X-Ray Analysis of the (1:1) Addition Compounds of 1,4-Dioxan with Oxalyl Chloride resp. Oxalyl Bromide

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Results obtained from two-dimensional X-ray investigations of the two (1:1) addition compounds formed by 1,4-dioxan with oxalyl chloride and oxalyl bromide are reported. Lattice parameters are listed in Table 1.

The two (isomorphous) structures both exhibit endless chains of alternating donor and acceptor molecules joined by bonds connecting oxygen and halogen atoms. In the oxalyl chloride compound the oxygen-halogen distance is not significantly different from that expected for a van der Waals interaction, whereas the corresponding interatomic distance in the oxalyl bromide compound is significantly shorter than the radius sum and approximately equal to the oxygen-bromine distance observed in the crystals of oxalyl bromide itself.[5]

Results of structure investigations of solid addition compounds formed by n donors and halide molecules, particularly iodoform, were published several years ago.[1] It was felt that such investigations should be extended to include addition compounds containing halides of carboxylic acids, and halides of oxalic acid were chosen for this purpose because the 1:1 addition compounds with 1,4-dioxan had already been described.[2] These compounds appeared to offer the possibility that both kinds of molecules are situated in crystallographic centres of symmetry, in which case the analysis might be facilitated.

Two-dimensional X-ray work was finished and a few details were published in 1961.[3] Here, further details are being presented.

The oxalyl chloride used for preparing the addition compound was a commercial product which was first carefully distilled. The bromide was prepared as described by Staudinger [4] by passing a stream of carefully dried hydrogen bromide into the chloride at 0°C. Crystals of the addition compounds were obtained as described by Varvoglis:[2] To a solution of carefully dried dioxan in light petroleum (b.p. 30—50°C) a solution in the same solvent of oxalyl halide was added drop by drop, passing at the same time a stream of dry nitrogen gas through the dioxan solution. During this procedure colourless, needle-shaped crystals of the addition compound were deposited from the

Table 1. Lattice parameters.

Oxalyl chloride-1,4-dioxan		Oxalyl bromide-1,4-dioxan
a	7.58 Å	7.67 Å
b	10.30 Å	10.90 Å
c	7.09 Å	7.14 Å
β	126.5°	127.2°

gas phase at the end of the funnel containing the oxalyl halide solution. Some difficulties had to be overcome before a method was developed which made possible the transfer of selected crystals to thin-walled capillary tubes and the sealing of the tubes without admitting traces of moisture to the crystals. Eventually this was achieved and crystals could be kept in the tubes ready for X-ray examination for several weeks.

The intensity material used in the analysis was collected partly from Weissenberg, partly from precession diagrams. $CuK\alpha$-radiation was used in the first case; in the second case $MoK\alpha$-radiation. Weissenberg diagrams were partly of the ordinary kind, partly taken with an integrating camera, in both

Table 2. Final atomic parameters for the oxalyl chloride compound (A) and the oxalyl bromide compound (B), and estimated standard deviations for the positions.

A	x	y	z	e.s.d. (Å)	$\overline{B}$
Halogen	0.030	0.1920	0.128	0.006	3.0
O(dioxan)	0.309	0.438	0.437		2.9
O(oxalyl)	−0.208	0.071	−0.263	0.013	2.6
C_1(dioxan)	0.309	0.505	0.252		3.6
C_2(dioxan)	0.484	0.606	0.348	0.021	3.4
C(oxalyl)	−0.077	0.061	−0.063		2.9

$R(0kl) = 10.8 \%$ $R(hk0) = 12.2 \%$

B	x	y	z	e.s.d. (Å)	$\overline{B}$
Halogen	0.043	0.1955	0.147	0.009	3.4
O(dioxan)	0.297	0.442	0.432		5.4
O(oxalyl)	−0.219	0.068	−0.253	0.037	4.7
C_1(dioxan)	0.297	0.507	0.241		5.9
C_2(dioxan)	0.503	0.600	0.370	0.050	2.2
C(oxalyl)	−0.068	0.055	−0.068		3.2

$R(0kl) = 15.9 \%$ $R(hk0) = 11.0 \%$

Table 3. Some distances (Å) and bond angles (°). Figures in parentheses are estimated standard deviations.

	Oxalyl chloride compound	Oxalyl bromide compound
Hal-O(dioxan)	3.18 (0.02)	3.21 (0.04)
Hal-C(oxalyl)	1.70 (0.03)	1.96 (0.06)
O(dioxan)-Hal-O(oxalyl)	180 (2)	165 (3)

cases employing the multiple film method. Integrated Weissenberg and precession diagrams were measured photometrically.

Diagrams of the oxalyl bromide compound were taken at room temperature. In the case of the oxalyl chloride compound a moderate cooling (to $-20°$ or $-40°C$) was found to be an advantage because of its stabilizing effect on the crystals.

The lattice constants of the two addition compounds are listed in Table 1. The space group is $P2_1/c$ and the number of formula units in the unit cell is $Z = 2$ in both cases. It was therefore assumed that the crystals are isomorphous. If the structures are not of a disordered type both kinds of molecules must be centrosymmetrical. The analyses of the two crystal structures were carried out at the same time and it was found convenient to start with the $0kl$-zone of the oxalyl bromide compound and to take advantage of the fact that the contribution to the intensities from the halogen atoms is here considerably larger than in the oxalyl chloride compound. Patterson syntheses followed by successive Fourier syntheses were carried out also for the $hk0$-zones. Additional intensity data were obtained from precession diagrams in order
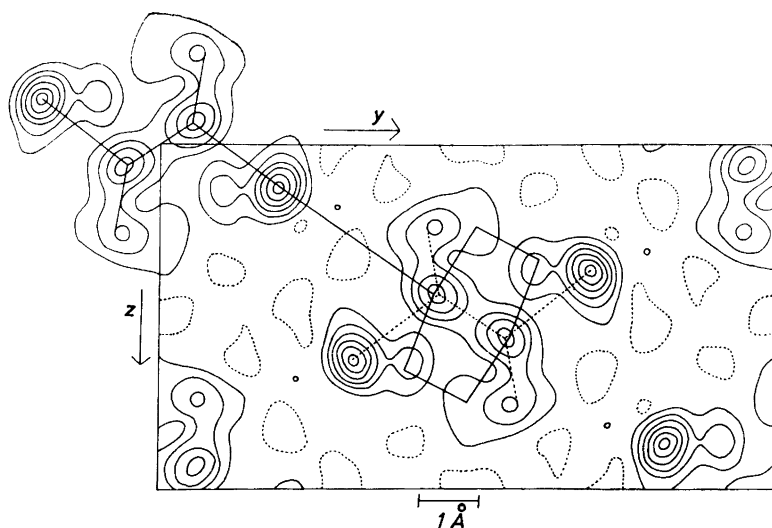

Fig. 1. Electron density projection along the *a*-axis of the oxalyl chloride compound. Contour intervals of 4 e.$Å^{-2}$.

Table 4.

a. Observed and calculated structure factors for 1,4-dioxan-oxalyl chloride
$hk0$-projection

h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c
0	2	42	37	2	7	< 5	−1	4	8	10	−8
0	4	4	6	2	8	12	−9	4	9	8	8
0	6	5	−6	2	9	< 5	1	4	10	8	7
0	8	36	−33	2	10	15	13	5	0	< 5	0
0	10	11	9	2	11	7	−7	5	1	8	−9
0	12	< 4	−4	2	12	6	−4	5	2	13	−16
1	0	44	46	3	0	29	31	5	3	12	14
1	1	< 3	−3	3	1	12	−12	5	4	< 5	−1
1	2	46	−40	3	2	7	−9	5	5	8	8
1	3	12	12	3	3	11	13	5	6	< 5	−1
1	4	14	8	3	4	< 4	1	5	7	6	−7
1	5	< 4	−1	3	5	9	8	5	8	7	−6
1	6	14	13	3	6	20	18	5	9	5	5
1	7	10	−8	3	7	5	−5	6	0	9	10
1	8	28	−26	3	8	13	−13	6	1	6	−8
1	9	< 4	0	3	9	8	8	6	2	< 5	1
1	10	8	5	3	10	6	5	6	3	12	11
1	11	< 5	−1	3	11	6	−3	6	4	< 5	−1
1	12	6	−3	4	0	24	28	6	5	9	9
2	0	16	17	4	1	21	−22	6	6	< 5	−2
2	1	< 3	3	4	2	8	−8	6	7	< 6	−4
2	2	52	−52	4	3	7	−7	7	0	< 5	−3
2	3	29	34	4	4	< 5	0	7	1	5	−8
2	4	16	−11	4	5	6	−5	8	0	6	−5
2	5	25	24	4	6	< 5	−1	8	1	5	−7
2	6	14	14	4	7	10	−10				

$0kl$-projection

k	l	F_o	F_c	k	l	F_o	F_c	k	l	F_o	F_c
1	1	60	63	10	2	< 6	−4	8	4	9	11
2	1	9	−8	11	2	14	−12	9	4	< 6	−1
3	1	19	−15	12	2	< 5	−1	10	4	9	−8
4	1	54	52	1	3	< 5	−1	1	5	8	−10
5	1	14	12	2	3	15	−12	2	5	21	23
6	1	< 5	1	3	3	25	25	3	5	7	8
7	1	22	−21	4	3	20	22	4	5	< 7	0
8	1	< 6	7	5	3	17	−16	5	5	< 7	0
9	1	< 6	−4	6	3	< 6	−1	6	5	12	13
10	1	< 7	0	7	3	< 7	1	7	5	9	8
11	1	< 6	3	8	3	10	9	8	5	< 6	−1
12	1	14	−14	9	3	< 6	−3	9	5	< 6	−2
0	2	20	−18	10	3	< 5	1	0	6	8	9
1	2	42	−41	11	3	10	−7	1	6	10	14
2	2	10	−8	0	4	11	−12	2	6	8	−9
3	2	24	23	1	4	10	11	3	6	< 6	−1
4	2	< 5	−4	2	4	23	28	4	6	< 6	−1
5	2	20	20	3	4	16	17	5	6	< 5	0
6	2	< 5	−4	4	4	< 6	3	6	6	< 5	−2
7	2	10	−8	5	4	9	11	1	7	< 5	0
8	2	8	−6	6	4	7	−9	2	7	< 5	2
9	2	20	17	7	4	8	3	3	7	5	−8

b. Observed and calculated structure factors for 1,4-dioxan-oxalyl bromide

hk0-projection

h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c
0	2	12	−16	2	8	26	−25	4	9	18	18
0	4	22	22	2	9	18	18	4	10	<11	6
0	6	15	15	2	10	26	25	4	11	<11	−9
0	8	56	−51	2	11	13	−10	4	12	<10	−3
0	10	29	26	2	12	12	−9	5	0	<10	0
0	12	13	−13	2	13	<11	2	5	1	22	−32
0	14	19	−4	3	0	54	54	5	2	12	−10
1	0	110	108	3	1	48	−52	5	3	20	23
1	1	25	−27	3	2	26	−29	5	4	<10	−1
1	2	84	−88	3	3	21	25	5	5	<10	4
1	3	21	20	3	4	26	23	5	6	<10	2
1	4	25	24	3	5	11	10	5	7	12	−13
1	5	< 7	−4	3	6	18	22	5	8	<11	−9
1	6	27	30	3	7	19	−16	5	9	12	15
1	7	16	−17	3	8	20	−25	5	10	<10	1
1	8	49	−48	3	9	22	22	6	0	<10	2
1	9	<10	3	3	10	15	9	6	1	14	−21
1	10	25	19	3	11	12	−10	6	2	<10	−4
1	11	<11	−9	3	12	12	−5	6	3	14	16
1	12	14	−9	3	13	<11	4	6	4	<10	−1
1	13	<11	0	4	0	38	38	6	5	<11	8
2	0	73	71	4	1	42	−47	6	6	<10	−2
2	1	45	−36	4	2	<10	−6	6	7	<10	−6
2	2	85	82	4	3	<10	10	6	8	<10	0
2	3	53	49	4	4	<10	5	7	0	<10	−4
2	4	< 6	7	4	5	<10	−6	7	1	<10	−7
2	5	28	25	4	6	<10	0	8	0	<10	−6
2	6	21	21	4	7	20	−21	8	1	<10	−9
2	7	16	−10	4	8	10	−9				

0kl-projektion

k	l	F_o	F_c	k	l	F_o	F_c	k	l	F_o	F_c
1	1	67	77	11	2	24	−23	9	4	17	−14
2	1	51	−43	12	2	< 9	1	10	4	18	−21
3	1	42	−36	13	2	< 8	2	11	4	< 7	6
4	1	93	95	1	3	23	−22	1	5	< 9	−6
5	1	49	42	2	3	20	−18	2	5	32	37
6	1	39	−36	3	3	55	60	3	5	<10	4
7	1	42	−37	4	3	24	25	4	5	17	−23
8	1	23	21	5	3	47	−48	5	5	< 9	3
9	1	<10	−4	6	3	18	−7	6	5	28	34
10	1	10	5	7	3	43	31	7	5	14	4
11	1	12	7	8	3	36	16	8	5	13	−11
12	1	22	−23	9	3	<10	−7	9	5	< 7	2
13	1	12	−14	10	3	< 9	6	0	6	< 9	8
0	2	41	−41	11	3	16	−16	1	6	15	21
1	2	78	−91	12	3	< 7	4	2	6	17	−25
2	2	12	12	0	4	33	−43	3	6	< 9	−4
3	2	50	50	1	4	34	34	4	6	< 8	1
4	2	< 7	−8	2	4	42	43	5	6	< 7	2
5	2	26	21	3	4	<10	−2	6	6	9	9
6	2	22	−8	4	4	13	−3	7	6	< 6	7
7	2	31	−26	5	4	11	8	1	7	< 8	3
8	2	15	9	6	4	12	−12	2	7	< 8	−2
9	2	41	45	7	4	24	20	3	7	< 7	−14
10	2	15	−14	8	4	20	25				

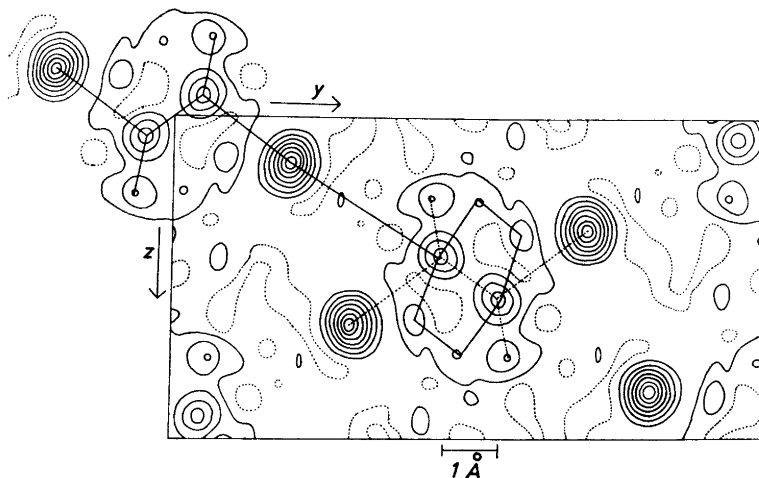*Fig.* 2. Electron density projection along the *a*-axis of the oxalyl bromide compound. Contour intervals of 8 e.$Å^{-2}$ for bromine atoms, 4e.$Å^{-2}$ for the lighter atoms.

to check the assumed mutual orientation of the *a* and *c* axes. The corresponding Fourier projections were not refined, because of the serious overlapping of atoms in these projections, but even here a satisfactory agreement between calculated and observed structure factors was achieved.

Using the preliminary coordinate values thus obtained and consulting the model of the free dioxan molecule derived by electron diffraction work [6] the final refinement of the two structures was performed by least-squares procedures. The atomic coordinates thus arrived at are listed in Table 2 which also contains standard deviation values and isotropic damping factors (*B*). Table 3 contains interatomic distances and valence angles, and in Table 4 observed and calculated structure factors are listed. Figs. 1 and 2 show the Fourier projections along the *a* axis for the chlorine and the bromine compound, respectively. In Fig. 3 a schematical drawing demonstrates the chains of alternating dioxan and halide molecules running along the [111]-direction.

The probable accuracy of the two-dimensional analysis is somewhat greater for the oxalyl chloride than for the oxalyl bromide compound.
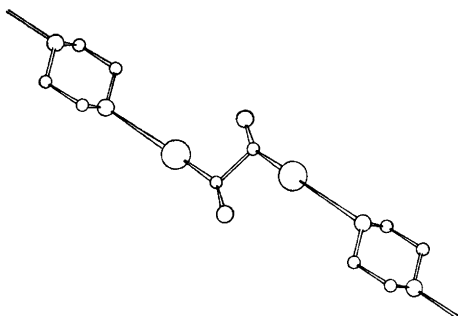

Fig. 3. Schematical drawing illustrating the chains of alternating oxalyl halide and dioxan molecules.

CONCLUSIONS

In both structures chains of alternating dioxan and oxalyl halide molecules are found to be present. It appears obvious that bonds are formed between oxygen and halogen atoms and approximately linear arrangements O———Br—C are indeed present. The O——Hal distance is nearly the same in the two compounds as might also have been expected because the bond in question should be stronger for a bromine than for a chlorine atom. In the chlorine compound, however, the bond length is nearly that expected for a van der Waals interaction whereas a significant shortening is observed in the oxalyl bromide compound. It may be pointed to the observation that bonds of a similar length between (carbonyl) oxygen and bromine are found in the crystal structure of oxalyl bromide itself but not in the structure of oxalyl chloride.[5]

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