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Crystal Structure of the Addition Compound Benzene-Chlorine (1:1)

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The crystal structure of an equimolecular addition compound benzene-chlorine has been determined using single crystal Weissenberg technique and working at low temperatures, mainly about −90°C. The crystals are *monoclinic* (space group *C*2/*m*) and isomorphous with those of the corresponding benzene-bromine compound [2]. Chains of alternating benzene and chlorine molecules are present in the crystal, the Cl—Cl distance is 1.99 Å and the distance from one particular chlorine atom to the nearest benzene plane (3.28 Å), a little shorter than the corresponding distance in the bromine compound.

A considerable amount of experimental material has been gathered during the last few years concerning crystal structures of charge transfer compounds in which molecules of the heavier halogens and iodo monochloride are the electron acceptors. The most conspicuous results of these investigations are the facts that in all compounds so far investigated the arrangement, donor atom-halogen-halogen, is *linear*, and that both atoms of a particular halogen molecule may be capable of forming bonds to donor atoms.

Recently X-ray work has been started on addition compounds formed by *chlorine*. The first crystal structure to be studied was that of the 1:1 compound formed by 1,4-dioxan and chlorine [1]. It could be shown that this compound is isomorphous with the corresponding bromine compound and a proof of the existence of chlorine molecule bridges between oxygen atoms was thereby given. The next step in our research programme was to look for a possible solid compound between benzene and chlorine. We actually succeeded in growing crystals of a 1:1 compound and in determining its crystal structure.

The procedure followed was very similar to that briefly described for the benzene-bromine compound [2]. By cooling an equimolecular mixture of benzene and chlorine in a capillary tube to temperatures below −50°C (m.p. −40°C) single crystals of the 1:1 compound could be grown which were suitable for X-ray analyses in a Weissenberg camera. Photographs with Cu*K*-radiation

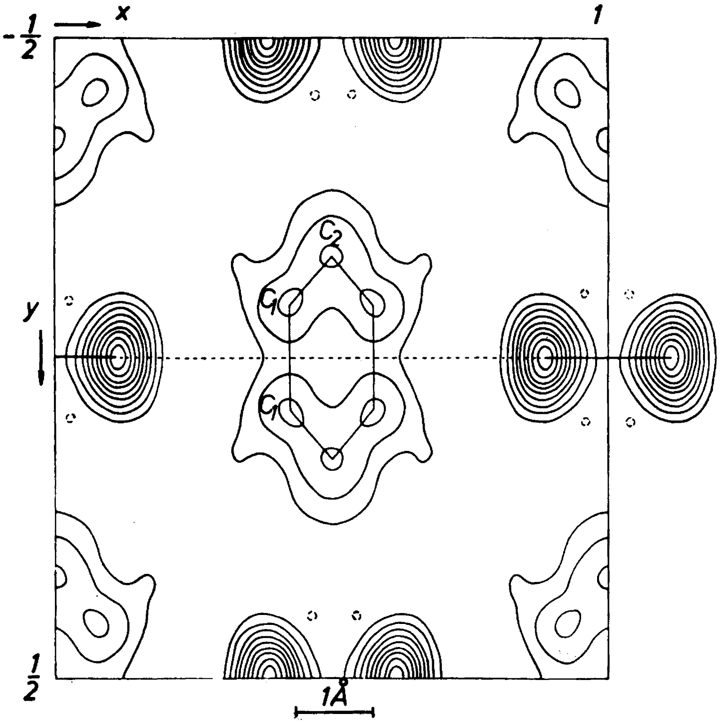

Fig. 1. Fourier along [001]. Contour intervals 2 e . Å^{-2}. Zero contour broken.

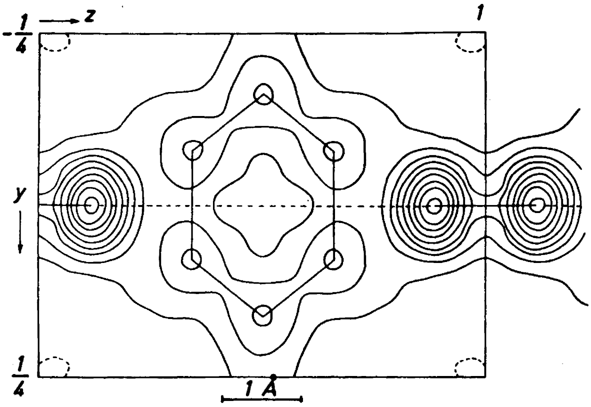

Fig. 2. Fourier projection along [100]. Contours as in Fig. 1.

Table 1. Atomic coordinates in fractions of the cell-edges. Origin at a center of symmetry.

Atom	x	y	z
Cl	0.116_5	0.000	0.116_5
C_1	0.575	0.080	0.342
C_2	0.500	0.161	0.500

and rotation about three different crystallographic directions were obtained at temperatures mainly at about -90°C.

The crystals turned out to be monoclinic, space group $C2/m$ with lattice parameters: $a = 7.41$ Å, $b = 8.61$ Å, $c = 5.65$ Å, $\beta = 99.5$°. With these parameters and assuming the unit cell to contain two molecules of either kind a density of 1.40 g/cm^3 is computed. This conforms to the expected density of a compound containing equal numbers of the two kinds of molecules. These findings make it appear extremely probable that the crystalline chlorine-benzene compound is isomorphous with the bromine-benzene compound previously investigated.

From zero layer line Weissenberg diagrams with rotation about [001], [100] and [10$\bar{1}$] intensity data were derived which could be used for the computation of electron density projections. It was assumed that the structure is indeed closely similar to that of the benzene-bromine compound[2]. The final Fourier maps with projections along [001], [100], and [10$\bar{1}$] are reproduced in Figs. 1—3. The number of reflexions observed in the ($hk0$) zone is 28 (theor. 48), in the ($0kl$) zone 26 (theor. 39) and in the (hkh) zone 19 (theor. 27). The atom form factors were taken from McWeeney[3] (hydrogen), Berghuis *et al.*[4] (carbon) and International Tables[5] (chlorine).

In Table 1 the atomic coordinates derived from the Fourier projections are listed. On computing the reliability factors it was found that the agreement between observed and calculated F-values improved on including the contribution from the hydrogen atoms, the coordinates of which were taken from a model. The R-values obtained were:

$$[001]\ 11.0\ \%; \qquad [100]\ 7.3\ \%; \qquad [10\bar{1}]\ 11.3\ \%$$

When calculationg the R-values a few strong reflexions which are suffering from extinction effects were omitted. Calculated and observed F-values are listed in Table 2. The following (anisotropic) temperature factors were introduced:

$$B_{100} = 3.2\ ; \quad B_{010} = 7.8\ ; \quad B_{001} = 5.2$$

The experimental results thus indicate anisotropic vibrations of the chlorine atoms, the vibrations being more pronounced perpendicular to [101] (the Cl—Cl direction) than along this direction. It appears justified, however, to assume that the thermal vibrations are independent of the direction within planes perpendicular to [101] (parallel to the benzene rings). This assumption actually conforms very well to the experimentally observed damping of the X-ray reflections.

Table 2. Observed and calculated structure factors. The figures represent one half of the absolute values. F —'s suffering from extinction are marked with an asterisk.

h k l	Fobs	Fcalc
	(h k 0) zone	
2 0 0	20.6	22.1
4 0 0	15.7	−17.0
6 0 0	5.2	−5.2
8 0 0	4.8	4.7
1 1 0	<0.8	1.1
3 1 0	14.9	−16.0
5 1 0	8,5	−8.0
7 1 0	4.2	5.4
9 1 0	2.7	4.1
0 2 0	25.0 *	29.9
2 2 0	3.3	3.2
4 2 0	18.1	−16.0
6 2 0	6.2	−5.7
8 2 0	3.6	3.0
1 3 0	20.1	19.0
3 3 0	6.1	−4.4
5 3 0	5.7	−5.4
7 3 0	4.1	4.1
9 3 0	<1.8	3.8
0 4 0	8.6	7.5
2 4 0	<2.0	−2.4
4 4 0	8.6	−9.4
6 4 0	2.2	−1.6
8 4 0	2.4	3.2
1 5 0	11.0	10.1
3 5 0	4.9	−4.8
5 5 0	6.4	−6.9
0 6 0	6.2	3.0
2 6 0	<2.0	0.4
4 6 0	2.2	−2.8
6 6 0	2.0	1.2
1 7 0	3.8	4.4
3 7 0	<2.0	−2.9
5 7 0	2.5	−3.7
7 7 0	<1.2	−0.26
0 8 0	2.1	1.9
2 8 0	<2.2	−0.36
4 8 0	<1.9	−2.00
1 9 0	<2.0	2.00
010 0	<2.0	1.0
	(0 k l) zone	
0 2 0	31.2	30.0
0 4 0	6.9	7.4
0 6 0	5.1	4.8
0 8 0	1.7	1.7
010 0	<1.4	0.9
0 0 1	1.0	−0.7
0 2 1	17.1	17.7
0 4 1	14.0	13.6
0 6 1	4.9	5.0
0 8 1	1.9	2.5
010 1	<1.1	0.8
0 0 2	2.1	3.1
0 2 2	3.6	−3.0
0 4 2	1.8	0.5
0 6 2	3.1	3.0
0 8 2	<1.0	0.4
0 0 3	5.1	−4.3
0 2 3	2.2	−2.4
0 4 3	5.2	−4.9
0 6 3	5.2	−5.4
0 8 3	1.5	−1.4
0 0 4	8.6	−9.4
0 2 4	9.9	−10.0
0 4 4	5.3	−5.2
0 6 4	<1.5	−1.2
0 8 4	<1.2	−1.2
0 0 5	6.3	−6.8
0 2 5	3.8	−4.0
0 4 5	2.7	−2.3
0 6 5	1.4	−1.8
0 0 6	1.4	1.2
0 2 6	<1.4	−0.5
0 4 6	<1.2	−1.2
0 0 7	<0.9	0.2
	(h k h) zone	
2 0 2	8.2	−6.4
4 0 4	5.7	6.2
1 1 1	20.6	20.0
3 1 3	2.1	−2.0
5 1 5	<1.2	1.0
0 2 0	25.0 *	30.8
2 2 2	15.3	−13.8
4 2 4	3.7	4.1
1 3 1	3.2	−2.8
3 3 3	4.2	−4.6
0 4 0	7.3	7.6
2 4 2	11.9	−12.0
4 4 4	2.9	3.7
1 5 1	2.1	−1.7
3 5 3	1.5	−1.2
0 6 0	5.2	3.8
2 6 2	4.3	−5.1
4 6 4	2.0	3.3
1 7 1	<2.1	−0.5
3 7 3	<2.0	−0.4
0 8 0	1.7	−2.5
2 8 2	1.7	−1.7
1 9 1	<2.1	−0.5
010 0	<1.9	0.6

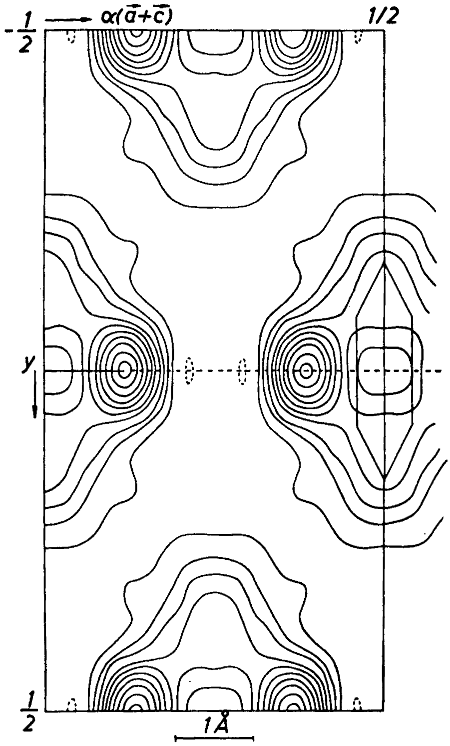

Fig. 3. Fourier projection along [10$\bar{1}$]. Contours as in Fig. 1.

All our findings thus confirm the expected close analogy between the structures of the benzene compounds of chlorine and bromine. In both cases the thermal movement of the atoms takes place preferably parallel to the benzene planes. The Cl—Cl bond direction is at least very nearly perpendicular to the benzene rings. The distance from a particular chlorine atom to the nearest benzene ring is 3.28 Å and thus 0.08 Å shorter than the corresponding distance in the bromine compound [2]. The observed Cl—Cl distance is 1.99 Å and thus identical with the spectroscopical value for the free molecule. In Table 3 the angles and interatomic distances in the benzene ring have been listed. The standard deviations of the reported distances are the following:

Cl—Cl 0.013 Å; C—Cl 0.026 Å; C—C 0.034 Å.

Table 3. Interatomic distances and angles within the benzene ring.

Bond	Bond length (Å)	Angle	
C_1-C_1	1.38	$C_1-C_1-C_2$	120.7°
C_1-C_2	1.37	$C_1-C_2-C_1$	118.6°

The present structure thus affords a second example of a chlorine molecule bridge in an addition compound, and of isomorphism between addition compounds in which chlorine and bromine are the electron acceptors. It is to be expected that many new examples will be found in the future. The reason for this isomorphism is no doubt, that the lengthening of the bond between donor molecule and chlorine is compensated by the smaller atomic radius of the chlorine atom.

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