The Structure of Bromine 1,4-Dioxanate

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The structure of the solid compound containing equal numbers of bromine and 1,4-dioxan molecules has been determined by X-ray analysis. The monoclinic structure — space group C_{2h}^3-C2/m — is based on a *c*-centered unit cell containing *two* molecules of each species and having the dimensions: $a = 9.65$, $b = 9.05$, $c = 4.25$. The β angle is 91.4°. It was not necessary to take advantage of the fact that the corresponding iodine compound has a similar unit cell in order to derive approximate coordinates for the bromine atoms. The signs of the structure factors derived from these bromine coordinates alone were used when carrying out the Fourier syntheses which led to the electron density maps reproduced in Fig. 1. The calculation of the signs of structure factors using atomic coordinates of bromine, oxygen and carbon derived from these maps did not alter any of the signs used in the *c*-axes synthesis. The atomic coordinates are:

Br	$x = 0.1125$,	$y = 0$,	$z = 0.100$
O	$x = 0.3795$,	$y = 0$,	$z = 0.319$
C	$x = 0.422$,	$y = 0.133$,	$z = 0.466$

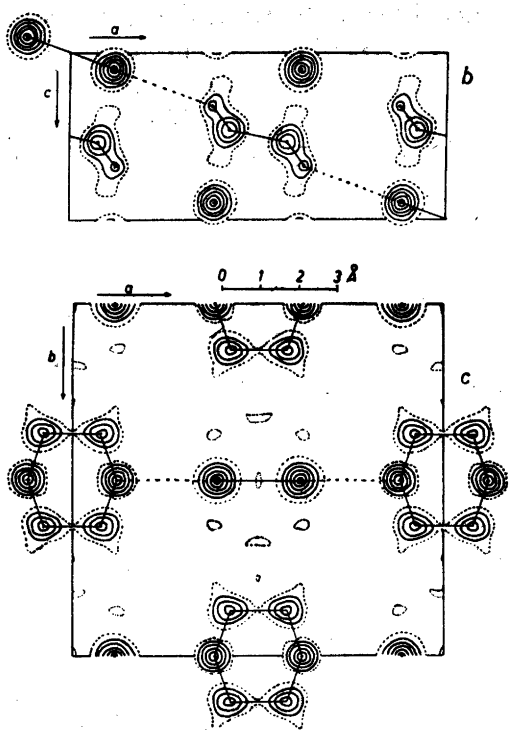

Fig. 1. Electron density maps projected: b. along b *axis, c. along* c *axis. Interval between drawn contour lines about six times larger for bromine than for carbon and oxygen atoms.*

The Br-Br distance within the bromine molecule is found equal to 2.31 Å, a value slightly larger than that of the free molecule (2.28). The line joining the oxygen atoms of two neighbouring dioxan rings contains the two bromine atoms of a Br_2 molecule. The O-Br distance is only 2.71 Å. This is the most striking feature of the whole structure as it indicates a very strong interaction between the bromine and oxygen atoms. The O-Br bond is *not* situated in the plane containing the oxygen atom and the two adjacent carbon atoms. The consequences of these findings will be discussed in a forthcoming, more detailed publication.

Taking into account the dominating influence of the bromine atoms on the diffraction of the X-rays it cannot be expected that the coordinates of the carbon or oxygen atoms are very accurate. Nevertheless the observed distances and angles within the ("chair"-formed) dioxan ring appear rather acceptable: C—C = 1.54, C—O = 1.41 and the angles C—C—O and C—O—C 111° and 116.6°, respectively.

In order to establish whether the structures of molecular compounds between 1,4-dioxan and halides of electropositive elements are based also on strong interaction between halogen and oxygen, work has been started on such compounds. Preliminary results indicate that the structure of the compound with mercuric chloride may have a structure resembling the structure of the bromine compound.

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