

Crystal Structure of the 1:1 Addition Compound Formed by Acetone and Bromine

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The crystal structure of the equimolecular compound containing acetone and bromine has been determined at temperatures near -30°C using Weissenberg technique (CuK-radiation) and precession technique (MoK-radiation). The space group is $C2/c$ and the lattice parameters: $a = 7.12 \text{ \AA}$; $b = 7.48 \text{ \AA}$; $c = 12.90 \text{ \AA}$; $\beta = 111.5^{\circ}$. Endless chains are present in this structure, bromine atoms and the carbonyl carbon and oxygen atoms of each chain being coplanar. Each oxygen atom is linked to two neighbouring oxygen atoms of the same chain by halogen molecule bridges and the O—Br—Br—O arrangements are linear. The observed Br—Br distance was found equal to the distance observed in free bromine molecules (2.28 \AA), the O—Br distance 2.82 \AA . This structure affords the first example of two halogen molecule bridges starting from a common oxygen atom.

Results obtained in previous investigations of the crystal structure of addition compounds containing halogen molecules and electron donor molecules like ethers, amines and aromatic hydrocarbons made it appear of interest to include at least *one* addition compound between halogen and ketone in our research programme¹. It would appear probable that in such compounds "halogen molecule bridges" are formed between keto oxygen atoms belonging to neighbouring ketone molecules. There is no doubt a marked tendency to establish endless chains of alternating halogen and donor molecules in addition compounds. In the case of ketones, however, such chains could not be formed unless both lone electron pairs of a particular keto oxygen atom are capable of forming electron transfer bonds at the same time.

We have chosen the 1:1 addition compound of acetone and bromine as an example. According to Mass and McIntosh² this compound has a melting point of -8°C and the X-ray analysis of single crystals should therefore not be more difficult than for several other substances which have already been successfully investigated.

On cooling equimolecular mixtures of the two components in thin capillary tubes it was found that single crystals could indeed be grown which appeared

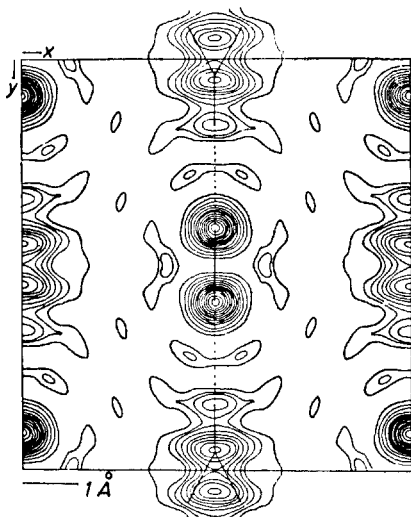


Fig. 1. Fourier projection along the c axis. First contour line represents $4 \text{ e} \cdot \text{Å}^{-3}$. Contour intervals $2 \text{ e} \cdot \text{Å}^{-3}$ for light atoms, $10 \text{ e} \cdot \text{Å}^{-3}$ for bromine.

satisfactory for our purpose. When using Weissenberg technique, however, it is useful that crystals are available that have one of their crystallographic axes approximately parallel to the axis of the capillary tube. In our case we succeeded in producing crystals which fulfilled this requirement with respect to one crystallographic direction only, the c -axis. The material obtained from Weissenberg diagrams with CuK -radiation had therefore to be supplemented by material obtained using a precession camera and MoK -radiation.

No efforts were made in order to keep the crystal at a constant temperature during the exposure, but the temperature was never far from a mean value of about -30°C .

According to the X-ray data the addition compound is monoclinic and the space group either $C2/c$ or C/c . The lattice parameters are:

$$a = 7.12 \text{ Å}; \quad b = 7.48 \text{ Å}; \quad c = 12.90 \text{ Å}; \quad \beta = 111.5^\circ$$

The density of the crystals was not determined experimentally, but a reasonable value is 2.1 which leads to a number of four molecules of each kind in the unit cell.

From a two dimensional Patterson synthesis preliminary x and y coordinates of the bromine atoms were determined and a Fourier map with projection along $[001]$ was worked out. It was assumed that the space group is $C 2/c$ and the signs of the structure factors were determined from the coordinates of the bromine atoms alone, neglecting contributions from the lighter atoms. The resulting electron density map is reproduced in Fig. 1. No changes of structure factor signs occurred after introducing the contribution from carbon and oxygen atoms. Fig. 1 thus represents the final electron density projection along $[001]$. The R -factor of this projection is 0.13. The heavy peaks correspond to double bromine atoms, the overlapping of the atoms being complete or at least almost so. Approximate x and y coordinates of the lighter

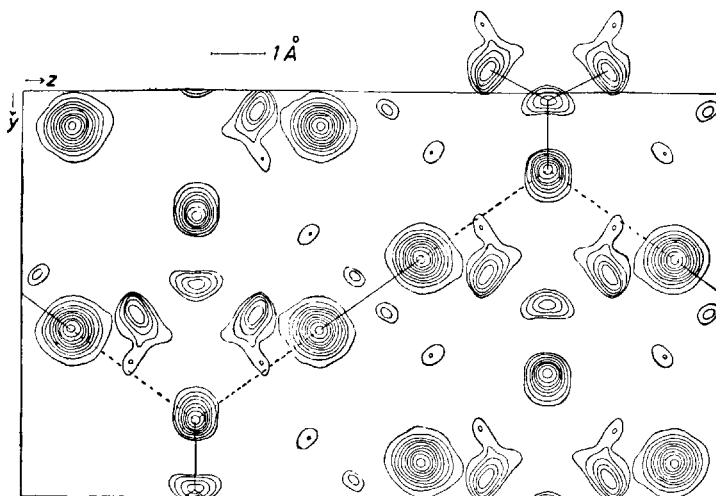


Fig. 2. Fourier projection along the a axis. First contour line represents $4 \text{ e} \cdot \text{Å}^{-2}$. Contour intervals $1 \text{ e} \cdot \text{Å}^{-2}$ for light atoms, $6 \text{ e} \cdot \text{Å}^{-2}$ for bromine.

atoms may also be obtained from this projection. The C—O distance of the carbonyl group is in good agreement with the value deduced from the [100] projection (1.22 Å).

Before starting to work out the Fourier projection along [100] the corresponding Patterson map was computed in order to determine the z coordinates and verify the y coordinates already determined. Neglecting again the lighter atoms the Fourier chart reproduced in Fig. 2 was obtained. More accurate values for the coordinates of the light atoms were worked out by computing a difference synthesis with subtraction of the contribution from the bromine atoms. This procedure led to some modifications of the coordinates determined from the original map and also to minor corrections of the bromine parameters. With the new parameter values the R factor for the [100] projection dropped from 0.12 to 0.10. The final parameters for both the bromine and the light atoms are listed in Table 1.

The fall in observed X-ray intensities for increasing reflexion angles turned out to be smaller for the bromine acetone compound than for most addition

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

Atom	x	y	z
Br	0.000	0.091	0.071
O	0.000	0.307	0.250
C ₁	0.000	0.469	0.250
C ₂	0.062	0.577	0.169
C ₃	-0.062	0.577	0.331

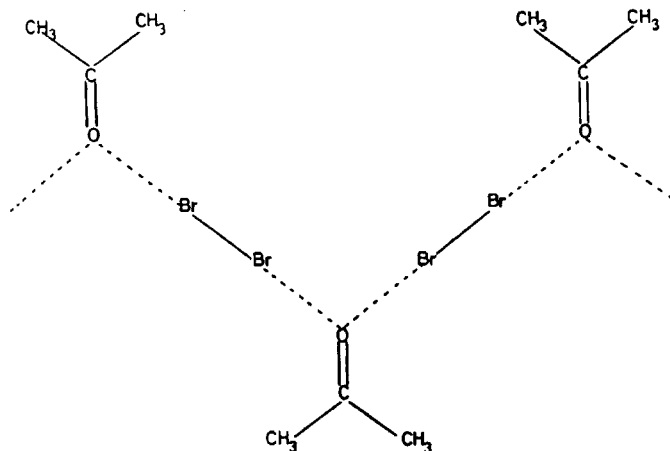


Fig. 3. The planar chains.

compounds with halogens previously investigated (B values 2.1 and 2.3 for the projection along [100] and [001]), respectively. This is probably due to the presence of the fairly rigid planar double chains present in the acetone-bromine structure (see below).

There is actually very strong evidence that not only are the bromine atoms lying in the (100) plane but also the carbon and oxygen atoms of keto groups belonging to a particular chain. The coordinate values of the latter atoms are listed in the upper part of Table 1. From these values follows a Br-Br bond distance of 2.28 Å. Allowing for probable errors in the bromine coordinates it may at least be stated that this distance cannot be substantially greater than the corresponding bond distance in the "free" molecule which is indeed 2.28 Å. The distance between a bromine atom and the nearest oxygen atom to which it is directly attached becomes 2.82 Å, a value somewhat larger than the O-Br distance observed in the addition compound between 1,4-dioxan and bromine namely 2.71 Å. The standard deviation in the Br-Br distance is 0.006 Å, in the O-Br distance 0.028 Å.

Table 2. Interatomic distances and angles.

Bond	Bond length (Å)	Sum of covalent radii (Å)	Angle
Br-Br	2.28	2.28	Br-Br-O 180°
Br-O	2.82	1.80	Br-O-Br 110°
O-C ₁	1.22		C ₂ -C ₁ -C ₃ 112°
C ₁ -C _{2(s)}	1.51	1.54	
C ₁ -C ₃	2.56		
C ₂ -Br	3.77		
C ₃ -Br	3.73		

Table 3. Observed and calculated structure factors. The figures represent one fourth of the absolute values.

hkl	F_{obs}	F_{calc}	hkl	F_{obs}	F_{calc}
	(hk0) zone				
200	61.7	71.9	041	19.5	-19.3
400	40.9	43.0	061	5.2	5.1
600	24.8	22.9	081	8.5	8.7
800	11.2	15.1	002	21.1	23.1
110	31.3	36.7	022	15.0	14.8
310	28.8	32.4	042	18.5	-17.9
510	23.7	24.1	062	15.6	-16.3
710	12.1	16.0	082	<4.9	-0.1
910	4.6	9.1	023	41.0	-49.3
020	28.7	29.1	043	24.7	-25.9
220	24.7	23.0	063	<4.7	6.5
420	18.8	14.4	083	12.6	15.1
620	10.3	8.7	004	11.1	-4.8
820	4.0	5.3	024	9.7	-6.6
130	8.8	-4.3	044	9.5	7.2
330	8.1	-3.1	064	5.2	6.4
530	5.8	-2.5	084	<4.7	0.4
730	<2.1	-1.7	025	24.3	-24.8
040	27.6	-28.5	045	17.7	-19.3
240	25.1	-25.1	065	9.0	7.8
440	20.8	-18.1	085	12.8	11.5
640	11.2	-11.8	006	37.9	-40.1
840	5.7	-7.3	026	12.4	-11.2
150	33.2	-33.2	046	16.9	12.8
350	27.2	-26.6	066	15.0	14.5
550	20.3	-20.9	086	<4.7	1.1
750	10.1	-14.3	027	6.9	-5.1
060	26.8	-25.2	047	<4.4	-0.5
260	25.6	-22.5	067	<4.8	-1.3
460	19.1	-16.6	008	28.8	-28.0
660	10.8	-10.8	028	11.7	-13.2
170	14.5	-13.2	048	15.7	16.9
370	11.5	-12.4	068	15.7	18.2
570	7.6	-10.7	029	20.8	20.6
080	6.3	-3.8	049	10.9	11.9
280	4.9	-3.6	069	<4.9	-1.9
190	7.7	6.5	0010	13.9	-11.1
390	5.4	5.5	0210	<4.6	-2.8
			0410	<4.9	2.7
			0610	<4.9	3.4
			0211	19.6	18.9
			0411	14.0	15.0
			0611	<4.8	-4.7
			0012	18.3	17.9
			0212	<4.9	5.3
			0412	<4.9	-6.3
			0213	6.9	6.6
			0413	<4.7	3.2
			0014	13.4	11.8
			0214	<4.7	4.7
hkl	F_{obs}	F_{calc}			
	(0kl) zone				
020	27.9	27.0			
040	24.9	-25.9			
060	22.2	-25.6			
080	4.5	-5.1			
021	23.9	-22.5			

The O—Br—Br—O arrangement is linear. The angle between the two O—Br—Br—O lines meeting in a particular oxygen atom is 110° . The arrangement of the carbonyl and bromine atoms in the plane of the chains (*cf.* Fig. 3) thus appears to be determined in a very simple way by the position of the two lone electron pairs of the oxygen atom and the linearity of the O—Br—Br—O arrangement. The presence of halogen-molecule bridges between oxygen atoms of neighbouring acetone molecules was not unexpected; the new feature of this structure is the fact that a particular oxygen atom may indeed serve as a "bridge-head" for *two* such bridges.

The only atoms of the chains which do not appear to be situated in the (100) planes are those of the methyl groups. The angle between the C—C bonds and the plane of the chains is 16° . The reason for this tilting of the methyl groups is probably to be sought in the circumstance that only in this way the distance from the methyl carbon atom to the two nearest bromine atoms belonging to neighbouring chains will be of equal length and correspond to the accepted "van der Waals distance".

The relatively slow fall in X-ray intensities for increasing reflexion angles mentioned above indicates more moderate thermal vibrations than those met with in many other addition compounds. This finding must no doubt be a consequence of the particular form of chains present in the structure which should be expected to facilitate vibrations perpendicular to the plane. Actually, the observed anisotropy of the thermal vibrations is in accord with this view, the vibration parallel to the x -axis being more pronounced than in directions perpendicular to the x -axis.

Table 2 contains a list of observed interatomic distances and angles. In Table 3 observed and calculated structure factors are listed. The number of reflexions observed in the ($hk0$) zone is 37 (theor. 39), in the ($0kl$) zone 40 (theor. 60). The f -curves used in this calculations are those given in the *Internationale Tabellen* (1935).

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