar{4}$	7	18.9	520	abs.	-2.2
11.0.2	5	-15.4	11.0. $\bar{4}$	4	13.0	620	10	15.6
12.0.2	4	-6.1	12.0. $\bar{4}$	5	15.2	720	5	7.6
13.0.2	5	-13.2	13.0. $\bar{4}$	5	12.2	820	8	21.6
14.0.2	4	-13.1	14.0. $\bar{4}$	4	8.2	920	6	15.7
						10.2.0	8	23.7
10 $\bar{2}$	20	-15.6	106	15	-23.5	11.2.0	5	13.3
20 $\bar{2}$	7	-6.0	206	13	-17.2	12.2.0	4	9.4
30 $\bar{2}$	43	-36.6	306	10	-27.9	16.2.0	5	-7.1
						17.2.0	4	-6.9

hkl	$F_{obs.}$	$F_{calc.}$	hkl	$F_{obs.}$	$F_{calc.}$
406	4	-12.6	130	8	9.6
506	3	-13.6	230	15	14.6
806	4	4.8	330	15	6.2
906	6	11.9	430	18	21.6
10.0.6	4	6.1	530	11	13.3
11.0.6	3	11.1	630	11	18.3
			730	7	8.7
10 $\bar{6}$	11	-13.7	12.3.0	5	-8.9
20 $\bar{6}$	8	-5.4	13.3.0	6	-4.2
30 $\bar{6}$	6	9.5	14.3.0	7	-9.4
40 $\bar{6}$	6	5.5	15.3.0	6	-6.6
50 $\bar{6}$	10	15.7			
60 $\bar{6}$	11	11.2	140	13	9.3
70 $\bar{6}$	15	23.0	240	13	11.1
80 $\bar{6}$	12	14.4	340	6	2.4
90 $\bar{6}$	12	16.4	440	5	1.2
10.0. $\bar{6}$	8	11.9	540	abs.	-1.0
12.0. $\bar{6}$	4	10.9	640	6	-7.1
			740	4	-5.6
208	4	-2.9	840	4	-9.3
308	4	-7.6			
408	5	-12.5	150	abs.	-0.7
508	3	-6.6	250	5	-5.6
608	3	-10.9	350	5	-2.8
708	3	-5.8	450	7	-5.9
			550	5	-8.6
10 $\bar{8}$	4	4.5	650	4	-3.2
20 $\bar{8}$	4	15.7			
30 $\bar{8}$	6	9.9	160	3	-0.3
40 $\bar{8}$	8	13.5	560	4	-0.2
50 $\bar{8}$	8	8.5			
60 $\bar{8}$	9	7.8	011	abs.	-0.2
70 $\bar{8}$	11	5.8	012	71	31.0
80 $\bar{8}$	3	-2.1	013	12	-6.1
			014	18	10.7
1.0. $\bar{10}$	3	9.1	015	6	4.1
2.0. $\bar{10}$	3	6.6	016	6	-8.2
3.0. $\bar{10}$	3	5.0	017	6	0.3
4.0. $\bar{10}$	3	3.8	018	6	-10.7
110	34	-18.7	021	33	-19.4
210	61	-40.9	022	11	-2.2
310	28	-26.5	023	18	-18.4
410	43	-51.9	024	25	29.5
510	17	-30.7	025	abs.	5.5
610	28	-41.2	026	7	13.9
710	9	-22.9	027	4	8.7
810	7	-15.5			
910	3	-7.1	031	12	9.3
10.1.0	3	5.4	032	47	-21.7
11.1.0	4	5.6	033	6	3.0
12.1.0	6	16.2	034	15	-8.8
13.1.0	4	7.8	035	15	-13.1
14.1.0	5	15.3	038	4	7.2
15.1.0	4	10.2			
			041	7	14.8
120	36	-19.2	042	8	7.1
220	50	-29.1	043	15	20.7
320	15	-13.1	044	5	-9.6
420	15	-15.6			
520	abs.	-2.2	051	15	-13.0
620	10	15.6			
720	5	7.6	061	4	-11.6
820	8	21.6	063	11	-14.9
920	6	15.7			
10.2.0	8	23.7	071	10	7.0
11.2.0	5	13.3			
12.2.0	4	9.4			
16.2.0	5	-7.1			
17.2.0	4	-6.9			

The packing of the molecules in the crystal

There are four molecules in the unit cell, which are derived from a single molecule by operation of the glide and the two-fold screw axis. Figs. 5, 6 and 7 are labelled so that atoms derived from one another by the operation of a symmetry element are denoted by the same letter.

The iodoxy groups of the molecules approach one another very closely. The I to I distance between molecules (1) & (4) and (2) & (3) is 3.60 Å., whereas the usual I to I distance between different molecules is greater than 4.0 Å. An I to I distance of 3.79 Å. between different molecules has been observed in iodic acid, and this short distance was attributed to the effect of unshared electrons in the molecules.

The I to O₁ distance between molecules (1) & (4) and (2) & (3) is 2.72 Å. and the I to O₂ distance between molecules (1) & (2) and (3) & (4) is 2.87 Å., which distances are very much smaller than the sum of the iodine and oxygen ionic radii, namely 3.3 Å., but are comparable with the I to O distances observed between different molecules in iodic acid and potassium fluoriodate (see Table 2).

All the O to O distances are greater than 3.0 Å. except the distance from O₁ to O₁ of molecules (1) & (4) and (2) & (3) which is 2.62 Å. This is considerably shorter than the usual O to O distance between different molecules in organic compounds which is about 3.0 Å. and slightly shorter than the normal O to O distance between molecules in inorganic compounds which is 2.7 Å. It is, however, comparable to the O to O distance observed in ammonium paraperiodate, 2.60 Å., which is attributed to hydrogen bonding. This theory is quite inapplicable in the case of para-chloriodoxy benzene. The O to O distances of 2.76 and 2.78 Å. between different molecules in iodic acid have also been attributed to hydrogen bonding.

It can be seen that the I and O₁ atoms of molecules (1) and (2) form a very closely knit planar group, with the bonds from I to O₂ very nearly perpendicular to this plane. Since the plane (001) is a cleavage plane in the crystal, the strongest binding forces between different molecules are evidently in the plane formed by the I and O₁ atoms about a centre of symmetry.

Discussion of the structure

The very close approach of iodoxy groups to one another, and the large distances between neighbouring benzene rings and chlorine atoms indicates that the main binding forces in the crystal occur between adjacent iodoxy groups. A study of the crystal para-methyl-iodoxy benzene shows that it is identical with the crystal para-chlor-iodoxy benzene with regard to its unit cell, space group, and intensities of spectra. The replacement of the chlorine atom in the para-chlor-iodoxy benzene molecule with a methyl group thus has no effect on the packing of the molecules which must therefore be determined mainly by the iodoxy groups.

In iodic acid and ammonium paraperiodate, close approaches of neighbouring oxygen atoms were attributed to hydrogen bonding. This theory is obviously untenable in the case of para-chlor-iodoxy benzene, although the interatomic distances concerned are comparable with those observed in iodic acid and ammonium paraperiodate (see Table 2). The close approach of iodoxy groups to one another *may* be bound up with the 'lone pair' of electrons attached to each iodine atom forming an attractive force between these groups other than the ordinary van der Waals attraction between molecules. That there is some unusual attraction between neighbouring iodoxy groups cannot be disputed, but the nature of this force is a matter of conjecture.

In conclusion I wish to thank Prof. R. W. James for his constant interest and help throughout the course of this work and for the use of his unpublished *Crystalline State*, Vol. II. I also wish to thank Dr W. S. Rapsom for suggesting this problem, and for preparing the crystals.

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