

The 2:1 Addition Compound Methanol-Bromine, a Crystalline Substance Exhibiting Both Hydrogen and Halogen Molecule Bridges between Oxygen Atoms

P. GROTH and O. HASSEL

Universitetets Kjemiske Institutt, Oslo 3, Norway

The crystalline compound containing methanol and bromine molecules in the ratio 2:1 belongs to the monoclinic system, space group $P2_1/c$ with eight molecules in the unit cell. The parameters are

$$a = 16.07 \text{ \AA}; b = 11.16 \text{ \AA}; c = 8.16 \text{ \AA}; \beta = 92.3^\circ$$

Each oxygen atom is tetrahedrally surrounded by one methyl group and three bridges connecting it with oxygen neighbours — two hydrogen bridges and one bromine molecule bridge.

X-Ray work carried out during the last decade has revealed some important details regarding the atomic architecture of addition compounds in which "n donors" or " π donors" are bonded to acceptors of different kinds.¹ Among the most interesting — and unexpected — features discovered are the "halogen molecule bridges"² linking together donor molecules. When n donor atoms (like oxygen) are involved, *e.g.* in ethers or ketones, linear arrangements of atoms like O— — — Br— Br— — — O may result if a halogen acts as the acceptor molecule. Either one or two such bridges may start from a particular oxygen atom because it possesses two lone pairs of electrons. A nitrogen atom in amines or nitriles cannot be expected to form more than a single halogen molecule bridge. In solid halogen compounds formed by amines such bridges have so far not been observed, however. It appears likely that this finding may be explained by the remarkable strength of the charge transfer bond between an amine nitrogen atom and halogen. Nitriles, however, which show only a moderate donor strength are capable of participating in the formation of halogen molecule bridges.³

There is some reason for believing that a charge transfer bond formed between oxygen and bromine is energetically roughly comparable to a strong hydrogen bond. The question therefore arises if hydrogen bridges and bromine molecule bridges may perhaps both be found in addition compounds in which

Table 1. Observed and calculated structure factors of the $hk0$ -projection.
 $R = 8.9\%$

h	k	F_o	F_c	h	k	F_o	F_c
0	4	269	279	4	11	-26	-24
0	6	-118	-115	4	12	-25	-24
0	8	43	28	4	13	22	27
0	10	-43	-39	4	14	12	21
0	12	-31	-29	5	0	-13	-13
0	14	25	29	5	1	-5	-2
1	2	-10	-9	5	2	18	16
1	3	-21	-26	5	3	39	44
1	4	17	21	5	5	-69	-72
1	5	36	36	5	6	11	8
1	6	-16	-14	5	7	90	87
1	7	-39	-36	5	8	-27	-21
1	8	18	16	5	9	-96	-92
1	9	50	46	5	10	25	15
1	10	-14	-10	5	11	95	86
1	11	-60	-48	5	12	-17	-13
1	13	59	51	5	13	-78	-72
2	0	52	72	6	0	309	304
2	1	-172	-210	6	1	-239	-251
2	2	-74	-80	6	2	-226	-237
2	3	305	320	6	3	116	118
2	4	55	56	6	4	142	147
2	5	-173	-175	6	5	-84	-87
2	6	-18	-16	6	6	-77	-80
2	7	135	131	6	8	36	37
2	8	-24	-18	6	10	-22	-20
2	10	46	40	6	11	-13	-10
2	11	-30	-31	6	12	-8	-3
2	12	-42	-37	6	13	26	33
2	14	20	29	7	0	-20	-17
3	1	-11	-12	7	4	-13	-8
3	2	-12	-10	7	5	12	12
3	3	17	16	7	6	12	20
3	4	43	44	7	8	-24	-26
3	5	-31	-33	7	10	33	30
3	6	-88	-96	7	11	-26	-18
3	7	33	36	7	12	-21	-19
3	8	120	120	7	13	21	21
3	9	-34	-31	8	0	-88	-79
3	10	-118	-115	8	1	-269	-278
3	11	31	29	8	2	118	125
3	12	95	86	8	3	245	249
3	13	-13	-13	8	4	-88	-88
3	14	-38	-53	8	5	-162	-162
4	0	-138	-109	8	6	56	61
4	1	-16	-9	8	7	85	79
4	2	-54	-49	8	8	-40	-40
4	3	-42	-42	8	9	-17	-7
4	4	31	37	8	11	-29	-29
4	5	55	53	8	13	20	27
4	6	-22	-26	9	0	-20	-13
4	7	-55	-50	9	1	-15	-12
4	8	16	4	9	5	-28	-32
4	9	33	32	9	6	-19	-21
4	10	61	60	9	7	31	36

h	k	F_o	F_c	h	k	F_o	F_c
9	8	53	49	13	6	33	31
9	9	- 50	- 46	13	7	- 19	- 16
9	10	- 48	- 44	13	8	- 45	- 51
9	11	36	39	13	9	29	28
9	12	34	38	13	10	35	45
9	13	- 12	- 22	13	11	- 23	- 31
10	0	- 152	- 156	14	0	- 160	- 168
10	1	14	19	14	1	- 83	- 85
10	2	130	129	14	2	143	145
10	3	- 12	- 6	14	3	68	70
10	4	- 94	- 90	14	4	- 98	- 100
10	5	33	33	14	5	- 52	- 50
10	6	59	51	14	6	62	51
10	7	- 30	- 21	14	7	24	24
10	8	- 27	- 15	14	8	- 24	- 21
10	9	39	36	14	9	- 10	- 9
10	11	- 30	- 35	15	0	- 18	- 11
11	1	12	11	15	8	13	18
11	2	24	25	16	0	- 98	- 105
11	3	9	6	16	1	82	86
11	4	- 34	- 34	16	2	93	94
11	5	- 39	- 41	16	3	- 84	- 89
11	6	54	52	16	4	- 72	- 73
11	7	50	50	16	5	68	72
11	8	- 67	- 63	16	6	42	40
11	9	- 59	- 57	16	7	- 45	- 46
11	10	48	47	16	9	10	12
11	11	52	62	17	3	- 13	- 13
11	12	- 29	- 41	17	6	28	32
12	0	13	9	17	8	- 24	- 37
12	1	- 68	- 65	18	0	26	36
12	2	- 23	- 21	18	1	44	42
12	3	58	53	18	2	- 22	- 20
12	4	20	17	18	3	- 27	- 30
12	5	- 41	- 38	18	4	13	12
12	6	- 23	- 22	18	5	12	7
12	7	14	15	18	6	- 12	- 9
12	8	29	30	19	0	18	26
12	10	- 17	- 21	19	5	17	26
13	0	17	5	20	0	- 48	- 56
13	1	24	25	20	1	42	20
13	4	- 17	- 15	21	0	6	8
13	5	29	29				

hydroxy oxygen is the donor, bromine the acceptor. In order to answer this question the crystal structure of a previously known addition compound ⁴ containing methanol and bromine in the ratio 2:1 has been determined.

This compound has a melting point of -66°C and the X-ray investigation had to be carried out below that temperature, at about -90°C . It turned out to be somewhat more difficult, however, than we had expected from previous experience to grow good single crystals by cooling the liquid mixture in a capillary tube. In one particular case only, a crystal of high quality was obtained and a full set of very satisfactory diagrams was obtained for one particular zone, ($hk0$), using an integrating Weissenberg goniometer. At this stage

a most unfortunate disruption of the cooled air stream occurred, however, and the temperature of the sample rose above the melting point of the addition compound. Unfortunately, a series of attempts to grow a new crystal of a quality comparable to that of the lost crystal were not successful, however, and eventually we had to content ourselves with crystals of inferior quality in order to work out a second projection for the $(h0l)$ zone, using a precession camera.

The structure is monoclinic, space group $P2_1/c$. The density of the crystals is about 2.4 g/cm^3 and 8 formula units have to be accommodated in the unit cell having the parameters

$$a = 16.07 \text{ \AA} \quad b = 11.16 \text{ \AA} \quad c = 8.16 \text{ \AA} \quad \beta = 92.3^\circ$$

The projection along the c -axis was worked out starting with a Patterson syntheses which made possible approximate determinations of the x and y coordinates of the bromine atoms. The Fourier map indicated only roughly the positions of the light atoms, but after a series of least squares refinements the Fourier map reproduced in Fig. 1 was obtained. The R factor was 0.089.

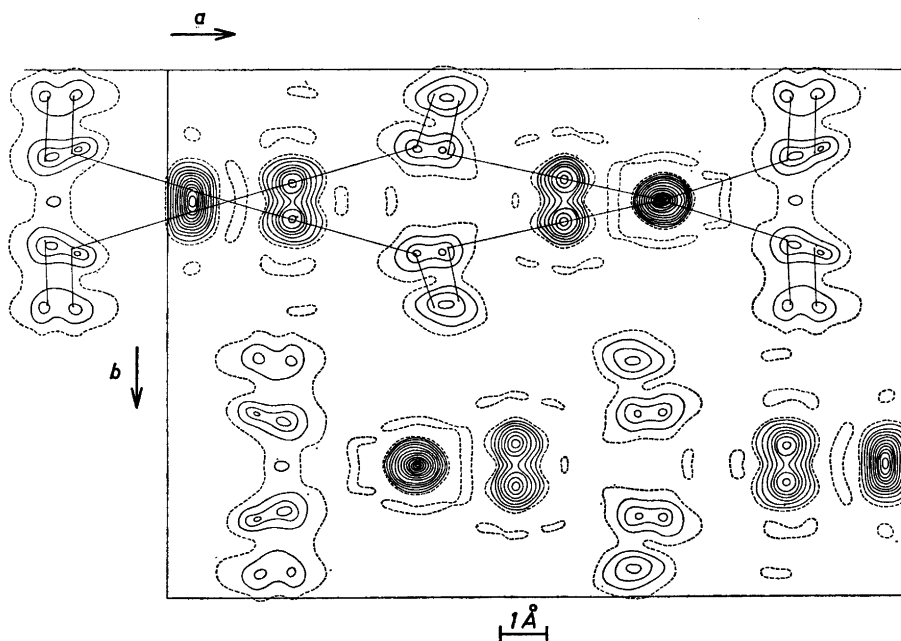


Fig. 1. Fourier projection along $[001]$.

As indicated above, the $[010]$ -projection was worked out on the basis of a single precession diagram and using a crystal of poorer quality. The R factor eventually obtained was a little below 0.12. The corresponding Fourier

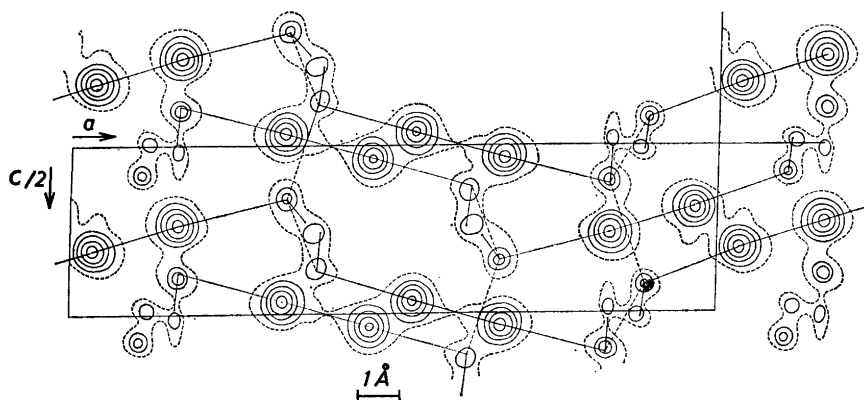


Fig. 2. Fourier projection along [010].

Table 2. Observed and calculated structure factors of the $h0l$ -projection.
 $R = 11.6\%$

h	l	F_o	F_c	h	l	F_o	F_c
-14	2	-21	-19	4	0	-63	-51
-11	2	-28	-31	4	1	-38	-41
-11	3	-25	-25	4	2	-32	-28
-10	1	27	26	4	3	-46	-33
-10	3	25	31	4	4	-41	-37
-9	1	75	84	5	1	-80	-88
-9	2	-41	-43	5	2	83	80
-8	1	35	40	5	4	31	31
-8	2	-37	-37	6	0	147	150
-6	1	58	61	6	1	-66	-69
-6	2	39	45	6	2	54	60
-6	3	18	22	6	3	-35	-30
-5	1	-79	-92	7	1	-33	-42
-5	2	-87	-91	7	2	20	22
-5	3	-22	-21	8	0	-46	-45
-4	1	57	61	8	1	-36	-38
-4	3	63	72	9	0	-9	-10
-3	2	-67	-67	9	1	67	73
-3	3	38	41	9	2	38	46
-3	4	-23	-29	9	3	21	28
-2	2	-34	-41	10	0	-67	-70
-2	4	-22	-21	10	2	-23	-25
-1	1	-87	-87	10	3	-41	-46
0	2	91	82	11	2	47	56
1	1	-165	-135	11	3	-20	-18
1	2	-54	-43	12	0	6	8
1	4	-23	-20	12	3	-20	-21
2	0	28	31	13	0	7	4
2	2	28	11	14	0	-68	-67
2	3	40	31	15	0	-8	-9
2	4	-36	-32	16	0	-45	-36
3	2	28	23	18	0	14	16
3	3	66	52	19	0	11	8
3	4	-24	-22				

Table 3. Final atomic coordinates.

	<i>x</i>	<i>y</i>	<i>z</i>
Br ₁	0.0362	0.2291	0.1845
Br ₂	0.1669	0.2846	0.2603
Br ₃	0.5333	0.2107	0.0399
Br ₄	0.6688	0.2542	-0.0297
O ₁	-0.117	0.159	0.086
O ₂	0.335	0.352	0.319
O ₃	0.375	0.159	0.116
O ₄	0.834	0.330	-0.119
C ₁	-0.109	0.043	-0.010
C ₂	0.359	0.449	0.270
C ₃	0.383	0.053	0.343
C ₄	0.846	0.450	-0.019

map is reproduced in Fig. 2. In Tables 1 and 2 structure factors observed (F_o) and calculated (F_c) are listed.

The atomic coordinates derived from the [001] and [010] projections are listed in Table 3. The accuracy of the bromine parameters is no doubt considerably higher than those of the light atoms and their values are therefore given with four figures, but only with three figures in the case of the lighter atoms.

Table 4. Interatomic distances and angles (mean values).

Br—Br	: 2.29 Å	Br—Br...O	: 177°
Br...O	: 2.78 Å	Br—O—C	: 109°
C—O	: 1.46 Å	Br—O...O	: 88°
O...O	: 2.62 Å	Br—O...O ₂	: 111°
		C—O...O	: 113°
		O...O...O	: 121°

Table 4 contains the interatomic distances and angles computed from the final (mean) coordinate values. The values obtained from crystallographically

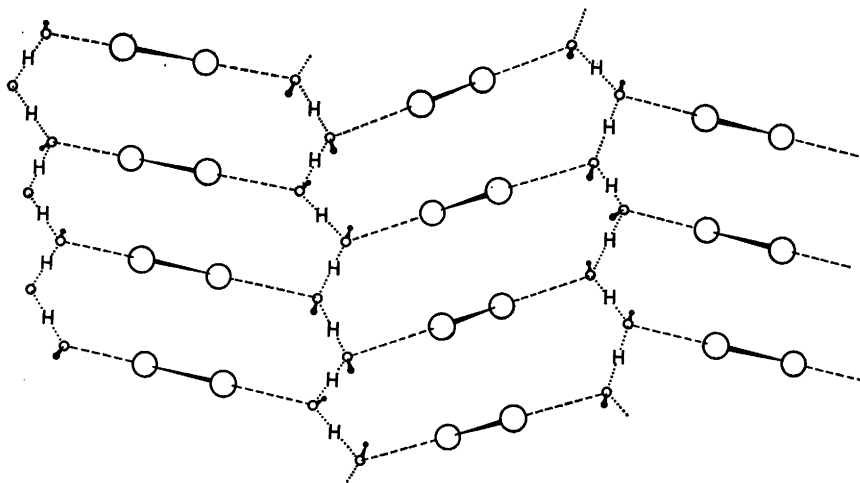


Fig. 3. Schematic drawing of the structure.

non-equivalent groups are in satisfactory agreement. The O—Br—Br—O arrangement is very nearly linear with an angle O—Br—Br equal to 177° (separate values 178° , 174° , 179° and 175°). The Br—Br distance is 2.29 Å and therefore not significantly larger than in the free molecule (2.28 Å). Each oxygen atom is tetrahedrally surrounded by its methyl group and by three bridges linking it to neighbouring oxygen atoms. Two of these bridges are ordinary hydrogen bridges, the third the bromine molecule bridge. The arrangement of the methanol and bromine molecules is visualized in Fig. 3 which shows the layers resulting from the two kinds of bridges between oxygen atoms. Between the layers van der Waals forces are active as may be concluded from calculating the relevant interatomic distances.

The aim of the present investigation, to answer the question if the two types of bridges — hydrogen bridges and bromine molecule bridges — may actually occur in one and the same crystal structure, has therefore been answered in the affirmative. This finding seems to confirm our suggestion that hydrogen bonds and charge transfer bonds between oxygen and bromine cannot differ very much energetically.

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Received October 26, 1963.