

## Interatomic Distances in Complexes Formed by n Donor Molecules and Iodine or its Monohalides

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Interatomic distances in trihalide ions and in n donor—IX complexes (X halogen) have been considered and “effective radii” of the iodine atom along its two bond directions discussed. A simple relationship between these radii has been shown to exist, which may serve as a basis for characterizing the strength of the charge-transfer bonds in question.

Crystal structures of a number of solid compounds formed by n donor molecules with halogen and interhalogen molecules have been investigated during the last fifteen years. In some cases isolated complexes like those expected to be present in solution have been observed in the crystalline state, in other cases further charge-transfer bonding leads to the formation of larger units and even of infinite chains. Comparatively simple rules could be formulated for the atomic arrangement due to bond formation and some indications of the donor atom-halogen and halogen-halogen distances to be expected in such compounds. As pointed out to us by Professor O. Foss the evaluation of the distance between the donor atom and the next nearest halogen atom in simple complexes or between two donor atoms connected by a halogen molecule bridge may be predicted with considerable success by attributing particular radii to halogen atoms involved in charge-transfer bonding, radii midway between covalent and van der Waals radii.

This procedure does not take into consideration the strength of the charge-transfer bond and refers to overall distances along the linear arrangement of the donor and the halogen atoms. Conspicuous is, however, a decrease in the donor-halogen separation and a lengthening of the halogen-halogen bond with increasing strength of the charge-transfer bond proper. Our discussion took advantage of the undeniable analogy existing between the bonding in trihalide ions and in the charge-transfer complexes here under consideration. The most extensive experimental material available is related to ions and complexes in which iodine is the “centre atom” and thus bonded to either two halogen atoms or to one n donor and to another halogen atom.

Trihalide ions with iodine as the centre atom and two halogen ligands of the same kind may be either symmetrical or non-symmetrical, the overall length of the ion being a little larger in the latter case. Of the two iodine-halogen distances one is larger than in the symmetrical ion, the other shorter, but not so much shorter that the overall length of the two types of ions is the same. In symmetrical ions the centre iodine atom appears to be nearly neutral and the two ligand atoms therefore both carry a negative charge of about 0.5 e.U. The net charges on the two ligand atoms are not the same in a non-symmetrical ion; the ligand atom nearest to the centre atom apparently carries a smaller negative charge than the second ligand atom. The effective "radius" of the centre atom in the direction pointing towards the more negative ligand atom is therefore larger than its "radius" in the opposite direction.

Both in trihalide ions and in complexes formed with IX molecules (X halogen) "effective radii"  $R_1$  and  $R_2$  of the iodine atom were evaluated by subtracting accepted covalent radii of the two atoms directly bonded to it from the observed interatomic distances. In a symmetrical trihalide ion the two values so obtained are of course identical, and are actually the same for the  $I_3^-$  and  $ICl_2^-$  ions = 2.90—1.33, resp., 2.55—0.99. In non-symmetrical

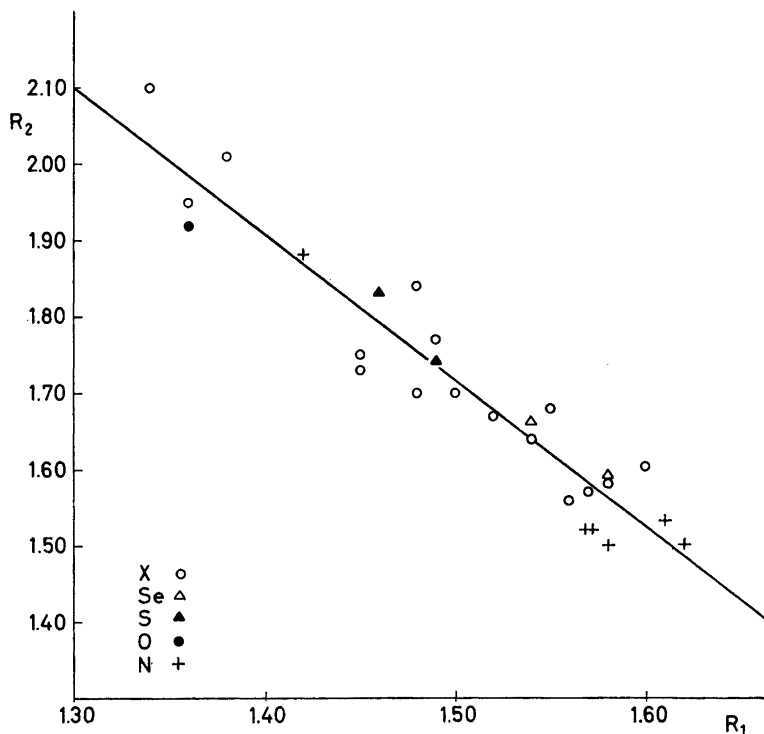


Fig. 1. "Effective radii"  $R_1$  and  $R_2$  of iodine as centre atom in trihalide ions and in IX complexes.

trihalide ions the effective radius of the central atom in the direction towards the more negative halogen atom is larger than 1.57 Å and in the opposite direction smaller than 1.57 Å. The extreme asymmetric arrangement is not observed in trihalide ions, however, but appears to be realized in the  $I_9^-$  ion.<sup>4</sup>

In n donor complexes formed with IX molecules a comparatively weak bonding results if oxygen is the donor atom. In such complexes the oxygen atom may be assumed to occupy the position corresponding to the more negative halogen ligand in non-symmetrical trihalide ions with the effect that the oxygen-iodine distance becomes comparatively large, the I—X distance, however, only slightly longer than the distance in the free IX molecule. At the other end of the sequence of donor molecule-IX complexes one finds the stronger complexes formed between tertiary amines and IX molecules. In these complexes the nitrogen atom appears to occupy a position corresponding to that of the less negative halogen ligand in non-symmetrical trihalide ions. The result is a lengthening of the I—X and a short N—I distance and probably a net charge on the X atom that even for X = I surpasses 0.5 e.U. This assumption is in harmony with the fact that halogen molecule bridges have never been observed between amino nitrogen atoms.

Table 1. Interatomic distances,  $R_1$  and  $R_2$  in complexes and ions with iodine as centre atom.

Compound	I—A (Å)	I—B (Å)	$R_2$	$R_1$	Ref.
As(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ·I <sub>3</sub>	I—I = 2.90	I—I = 2.90	1.57	1.57	1
NH <sub>4</sub> ·I <sub>3</sub>	I—I = 3.10	I—I = 2.82	1.77	1.49	5
Cs·I <sub>3</sub>	I—I = 3.03	I—I = 2.83	1.70	1.50	2
N(CH <sub>3</sub> ) <sub>4</sub> ·I <sub>5</sub>	I—I = 3.17	I—I = 2.81	1.84	1.48	6
N(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> ·I <sub>7</sub>	I—I = 2.91	I—I = 2.91	1.58	1.58	7
N(CH <sub>3</sub> ) <sub>4</sub> ·I <sub>9</sub>	I—I = 3.43	I—I = 2.67	2.10	1.34	4
(C <sub>2</sub> H <sub>5</sub> N)I·I <sub>7</sub>	I—I = 2.93	I—I = 2.93	1.60	1.60	8
Cs <sub>2</sub> I <sub>3</sub>	I—I = 3.00	I—I = 2.85	1.67	1.52	9
(CH <sub>3</sub> ) <sub>4</sub> N·ICl <sub>2</sub>	I—Cl = 2.55	I—Cl = 2.55	1.56	1.56	3
C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> ·2ICl <sub>2</sub>	{ I—Cl = 2.67	{ I—Cl = 2.54	1.68	1.55	10
	{ I—Cl = 2.63	{ I—Cl = 2.53	1.64	1.54	
C <sub>4</sub> N <sub>2</sub> H <sub>8</sub> ·2ICl <sub>2</sub>	I—Cl = 2.69	I—Cl = 2.47	1.70	1.48	11
α-ICl	{ I—I = 3.08	{ I—Cl = 2.44	1.75	1.45	12
	{ I—Cl = 3.00	{ I—Cl = 2.37	2.01	1.38	
β-ICl	{ I—I = 3.06	{ I—Cl = 2.44	1.73	1.45	13
	{ I—Cl = 2.94	{ I—Cl = 2.35	1.95	1.36	
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> ·2ICl	I—O = 2.57	I—Cl = 2.35	1.92	1.36	14
C <sub>4</sub> H <sub>8</sub> S <sub>2</sub> ·2I <sub>2</sub>	I—S = 2.87	I—I = 2.79	1.83	1.46	15
C <sub>4</sub> H <sub>14</sub> S·I <sub>2</sub>	I—S = 2.78	I—I = 2.82	1.74	1.49	16
C <sub>4</sub> H <sub>8</sub> Se <sub>2</sub> ·2I <sub>2</sub>	I—Se = 2.83	I—I = 2.87	1.66	1.54	17
C <sub>4</sub> H <sub>8</sub> Se·I <sub>2</sub>	I—Se = 2.76	I—I = 2.91	1.59	1.58	18
(CH <sub>3</sub> ) <sub>3</sub> N·I <sub>2</sub>	I—I = 2.83	I—N = 2.27	1.50	1.58	19
CH <sub>3</sub> ·C <sub>3</sub> H <sub>7</sub> N·I <sub>2</sub>	I—I = 2.83	I—N = 2.31	1.50	1.62	20
C <sub>5</sub> H <sub>5</sub> N·ICl	I—Cl = 2.51	I—N = 2.26	1.52	1.57	21
(CH <sub>3</sub> ) <sub>3</sub> N·ICl	I—Cl = 2.52	I—N = 2.30	1.53	1.61	22
C <sub>5</sub> H <sub>5</sub> N·IBr	I—Br = 2.66	I—N = 2.26	1.52	1.57	23
C <sub>5</sub> H <sub>5</sub> N·ICN	I—N = 2.57	I—C = 2.11	1.88	1.42	23

In Fig. 1 "effective radii"  $R_1$  and  $R_2$  of the iodine atom are plotted as abscissa and ordinate. The covalent radii employed in the calculations (in Å) are: I 1.33; Br 1.14; Cl 0.99; C (in CN) 0.69; N 0.69; O 0.65; S 1.04, and Se 1.17.

Table 1 contains the data on which Fig. 1 is based. The cross at  $R_1 = 1.42$ ,  $R_2 = 1.88$  represents the weak pyridine-iodine cyanide complex. For the dioxan-2 ICl complex distances derived by a refinement of the structure were used.

Taking into account probable errors in the interatomic distances the approach to a simple linear relation between  $R_1$  and  $R_2$  appears convincing. The equation obtained by a least squares computation is:

$$R_2 = -1.97 R_1 + 4.59$$

From Fig. 1 it is further seen that points representing the weakest complexes formed by n donor molecules and IX molecules are found in the top left part of the diagram, those representing the strongest complexes bottom right.

A discussion of ions and complexes in which bromine is the centre atom would be of interest, but unfortunately the experimental material available is still too incomplete for this purpose.

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