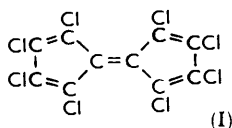


## 972. An X-Ray Determination of the Crystal and Molecular Structure of Perchlorofulvalene.

By P. J. WHEATLEY.

The crystal and molecular structure of perchlorofulvalene has been determined by two-dimensional X-ray diffraction methods. The two halves of the molecule are twisted through an angle of  $41^\circ$ . The chlorine atoms are all displaced from the plane of the five-membered ring of carbon atoms. The central C-C bond adopts a length of 1.49 Å.



THE preparation and properties of perchlorofulvalene (I) have recently been described.<sup>1</sup> The present paper gives an account of a two-dimensional X-ray determination of the crystal and molecular structure.

*Experimental.*— $C_{10}Cl_8$ .  $M = 403.8$ . Monoclinic.  $a = 14.96_2$ ,  $b = 7.90_0$ ,  $c = 11.80_3$  Å,  $\beta = 103^\circ 33'$ .  $U = 1356$  Å<sup>3</sup>.  $D_m = 1.98$  (by flotation in a mixture of ethyl iodide and 1,2-dibromoethane),  $Z = 4$ ,  $D_c = 1.977$ ,  $F(000) = 784$ . Space group  $C2/c$  ( $C_{2h}^2$ , No. 15).  $Cu-K\alpha$  radiation ( $\lambda = 1.542$  Å), single-crystal rotation and Weissenberg photographs.

The crystals are deep violet. Multiple-film Weissenberg photographs were taken round  $[b]$  and  $[c]$ . Relative intensities were estimated by visual comparison with standard charts prepared from the same crystals. Very small crystal fragments were used, and no correction was made for absorption ( $\mu = 146.8$  cm.<sup>-1</sup>). 102  $h0l$  and 74  $hk0$  reflexions were observed to be non-zero. In order to proceed with the analysis, it was assumed that the space group was  $C2/c$ , rather than  $Cc$ , and that the molecule could not possess a centre of symmetry because of the close approach of chlorine atoms in the two halves of the molecule, but could possess a two-fold axis. These assumptions were justified by the success of the analysis.

Sharpened Patterson syntheses were calculated for each projection, but could not be interpreted owing to the surfeit of heavy-atom vectors. Finally a suitable interpretation of the  $h0l$  zone was obtained from a consideration of the strength of the plane  $\bar{2}.0.4$ , monitored by the two planes 2.0.4 and 4.0.2. This projection was then refined by Fourier and difference techniques until  $R$  had fallen to 19%. It was then clear that no better agreement could be obtained without allowance for the anisotropic thermal motion of the chlorine atoms. Such an allowance could not be made without adequate computing facilities, and refinement was thus terminated. It was clear from the difference maps that the chlorine atoms were vibrating most freely in the plane of the ring and perpendicular to the C-Cl bonds.

In order to solve the  $hk0$  projection it was assumed that the centre of the molecule would lie close to  $y = 1/4$ . Again this assumption was justified, and refinement proceeded smoothly until  $R$  had dropped to 19%; then again anisotropic thermal motion prevented further improvement. The scattering factors used were those of Berghuis *et al.*<sup>2</sup> for the carbon atoms, and that of Tomiie and Stam<sup>3</sup> for the chlorine atoms. An isotropic temperature factor  $B = 2.67$  Å<sup>2</sup> was used for the  $h0l$  projection, and  $B = 4.05$  Å<sup>2</sup> for the  $hk0$  projection.

*Results.*—The co-ordinates of the atoms are given in Table 1, and the observed and calculated structure factors in Table 2. Figs. 1(a and b) show the final Fourier maps of the  $h0l$  and  $hk0$  projections respectively. Fig. 2 shows the bond lengths, the bond angles, and the numbering of the atoms. The agreement between the lengths of the C-Cl bonds is good, the average value being 1.692 Å. The central C-C bond is increased considerably from that of a standard double bond, and is close to the length found in biphenyl (1.49 Å).<sup>4</sup> The increase evidently reflects a decrease in conjugation resulting from the twisting of the two halves of the molecule. The lengths of the C-C bonds in the five-membered ring

<sup>1</sup> Mark, *Tetrahedron Letters*, 1961, 333.

<sup>2</sup> Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

<sup>3</sup> Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

<sup>4</sup> Almennigen and Bastiansen, *Kgl. Norske Videnskab. Selskabs Skrifter*, 1958, **4**, 1.

are in general agreement with those found in dimethylfulvene<sup>5</sup> if due allowance is made for the lower accuracy of the present analysis.

The five-membered ring of carbon atoms is found to be planar. The equation of the plane through C<sub>1</sub>, C<sub>3</sub>, and C<sub>4</sub> is

$$1.0528x - 2.8211y - 0.0337z + 5.9217 = 0.$$

This equation is obtained in terms of orthogonal axes in which [b'] and [c'] coincide with the original [b] and [c] respectively, and [a'] is perpendicular to [b'] and [c']. The orthogonal co-ordinates are also given in Table 1. The atoms C<sub>2</sub> and C<sub>5</sub> lie at distances 0.020 and 0.018 Å, respectively, from this plane. The angle between the planes of the rings is

TABLE 1.

Fractional co-ordinates (*x/a*, *y/b*, *z/c*) and orthogonal co-ordinates (*X*, *Y*, *Z* in Å).

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>X</i>	<i>Y</i>	<i>Z</i>
Cl <sub>1</sub> .....	0.166	0.406	0.415	2.415	3.207	4.316
Cl <sub>2</sub> .....	0.080	0.322	0.649	1.164	2.544	7.380
Cl <sub>3</sub> .....	-0.125	0.141	0.563	-1.818	1.114	7.088
Cl <sub>4</sub> .....	-0.183	0.119	0.272	-2.662	0.940	3.852
C <sub>1</sub> .....	-0.006	0.256	0.311	-0.087	2.022	3.692
C <sub>2</sub> .....	0.067	0.302	0.414	0.975	2.386	4.652
C <sub>3</sub> .....	0.028	0.276	0.509	0.407	2.180	5.910
C <sub>4</sub> .....	-0.061	0.215	0.474	-0.887	1.699	5.808
C <sub>5</sub> .....	-0.085	0.203	0.356	-1.236	1.604	4.500

TABLE 2.

Observed and calculated structure factors for one asymmetric unit.

<i>h0</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>h0l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>h0l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>h0l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>h0l</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>
2.0.0	7.2	11.4	12	2.8	-1.3	8	9.1	7.8	6	5.9	4.8	15	1.6	-1.0
4	18.5	-21.3	14	3.8	4.1	10	2.5	0.5	8	11.6	-10.4	17	1.1	-2.2
6	6.6	5.1				12	2.7	5.2	10	1.2	1.5			
8	13.2	-11.5	2.0.8	8.4	-8.0	14	5.4	5.3	12	9.7	6.8	2.4.0	14.4	12.6
10	1.6	1.7	4	5.2	-4.1	16	7.0	-6.6	14	1.7	-0.5	4	13.7	12.7
12	12.2	8.6	6	3.0	-2.7	18	2.7	-4.3	16	2.4	2.8	6	6.6	-6.9
14	2.1	-0.7	8	3.3	-5.6				18	1.4	-0.3	8	3.4	2.5
16	3.6	4.3	10	4.9	5.0	2.0.8	11.6	10.4				10	0.9	-0.3
18	1.7	-0.5	12	3.8	5.7	4	18.3	16.3	0.2.0	22.7	-24.5	12	1.4	-0.4
						6	2.9	-4.2	4	16.0	-15.3	14	3.4	2.7
0.0.2	7.6	6.5	2.0.10	10.7	-12.9	8	12.6	-10.5	6	1.5	0.3	16	1.4	-1.7
4	6.8	-4.5	4	5.8	9.0	10	4.3	-4.3	8	1.8	1.7	1.5.0	3.8	-4.4
6	9.7	-9.1	6	4.6	5.5	12	1.8	-2.5	10	0.8	1.3	3	1.6	-1.4
8	1.6	-3.3	10	1.5	1.0	14	3.6	4.8				5	1.1	1.2
10	5.0	-4.5				16	1.9	-0.4	1.1.0	1.4	-0.9	7	2.9	4.0
12	2.3	4.9	2.0.12	2.5	1.9	18	3.9	-3.6	3	5.7	-5.4	9	1.8	-2.0
14	3.5	5.9	6	2.8	4.9				5	0.9	0.4	13	2.2	1.5
						2.0.10	9.8	11.2	7	1.3	1.7	15	1.6	-2.0
2.0.2	11.5	12.2	2.0.2	5.8	4.9	4	4.7	1.1	9	5.3	5.6			
4	21.0	-23.6	4	8.7	10.4	6	9.5	9.4	11	0.8	-1.7	2.6.0	2.5	3.4
6	10.3	-11.5	6	4.0	6.7	8	1.8	3.9	13	6.6	-6.1	4	2.5	-3.5
8	18.4	18.7	8	4.4	-3.8	10	6.9	-7.6	15	3.0	2.6	6	9.6	-8.7
10	3.6	-1.3	10	15.3	-15.6	12	3.7	2.3	17	1.8	1.5	8	1.0	1.1
12	7.0	-6.8	12	4.7	-4.4	14	2.7	-3.9				10	1.6	1.3
16	7.4	-5.7	14	3.8	4.8	16	5.5	-3.6	2.2.0	20.5	-21.1	12	2.4	-1.4
			16	2.2	4.3				4	2.6	-1.3	14	1.7	1.7
2.0.4	22.7	23.1	18	1.9	1.9	2.0.12	3.8	-2.8	6	10.7	10.3			
4	3.3	3.4				6	2.8	-2.5	8	1.4	1.3	1.7.0	2.8	4.2
6	6.0	5.1	2.0.4	39.0	-37.2	10	7.4	7.8	10	2.5	-1.9	3	3.5	-4.9
8	3.1	1.3	4	18.0	15.6	14	5.7	-4.0	14	3.4	-2.9	5	1.4	1.1
10	4.5	-3.2	6	20.4	18.3				16	1.7	-0.9	7	3.2	3.2
12	5.1	-4.3	8	2.3	-1.8	2.0.14	2.6	2.8	18	1.4	1.2	11	1.2	-0.2
14	1.6	-3.8	10	6.3	6.5	4	2.3	-2.8				13	1.2	-1.2
16	2.1	2.6	12	10.5	-9.1	6	2.4	-1.0	1.3.0	1.5	1.0	2.3.0	1.5	-2.6
			14	7.9	-6.5	8	1.6	-3.1	3	12.3	11.4	6	3.0	4.6
2.0.6	18.3	18.2	16	6.9	4.0	10	2.1	1.4	5	2.0	-2.7	8	1.2	1.4
4	16.2	16.6	18	5.2	-4.4				7	6.1	-7.0	10	1.6	0.6
6	16.0	-20.1				<i>h0l</i>			9	3.2	-3.2			
8	2.8	-4.3	2.0.6	10.5	10.9	2.0.0	8.2	11.4	11	2.2	2.6	5.9.0	1.2	-0.7
10	4.5	5.3	6	3.3	-5.3	4	16.7	-20.7	13	4.5	5.7	7	1.6	-2.2

40° 57'. The distances of the chlorine atoms from the above plane, and the angles made by the C-Cl bonds with the plane of the ring are given in Table 3. It is quite clear from Fig. 1(b) that the chlorine atoms cannot all lie in one plane, and it is found that the two atoms on one side of the ring both lie below the plane of the carbon atoms, and the two atoms on the other side lie above this plane. This may be contrasted with the situation

<sup>5</sup> Norman and Post, *Acta Cryst.*, 1961, **14**, 503.

TABLE 3.

Distances from the plane through atoms C<sub>1</sub>, C<sub>3</sub>, and C<sub>4</sub>, and the angles made by the C-Cl bonds with this plane.

Atom .....	C <sub>2</sub>	C <sub>5</sub>	Cl <sub>1</sub>	Cl <sub>2</sub>	Cl <sub>3</sub>	Cl <sub>4</sub>
Distance (Å) .....	+0.020	-0.018	-0.242	-0.093	+0.208	+0.112
Angle .....	—	—	8° 13'	3° 09'	7° 06'	3° 48'

in C<sub>6</sub>Cl<sub>6</sub> which possesses a centre of symmetry,<sup>6</sup> thus implying chlorine atoms lying alternately above and below the plane. A similar distribution of chlorine atoms was also assumed in the electron-diffraction work.<sup>7</sup> In the latter investigation it was found that the C-Cl bonds make an angle of 12° with the plane of the ring. The values obtained here are always less than this, which may be attributed to the larger Cl...Cl separations to be expected in a five-membered ring.

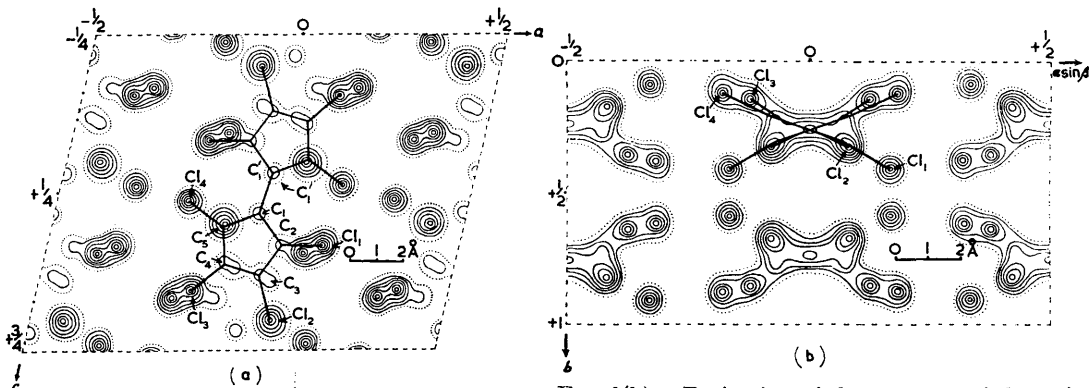


FIG. 1(a). Projection of the contents of the unit cell down [b].

FIG. 1(b). Projection of the contents of the unit cell down [c].

(The contours are drawn at equal arbitrary intervals.)

The distances between non-bonded chlorine atoms all seem reasonable. The shortest distance (3.216 Å) occurs between the atoms that are responsible for the twisting of the two rings out of co-planarity. The next shortest distances (3.320, 3.344, 3.375 Å) occur between chlorine atoms attached to the same ring. There are ten distances of less than 4 Å between chlorine atoms in different molecules, the two shortest of these being 3.473 and 3.534 Å.

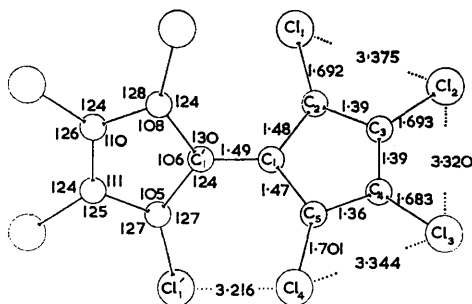


FIG. 2. The numbering of the atoms, the bond angles, and the bond lengths.

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<sup>6</sup> Lonsdale, *Proc. Roy. Soc.*, 1931, A, **133**, 536.

<sup>7</sup> Bastiansen and Hassel, *Acta Chem. Scand.*, 1947, **1**, 489.