Lengths of Bonds Connecting Group VI Atoms and Iodine Atoms in Addition Compounds

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A number of solid compounds formed by donor molecules and halide molecules are known and their crystal structures have been determined in some cases, particularly for compounds in which iodine derivatives of hydrocarbons act as acceptors. It has thus been possible to formulate general principles determining the atomic arrangement, and the prediction of new compounds and even of their structure have become possible. In this connection observed distances between donor atom and iodine are of interest. We present in a table a set of such distances and include some figures which have not previously been published.

1. Oxygen-iodine distances:	
1,4-dioxan · I.	2.81 Å
1,4-dioxan · CHI.	2.94 Å
cyclohexane-1,4-dione $\cdot C_2I_3$	2.93 Å
2. Sulphur-iodine distances:	
$1,4$ -dithiane $\cdot 2I_2$	2.87 Å ¹
1,4-dithiane · CoI.	$3.26 \; { m \AA}$
$1,4$ -dithiane · CHI_3	3.32 Å 4
3. Selenium-iodine distances:	
1,4-diselenane · 2I,	2.83 Å 2
1,4-diselenane · C.I.	3.35 Å
,	(3.47 Å ⁵
$1,4$ -diselenane · $2CHI_3$	3.51 Å
$1,4$ -diselenane · C_2I_4	3.43 Å

It appears that the nature of the atom responsible for the donor properties is of much greater importance than is the chemical constitution of the donor molecule. The structure of the acceptor molecule, whether it is derived from a saturated aliphatic hydrocarbon, an olefinic or acetylenic hydrocarbon, also appears to be of secondary importance for the donor atom-iodine distance.

The only structure determination familiar to us which does not fit into a scheme based on such considerations is that reported for the 1,4-dioxan-diiodoacetylene compound which leads to an oxygen-iodine separation of only 2.65 Å, a value about 0.25 Å shorter than expected. However, the value obtained in the same investigation for the distance between the two iodine atoms in the diiodo-acetylene molecule is shorter than 5 Å, a value which is somewhat difficult to accept. In two independent electron diffraction analyses the values 5.15 resp. 5.16 Å were obtained, and values found in X-ray investigations of addition compounds are all in the range between 5.13 and 5.17 Å.

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- Chao, G.Y. and McCullough, J.D. Acta Cryst. 13 (1960) 727.
- Chao, G.Y. and McCullough, J.D. Acta Cryst. 14 (1961) 940.
- Groth, P. and Hassel, O. Acta Chem. Scand. 19 (1965) 1733.
- Bjorvatten, T. and Hassel. O. Acta Chem. Scand. 15 (1961) 1429.
- Bjorvatten, T. Acta Chem. Scand. 17 (1963) 2292.
- Gagnaux, P. and Susz, B.-P. Helv. Chim. Acta 43 (1960) 948.

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