QUARTERLY REVIEWS

DIRECT STRUCTURAL EVIDENCE FOR WEAK CHARGE-TRANSFER BONDS IN SOLIDS CONTAINING CHEMICALLY SATURATED MOLECULES

By O. HASSEL and CHR. RØMMING

(DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OSLO, BLINDERN, NORWAY)

A NUMBER of addition compounds formed by two molecular species each of which is usually regarded as being chemically "saturated" have been known for many years. In some cases the mechanism leading to their formation appears rather straightforward because one of the molecular species contains atoms known to be able to extend their valency shell to include a larger number of electrons than that present in the same atom in its original state. Such molecules are often described as "electron acceptors" or simply "acceptors"[1] and belong to the class of Lewis acids. If the other molecular species contains atoms in which "lone pairs" of electrons are present this molecule may have "electron donor" properties. A dative covalent bond between the donor and the acceptor molecule may then be formed, in some cases sufficiently stable to exist not only in the solid state and in solution but even in the vapour state. Among the best known examples of the latter kind are the addition compounds formed by the trihalides of boron with, *e.g.*, ammonia, amines, and some oxygen-containing molecules. Numerous addition compounds of this kind have been prepared and it has often been possible to study their dissociation equilibria in solution and sometimes in the vapour at varying temperatures and concentrations, and thus to determine the enthalpy changes accompanying the formation of the addition compound. The molecular structure of the boron halide compounds has been determined in some cases by direct methods, and the structures actually correspond to those which would be expected if a covalent bond is established between the electron donor atom and the boron atom, the latter possessing a tetrahedral arrangement of ligands in the addition compounds.

It is easy to understand that chemists have often favoured concepts according to which the formation of addition compounds by donor molecules like those mentioned above, even with partner molecules not containing electron sextet atoms, is regarded as more or less analogous to the process leading to the formation of the boron halide compounds. They have thus been inclined to regard the rôle of the two reaction partners as that of a Lewis base and a Lewis acid respectively.

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[1] The terms "electron donor" and "electron acceptor" were introduced by Sidgwick ("The Electronic Theory of Valency," Oxford, 1929); an extended definition is however given by Mulliken, *J. Phys. Chem.*, 1952, **56**, 801.

More than half a century ago the structures of the addition compounds formed by amines and halogens were discussed by A. Hantzsch.[2] He pointed out that the nitrogen atom in these compounds should not be regarded as quinquevalent and thus as forming bonds with both halogen atoms, but rather as in salt-like compounds containing a halogen-substituted ammonium cation and a halogen anion.

The study of addition complexes formed in solutions and liquid mixtures originated in observations of the striking colour difference observed between solutions of iodine in different solvents so familiar to every chemist for a very long time. A number of solvents like aliphatic hydrocarbons, carbon disulphide, carbon tetrachloride, and chloroform give violet solutions the colour of which resembles that of iodine vapour. Solutions of iodine in acetone, alcohols, ethers, amines, and benzene, on the other hand, are brown or reddish brown.

A survey of the more important investigations up to 1948 which relate to solutions of iodine in different solvents has been published by Kleinberg and Davidson.[3] It is stated that iodine is diatomic in all solutions, but that it is linked to solvent molecules in equilibrium with free iodine molecules in the brown solutions. In solvents which give brown solutions the solvent molecule contains a chemical element capable of forming co-ordinate covalent bonds. The iodine is in this case chemically more reactive than in the violet solutions.

In 1949 Brackman[4] discussed in general terms the colour effects produced in liquid mixtures of different molecules now designated as Lewis acids (including the halogens) and nucleophilic substances including aromatic hydrocarbons. The colour effects are attributed to "complex resonance," which is defined as a covalent binding between two molecules the character of which is intermediate "between that of a single bond and no bond at all." Brackman stresses the fact that absorption bands are observed in the spectra of the mixtures which are not found for the pure components and which must be attributed to a complex formed between them.

Spectrophotometric measurements dealing with solutions of iodine in benzene and in some benzene derivatives have been carried out by Benesi and Hildebrand[5,6] who also report new absorption bands in the ultraviolet region. From these measurements they were able to determine the equilibrium constants of the 1:1 addition reactions. A fair amount of spectrophotometric measurement in solutions has been carried out by other investigators using the Benesi–Hildebrand method or a modification of it, and values of the enthalpy and entropy changes accompanying the complex formation have been determined.

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[2] Hantzsch, *Ber.*, 1905, **38**, 2161.

[3] Kleinberg and Davidson, *Chem. Rev.*, 1948, **42**, 601.

[4] Brackman, *Rec. Trav. chim.*, 1949, **68**, 147.

[5] Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1948, **70**, 2832.

[6] Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

Molar ΔH-values for the formation of addition complexes in solution are of considerable interest when trying to compare the relative strengths of bonds between donor and acceptor molecules. From figures quoted in the literature it follows that the value for the iodine complex of benzene is somewhat below 1 kcal., the values for ethers ranging from 3·5 to 6 kcal.[7] Larger values are found in the case of amines, from 7 to 12 kcal.[8]

A quantum mechanical theory of the complex resonance has been worked out by Mulliken.[9] In this theory a resonance between a "no-bond" structure (D,A) and a dative structure (D^+–A^-) is postulated. Here D denotes the donor and A the acceptor molecule. The contribution from the first-mentioned structure to the wave function describing the charge-transfer complex is believed to be much greater than the contribution from the "dative" structure, at least if we restrict our considerations to the "loose" complexes with which we are concerned in the present review. A remarkable consequence of this theory is the existence of an excited state of the complex and an electronic absorption spectrum corresponding to transitions from the ground state to the excited state just mentioned. According to Mulliken's approximate computation this absorption spectrum ("charge-transfer spectrum") which cannot be attributed to either of the two components forming the complex should give rise to very high absorption intensities. It might be added that, according to the theory, charge-transfer resonance requires the wave functions of the "no-bond" and "dative" structure to belong to the same group-theory symmetry class. This restriction should in special cases be of some help when discussing the configuration to be expected for a charge-transfer complex.

The infrared absorption spectra have also served as a basis for suggestions of models of the complexes formed by halogens and a series of donor molecules. Reid and Mulliken[10] were led to the assumption that in the pyridine–iodine complex one of the iodine atoms is directly linked to the nitrogen atom and situated in the plane of the pyridine ring, whereas the second halogen atom which is believed to carry a negative charge is attracted to the (positively charged) nitrogen atom and situated in a plane perpendicular to that of the pyridine ring (Fig. 1). In the case of donor atoms possessing two lone pairs (oxygen in ethers or ketones) it is assumed[11] that both halogen atoms are linked to this atom in the same way. In the case of an ether, ROR′, the Hal–Hal axis was believed to be perpendicular to the C–O–C plane, in the case of a ketone it was believed to be situated in the plane containing the C–C(:O)–C arrangment (Fig. 2). Against models in which both halogen atoms are bonded to a particular donor

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[7] de Maine, *J. Chem. Phys.*, 1957, **26**, 1192, 1199.

[8] Yada, Tanaka, and Nagakura, *Bull. Chem. Soc. Japan*, 1960, **33**, 1660.

[9] Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, and later publications. For review articles see Andrews, *Chem. Rev.*, 1954, **54**, 713; McGlynn, *ibid.*, 1958, **58**, 1113.

[10] Reid and Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 3869.

[11] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600.

atom the argument has been raised[12] that they would involve improbably small angles donor–halogen–halogen and halogen–donor–halogen. Nevertheless, such models have sometimes been presented (*e.g.*, ref. 13) as more or less conclusive in textbooks or monographs.

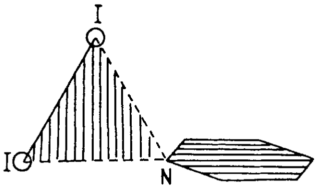

FIG. 1. *Model originally suggested*[10] *for the pyridine–iodine complex. (Reproduced with permission.)*

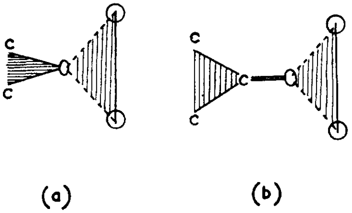

FIG. 2. *Models originally suggested*[11] *for the halogen complexes of* (a) *an ether,* (b) *a ketone. (Reproduced with permission.)*

Mulliken's original suggestion regarding the benzene–iodine complex was of an arrangement in which the axis of the iodine molecule is parallel to the benzene plane ("resting" model; Fig. 3a). This view could not be

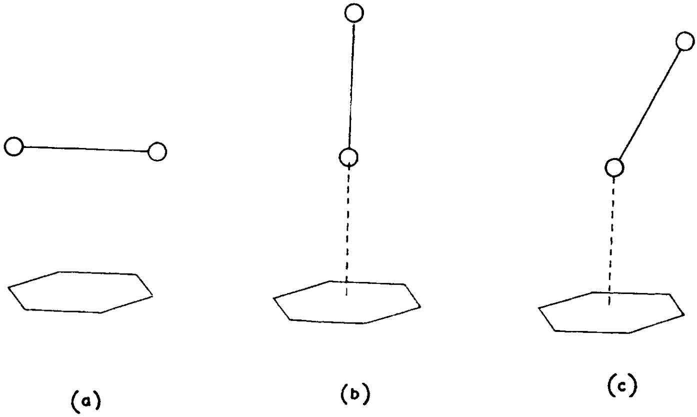

FIG. 3. (a) "*Resting*", (b) "*axial*", *and* (c) "*oblique*" *models of the benzene–halogen complex.*

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[12] Hassel, *Svensk Kem. Tidskr.*, 1960, **72**, 88.

[13] Sneed, Maynard, and Brasted, "Comprehensive Inorganic Chemistry, III, The Halogens," New York, 1954.

substantiated, however, by Collin and D'Or[14] who have carried out infrared spectroscopic work on the benzene–chlorine complex, and Mulliken[15] subsequently suggested an "oblique" model (Fig. 3c) in which one iodine atom is placed on the chief axis of the benzene molecule. Further infrared investigations by Ferguson[16] seemed to be strongly in favour of the "axial" model (Fig. 3b) in which both iodine atoms lie on the benzene chief axis, which thus retains its six-fold symmetry. The question has been reviewed by McGlynn.[17]

It is interesting to note that even complexes formed by molecular species (*e.g.* 1,4-dioxan and iodine, or benzene and iodine) both lacking dipole moments have sometimes been found to exhibit appreciable dipole moments.[18] It thus appears very likely that bonds established between a halogen molecule and some of the molecular species mentioned above are closely associated with a transfer of electronic charge from one of the two partners (the donor) to the other (the acceptor). In the complexes formed by Lewis bases like amines or ethers with a halogen molecule it is now generally believed that negative charge is transferred from the nitrogen or oxygen atom to the halogen molecule. The idea that one of the iodine atoms should, before forming a bond to the donor atom, be in a sextet configuration[19] (I^+I^-) would be likely to imply that in the complex the iodine atom which is not directly linked to the donor atom would carry a negative charge. Although indications exist that in pyridine a conducting solution is produced by addition of iodine, it appears very questionable whether or not a strong negative charge on one of the iodine atoms may in general be expected in the complex. The existence of "halogen molecule bridges" between oxygen or nitrogen atoms (see below) does not appear to conform with the assumption of a marked negative charge on the halogen not linked to the donor atom.

In order to be able to draw advantage from the more direct interferometric methods, particularly those with *X*-rays or neutron beams, it was felt that crystal structure analyses should be carried out on solid addition compounds expected to exhibit weak charge-transfer bonds. Since 1954 a number of papers dealing with compounds corresponding to the "loose" complexes mentioned above have appeared, and the aim of this article is to sum up the results so far obtained regarding the atomic arrangements in the solid state and to discuss their significance for the "charge-transfer" bond.

It should be emphasised that in many cases crystallographic investigation of addition compounds involves single-crystal work at well below room temperature, in some cases even at very low temperatures which may

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[14] Collin and D'Or, *J. Chem. Phys.*, 1955, **23**, 397.

[15] Mulliken, *J. Chem. Phys.*, 1956, **23**, 397.

[16] Ferguson, *J. Chem. Phys.*, 1956, **25**, 577 and later publications.

[17] McGlynn, *Chem. Rev.*, 1958, **58**, 113.

[18] Syrkin and Anisimova, *Doklady Akad. Nauk. S.S.S.R.*, 1948, **59**, 1457; *Chem. Abs.*, 1948, 6593.

[19] Ketelaar, "Chemical Constitution," Amsterdam, 1953, p. 343.

mean that it is very difficult to obtain crystals comparable in quality to those easily obtainable from crystals melting above room temperature. In some cases therefore, the investigators have been obliged to content themselves with intensity measurements which would perhaps not have been considered quite satisfactory in the case of ordinary-temperature work dealing with really good crystals. On the other hand the work on addition compounds containing one of the two heavier halogens has the advantage that it makes possible the use of the "heavy atom method", and thus facilitates the first steps of the structure determination. Many addition compounds with a melting point well above room temperature are comparatively unstable, however, and some of them are characterised by large amplitudes of thermal vibrations of the atoms (sometimes anisotropic) which also makes it desirable to carry out the *X*-ray work at low temperatures. The accuracy actually obtained in two-dimensional *X*-ray studies may in general be expected to be of the order 0·02—0·03 Å for the halogen–halogen distances and better than 0·1 Å in the case of halogen–donor distances.

Halogen Compounds of Ethers, Ketones, and Sulphides

The first halogen addition compound to be selected for *X*-ray investigation was the 1:1 compound formed by 1,4-dioxan with bromine.[20] The crystal structure investigation revealed the presence of endless chains consisting of alternating dioxan and bromine molecules, and "halogen molecule bridges" between ether oxygen atoms belonging to the nearest dioxan neighbours within a particular chain. The arrangement oxygen–bromine–bromine–oxygen is linear (Fig. 4). The Br–Br distance was found to be only slightly larger than that observed in the free bromine molecule, the oxygen–bromine separation (2·71 Å) being intermediate between the values expected for a van der Waals contact and a covalent bond. The direction of the O–Br bond relative to the dioxan molecule corresponds roughly to one of the equatorial C–H bond directions in cyclohexane. This is not very surprising if the electron cloud representing one of the lone pairs present in the ether oxygen atom is responsible for the O–Br bond which is obviously present in the addition compound. The most surprising result of the investigation is perhaps the fact that both atoms belonging to a particular bromine molecule may simultaneously be involved in bond formation with oxygen atoms. It has been shown that

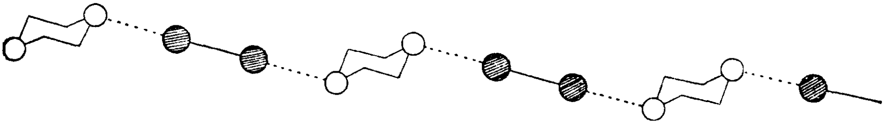

FIG. 4. 1,4-*Dioxan–bromine compound.*

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[20] Hassel and Hvoslef, *Acta Chem. Scand.*, 1954, **8**, 873.

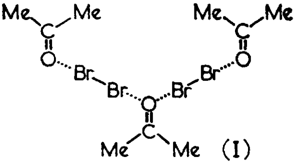
dioxan forms 1:1 addition compounds also with iodine and with chlorine and that the crystals of these compounds are isomorphous.[21] The halogen–oxygen bond lengths are not very different in those compounds, a fact which indicates that a bond to oxygen is stronger for a heavier than for a lighter halogen atom.

Facts are lacking, but it appears questionable whether or not structures resembling those just described may actually be obtained with molecules like iodine monochloride containing two different halogen atoms. The crystalline product most easily obtained when bringing together dioxan and iodine monochloride vapours contains the two molecular species in the proportion 1:2. In these crystals[22,23] bonds corresponding roughly to "equatorial" directions link iodine atoms to ether oxygen atoms, and the arrangement oxygen–iodine–chlorine is again linear or at least nearly so. According to observations made in the case of the dioxan–halogen compounds mentioned above it is not surprising that the ether oxygen atoms are linked to iodine rather than to chlorine in the dioxan,2ICl compound (compare the compound pyridine,ICl discussed below).

The observed halogen molecular bridges between ether oxygen atoms certainly show some similarity to the hydrogen bridges present in the dioxan–sulphuric acid (1:1) compound, the crystal structure of which contains infinite chains of alternating acid and ether molecules depending on comparatively strong hydrogen bonds between ether oxygens and the two hydroxyl-oxygen atoms of the sulphuric acid.[24]

This analogy between hydrogen and halogen molecular bridges will be brought out even more convincingly if the suggestion[12] is confirmed in the complete *X*-ray analysis that every oxygen atom in the compound $2CH_3{\cdot}OH,Br_2$ (m.p. −68°) is (tetrahedrally) linked to three neighbouring oxygens by two hydrogen bridges and one bromine molecule bridge.

The "halogen molecule bridges" of the dioxan–halogen addition compounds are not confined to halogen compounds formed by ethers but have been found also in the solid 1:1 addition compound formed by acetone and bromine.[25,26] The structure of this compound contains endless chains built up of alternating acetone and bromine molecules of type (I),



(I)

in which the atoms of the carbonyl groups and the bromine atoms are

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[21] Hassel and Strømme, *Acta Chem. Scand.*, 1959, **13**, 1775.
[22] Hassel and Hvoslef, *Acta. Chem. Scand.*, 1956, **10**, 138.
[23] Hassel, *Proc. Chem. Soc.*, 1957, 250.
[24] Hassel and Rømming, *Acta Chem. Scand.*, 1960, **14**, 398.
[25] Hassel and Strømme, *Nature*, 1958, **182**, 1155.
[26] Hassel and Strømme, *Acta Chem. Scand.*, 1959, **13**, 275.

coplanar. Here, also, the O–Br–Br–O arrangement is linear and the angle Br–O–Br is approximately "tetrahedral" (observed 110°) and the O–Br distance (2·82 Å) is again significantly shorter than the van der Waals radius sum, but a little larger than the O–Br distance (2·71 Å) observed in the dioxan–bromine compound. These findings are perhaps not surprising if the two lone pairs of each keto-oxygen atom are regarded as responsible for the bonds to the nearest bromine atoms, but it appears remarkable that both electron pairs are actually capable of forming such bonds simultaneously. The O–Br bonds are probably somewhat weaker than corresponding bonds where only one electron pair of the keto-oxygen atom is involved in charge-transfer bond formation.

TABLE 1. *Bond lengths* (Å) *in addition compounds with ethers, ketones, and sulphides as donor molecules.*

Compound	Charge-transfer bond	Bond length	Sum of van der Waals radii[27]	Hal–Hal bond length	Bond length in free Hal	Angle donor–Hal–Hal	Ref.
1,4-Dioxan,Br_2	O–Br	2·71	3·35	2·31	2·28	180°	20
1,4-Dioxan,2ICl	O–I	2·57	3·55	2·33	2·32	*	22, 23
1,4-Dioxan,Cl_2	O–Cl	2·67	3·20	2·02	1·99	178°	21
1,4-Dioxan,H_2SO_4	O–H–O	2·51 2·59					24
Acetone,Br_2	O–Br	2·82	3·35	2·28	2·28	180°	25, 26
Benzyl sulphide,I_2	S–I	2·78	4·00	2·82	2·67	179°	23, 28
1,4-Dithian,I_2	S–I	2·87	4·00	2·79	2·67	178°	29, 30
1,4-Diselenan,I_2	Se–I	2·83	4·15	2·87	2·67	180°	29, 31

*Approximately linear

Some halogen addition compounds formed by sulphides and their selenium analogues have also been investigated in the crystalline state. In the 1:1 compound benzyl sulphide–iodine the S–I–I arrangement was found to be linear and to form angles of about 100° with the two C–S bond directions.[23,28] The same type of atomic arrangement has also been found[29,30,31] in the 1:2 addition compounds formed by dithian and diselenan with iodine. It is noteworthy that the S–I distance is very nearly the same for the benzyl sulphide and dithian compounds (2·82 and 2·79 Å respectively) and that the I–I distance is approximately 0·2 Å larger than that observed in the free iodine molecule (cf. Table 1). A lengthening of the halogen–halogen bond distance of this magnitude is not observed in addition compounds in which oxygen is the electron donor, but appears to

[27] Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, 1960.
[28] Rømming, *Acta Chem. Scand.*, 1960, **14**, 2145.
[29] McCullough, Chao, and Zuccaro, *Acta Cryst.*, 1959, **12**, 815.
[30] Chao and McCullough, *Acta Cryst.*, 1960, **13**, 727.
[31] Chao and McCullough, *Acta Cryst.*, in the press.

be the rule in addition compounds in which nitrogen is the donor (see below).

Halogen Addition Compounds of Amines, etc.

As mentioned above, Hantzsch[2] expressed the opinion that the 1:1 addition compounds formed by amines and halogens should be formulated as salt-like substances containing monohalogen-substituted cations and halogen ions. Until recently this view seems to have been shared by most chemists. However, results obtained in a recent series of crystal-structure determinations have clearly demonstrated that the substances in question are addition compounds analogous to those dealt with in the preceding sections. There is no indication of a tendency for the halogen atom not directly attached to nitrogen to approach this atom, and in the case of pyridine and other aromatic amines this "outer" halogen atom appears to be situated near the plane of the aromatic molecule.

The substances submitted to *X*-ray analysis are addition compounds formed by tertiary amines, aliphatic as well as aromatic, and bromine, iodine, or iodine monochloride. The first compound to be investigated was the 1:2 compound hexamethylenetetramine,$2Br_2$.[32] It was found that the two bromine molecules are both independently attached to tertiary nitrogen atoms, and in exactly the same way. The arrangement N–Br–Br is linear; three methylene groups and one Br_2 group surround a nitrogen atom tetrahedrally. More accurate measurements of the interatomic distances have been carried out in the case of the 1:1 addition compounds formed by trimethylamine and iodine or iodine monochloride.[33,34,35] Here, also, the tertiary nitrogen atoms is tetrahedrally surrounded by three (methyl) carbon atoms and one halogen atom (iodine). The arrangement N–I–I (N–I–Cl) is again linear as would have been expected (Fig. 5). The observed N–I distance is very nearly the same in both cases and practically identical with the distance found in halogen addition compounds formed by tertiary aromatic amines. In all cases this distance is close to 2·30 Å which is only 0·2—0·25 Å larger than the value expected for a truly covalent bond. This of course indicates a very strong interaction between the nitrogen atom and the iodine atom directly attached to it. A corresponding weakening of the I–I (I–Cl) bond is indicated by the

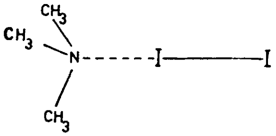

FIG. 5. *Trimethylamine–iodine compound.*

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[32] Eia and Hassel, *Acta Chem. Scand.*, 1956, **10**, 139.
[33] Hassel, *Mol. Phys.*, 1958, **1**, 241.
[34] Strømme, *Acta Chem. Scand.*, 1959, **13**, 268.
[35] Hassel and Hope, *Acta Chem. Scand.*, 1960, **14**, 391.

lengthening of this bond relative to its value (2·65 or 2·32 Å) in the free molecules by about 0·2 Å.

X-Ray results have also been reported for the 1:1 addition compounds pyridine–iodine monochloride[36] and γ-picoline–iodine.[37] In all addition compounds of halogens with aromatic tertiary amines so far investigated a linear arrangement nitrogen–halogen–halogen has been observed; the nitrogen–iodine distance is always about 2·30 Å and thus very nearly the same as in the addition compounds formed by aliphatic amines. A lengthening of the halogen–halogen bond distance is also found which is about the same as that observed in the case of aliphatic amines (compare Table 2).

TABLE 2. *Bond lengths* (Å) *in halogen addition compounds with amines.*

Compound	Charge-transfer bond	Bond length	Sum of van der Waals radii[27]	Hal–Hal bond length	Bond length in free Hal	Angle donor–Hal–Hal	Ref.
Hexamethylene-tetramine,$2Br_2$	N–Br	2·16	3·45	2·43	2·28	180°	32
Trimethylamine,I_2	N–I	2·27	3·65	2·83	2·67	179°	33, 34
Trimethylamine,ICl	N–I	2·30	3·65	2·52	2·32	180°	33, 35
Pyridine,ICl	N–I	2·26	3·65	2·51	2·32	*	36
γ-Picoline,I_2	N–I	2·31	3·65	2·83	2·67	*	37

*Approximately linear

One question appears to be of considerable interest in connection with the structures of halogen addition compounds formed by aromatic amines, namely the structure of addition compounds containing halogen and amine molecules in a ratio different from 1:1. The only substance of this kind so far investigated is the compound pyridine–$2I_2$.[38] As might have been expected it was found that we are here not concerned with an addition compound in the true sense of the word but rather with an ionic compound in which the pyridine molecules form part of a cation Py_2I^+. This ion has a centre of symmetry in the crystal and is at least very nearly planar. The anionic part of the crystal consists of a network in which linear I_3^- ions are linked together by iodine molecules.

So far little is known regarding the existence of halogen molecule bridges between nitrogen atoms. It seems improbable, however, that a very strong interaction between one of the halogen atoms of a halogen molecule and an adjacent donor atom accompanied by a corresponding weakening of the interhalogen bond will favour bond formation between the other halogen atom and a second donor atom of the same kind. Now, as it appears certain

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[36] Hassel and Rømming, *Acta. Chem. Scand.*, 1956, **10**, 696.
[37] Hassel, Rømming, and Tufte, *Acta Chem. Scand.*, 1961, **15**, 967.
[38] Hassel and Hope, *Acta Chem. Scand.*, 1961, **15**, 407.

that charge-transfer bonds formed between a tertiary nitrogen atom and iodine are comparatively strong, a halogen molecule bridge connecting two tertiary nitrogen atoms would be expected to be rather unstable. Actually, the only suggestion of a halogen molecule bridge between nitrogen atoms mentioned in the literature refers to the addition compound containing two molecules of acetonitrile and one molecule of bromine.[12] Further details of the crystal structure of this compound will be of particular interest. One would expect all the atoms of the $2CH_3{\cdot}CN,Br_2$ complex, apart from the hydrogen atoms, to be collinear in the crystal and the complexes to be held together by ordinary van der Waals forces.

Halogen Addition Compounds of Benzene

As already mentioned (p. 5) Mulliken's conclusion regarding the geometry of the 1:1 benzene–iodine complex has not been confirmed by later (infrared) spectroscopic work by Ferguson[39,40,41] who investigated ordinary benzene saturated with bromine or iodine and deuterated benzene saturated with iodine. The results of these investigations point to the symmetry C_{6v} and thus to the axial model of the two benzene–halogen complexes in question.

By cooling an equimolecular mixture of benzene and bromine in thin-walled capillary tubes Hassel and Strømme[33,42] were able to grow single crystals of a 1:1 compound and to carry out an X-ray crystallographic examination of it. Later, the same authors examined single crystals of the corresponding benzene–chlorine compound[33,43]. The two benzene–halogen compounds form isomorphous crystals belonging to the monoclinic system. Chains of alternating benzene and halogen molecules are present in the crystals, the ring planes of all benzene molecules are parallel, and each halogen molecule is symmetrically situated between two successive benzene molecules. The axes of the halogen molecules belonging to a particular chain coincide with the line running through the centres of the benzene molecules perpendicular to the planes of the benzene rings (Fig. 6).

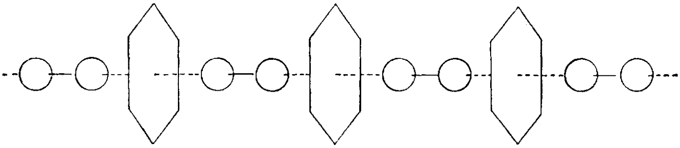

FIG. 6. *Benzene–halogen compounds.*

It appears most unlikely that the agreement between the axial model for the complex derived from infrared spectroscopic results and the chains

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[39] Ferguson, *J. Chem. Phys.*, 1956, **25**, 577, 1957; **26**, 1357.
[40] Ferguson and Matsen, *J. Chem. Phys.*,, 1958, **29**, 105.
[41] Ferguson and Matsen, *J. Amer. Chem. Soc.*, 1960, **82**, 3268.
[42] Hassel and Strømme, *Acta Chem. Scand.*, 1958, **12**, 1146.
[43] Hassel and Strømme, *Acta Chem. Scand.*, 1959, **13**, 1781.

just described should be incidental. In both cases all six electrons of the benzene molecule are expected to contribute equally to the formation of a charge-transfer bond. The arrangement found in the crystalline compound may thus be regarded as providing a new type of "halogen molecule bridge" between donor molecules. As with the dioxan–halogen compounds the observed donor–acceptor separation is only slightly larger in the bromine than in the chlorine compound, the effect of a difference in size of bromine and chlorine being nearly compensated by the increase in bond strength accompanying the replacement of a lighter halogen by a heavier one. The distance between a halogen atom and the nearest benzene plane is 3·36 Å in the bromine and 3·28 Å in the chlorine compound (the van der Waals separations[27] are 3·65 and 3·50 Å respectively). A weakening of the bond between the two halogen atoms due to the charge-transfer bonds is not indicated by the halogen–halogen bond length which is found (within the probable limits of error) to be identical with those of the free molecules.

It should, however, be added that the unusually large anisotropic vibrations of the halogens perpendicular to the chain axis observed in the solid state, particularly for the bromine compound, may be interpreted in terms of a statistical disorder due to possible positions of the halogen atom somewhat displaced from the chain axis.[42] Single-crystal diagrams taken at very low temperatures would probably settle this question.

Addition Compounds of Halide Molecules and Donors Containing Lone-pair Atoms

Well-crystallised addition compounds containing iodoform and quinoline molecules, or iodoform and sulphur (S_8) molecules in the proportion 1:3 have been known for a long time. The trigonal symmetry of the crystals and the fact that antimony tri-iodide forms a corresponding 1:3 addition compound with sulphur which is trigonal and has a rhombohedral unit cell roughly corresponding to that of the iodoform–sulphur compound made it appear reasonable to assume that all three iodine atoms belonging to a particular iodoform molecule form bonds with nitrogen or sulphur atoms in the two iodoform addition compounds.[23] In the 1:1 addition compound formed by iodoform and 1,4-dioxan, however, it would perhaps have been more natural to suggest the presence of bonds between the iodoform hydrogen atom and an ether oxygen atom like those expected to occur in the 1:1 complex formed by ether and chloroform and experimentally found in the solid 1:1 compound diethyl ether–bromodichloromethane.[23]

The *X*-ray examination of the two solid 1:3 addition compounds of iodoform has actually shown that the assumption of bonds between each iodine atom and a nitrogen or sulphur atom of the partner molecules was correct.[44,45,46] In addition to this it was found that the atomic arrange-

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[44] Bjorvatten and Hassel, *Acta. Chem. Scand.*, 1959, **13**, 1261.
[45] Bjorvatten, Hassel and Rømming, *Nature*, 1961, **189**, 137.
[46] Hassel, *Tidsskr. Kjemi Bergvesen Met.*, 1961, **21**, 60.

ment carbon–iodine–nitrogen (or sulphur) is at least very nearly a linear one.

It has further been reported that in the crystals containing equal numbers of dioxan and iodoform molecules each iodoform molecule is linked to two dioxan neighbours and *vice versa*, two of the iodine atoms belonging to a particular iodoform molecule forming bonds to ether oxygens. These bonds lead to the formation of endless chains of alternating dioxan and iodoform molecules. More details have been published about a new 1:1 compound containing 1,4-dithian instead of dioxan.[45,46] This compound, although not isomorphous with the dioxan–iodoform compound, is structurally closely related to it and the same type of chains are present. The dithian molecules are situated in centres of symmetry, the iodoform molecules in symmetry planes. In the two 1:3 compounds mentioned above all three iodine atoms of a particular iodoform molecule are linked to atoms belonging to neighbour molecules and isolated 1:3 molecular complexes are present. In the two 1:1 compounds, however, only two of the iodoform iodine atoms are involved in bond formation.

In Figs. 7 and 8 electron-density maps with projection along the trigonal axis are reproduced for the sulphur and for the quinoline 1:3 compound (iodine subtracted). The maps clearly demonstrate that symmetry planes

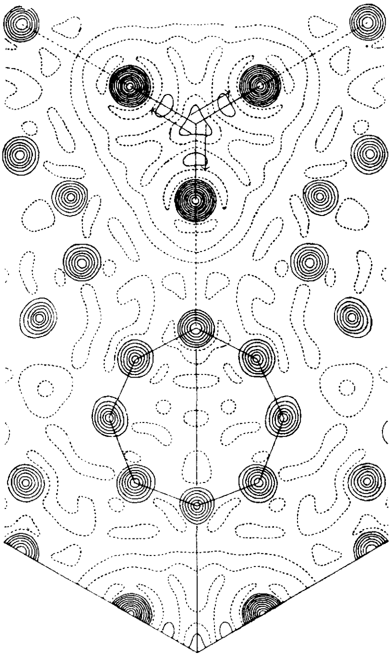

FIG. 7. *Electron density map of the iodoform–sulphur compound projected along the trigonal axis.*

present in the sulphur compound are lacking in the quinoline compound. Besides the linearity of the arrangements C–I . . . S or C–I . . . N another feature common to the structures of all the addition compounds

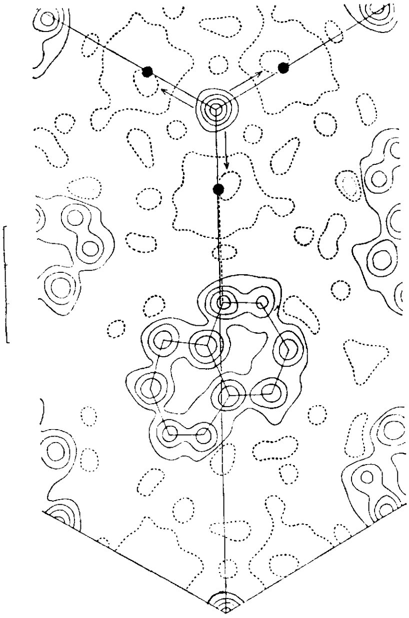

FIG. 8. *Electron density map* (*iodine subtracted*) *of the iodoform–quinoline compound projected along the trigonal axis.*

formed by iodoform and discussed above may also be mentioned; it further strengthens the argument in favour of a bond between iodine and sulphur (or nitrogen). The distance between the two atoms involved (cf. Table 3) is significantly shorter than that expected in the case of a regular van der Waals interaction.

The approximate linearity of the arrangement carbon–iodine–donor atom in the iodoform addition compounds has its counterpart in the addition compounds of oxalyl chloride and oxalyl bromide with 1,4-dioxan in which a nearly linear arrangement C–Cl···O has indeed been observed.[45] These two compounds are isomorphous, and the oxalyl halide molecules as well as the dioxan molecules are situated in symmetry centres. Both halogen atoms belonging to a particular halide molecule are linked to either oxygens of dioxan neighbours. These conditions lead to the formation of infinite chains of alternating donor (dioxan) and acceptor (oxalyl halide) molecules.

The strength of the bond between a halogen atom already linked to a carbon atom and a lone-pair donor atom certainly depends on the nature of both the donor and the halogen atom. The fact that the distance from an iodine atom in iodoform to a nitrogen or sulphur atom is always found to be significantly shorter than the sum of the van der Waals radii whereas the observed halogen–oxygen distances in the oxalyl halide–dioxan compounds are only slightly smaller than the sum of the corresponding radii clearly indicate that the charge-transfer bonds are much weaker in the latter case.

TABLE 3. *Distances in addition compounds of halides with various donors.*

Compound	Charge-transfer bond	Bond length (Å)	Sum of van der Waals[27] radii (Å)	Ref.
Quinoline,iodoform (3:1)	N–I	2·99	3·65	44
S_8,Iodoform (3:1)	S–I	3·44	4·00	45, 46
Dithian,iodoform (1:1)	S–I	3·29	4·00	45, 46
Dioxan,oxalyl bromide	O–Br	3·21	3·35	45
Dioxan,oxalyl chloride	O–Cl	3·18	3·20	45
Cyanogen iodide	N–I	2·8	3·65	47
Cyanogen bromide	N–Br	2·85	3·45	48
Cyanogen chloride	N–Cl	3·01	3·30	49
Cyanuric chloride	N–Cl	3·15	3·30	50
Oxalyl bromide	O–Br	3·27	3·35	51

The results obtained for the addition compounds formed by halide molecules and a number of electron donors would make it appear worthwhile to look for possible charge-transfer bonds even in crystals built up of *one* molecular species when the molecule in question contains both electron-accepting and electron-donating atoms. In the crystals of the oxalyl halides for example, it has been suggested[46] that charge-transfer bonds between keto-oxygen and halide atoms belonging to neighbouring molecules might play an important rôle. This suggestion has turned out to be correct, at least for the bromine compound.[51] The crystal structure of this substance actually contains (non-planar) sheets in which every molecule is linked to four neighbouring molecules by O···Br bonds of length 3·27 Å and with a nearly linear C–Br···O arrangement. The distances observed between atoms belonging to neighbouring sheets demonstrate that the interaction is of the van der Waals type.

Charge-transfer bonds must obviously be present also in the crystal structure of cyanuric chloride,[50,52] this time between nitrogen and chlorine atoms of neighbouring molecules. Here it results in sheets which appear to be strictly planar and a C–Cl···N arrangement which is probably exactly

[47] Ketelaar and Zwartsenberg, *Rec. Trav. chim.*, 1939, **58**, 448.
[48] Geller and Schawlow, *J. Chem. Phys.*, 1955, **23**, 779.
[49] Heiart and Carpenter, *Acta Cryst.*, 1956, **9**, 889.
[50] Hoppe, Lenné and Morando, *Z. Krist.*, 1957, **108**, 321.
[51] Groth and Hassel, *Proc. Chem. Soc.*, 1961, 343.
[52] Lonsdale, *Z. Krist.*, 1936, **95**, 471.

linear. Indeed, this structure provides the possibility of establishing the maximum number of charge-transfer bonds between nitrogen and halogen atoms. Both in the oxalyl bromide and in the cyanuric chloride structures the cohesion within the sheets depends mainly on these bonds. The structures of cyanuric bromide and iodide probably contain planar arrangements corresponding to that of the cyanuric chloride (Fig. 9).

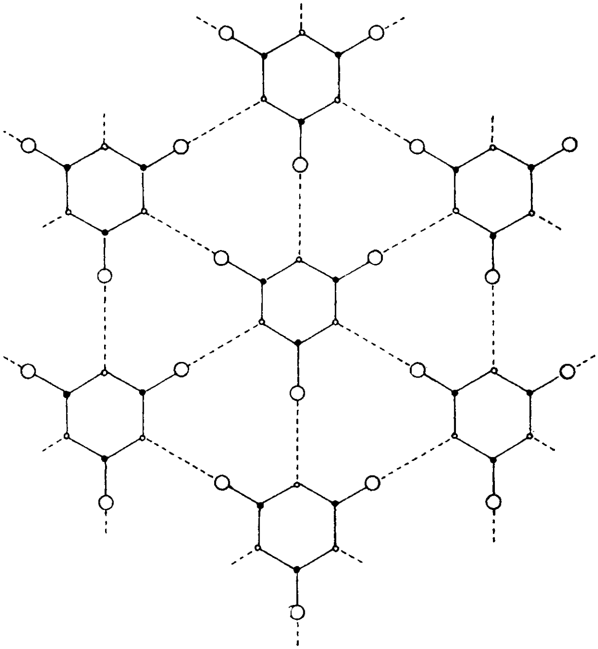

FIG. 9. *Atomic distribution within a plane layer of the cyanuric chloride crystal.*

The structures of the solid monomeric cyanogen halides are also interesting. In these crystals endless linear chains of the type ··Hal–C–N···Hal–C–N··· are present.[47,48,49] It has been suggested that in the free cyanogen halide molecules which are all linear a resonance exists between two structures, Hal–C≡N and Hal=C=N, which would lead to the suggestion that the halogen atom have acquired a certain positive, and the nitrogen atom a negative charge. This picture, which appears to be in accord with quadrupole resonance measurements,[48,53] may perhaps not be quite easy to reconcile with the linearity of the arrangement C–N–Hal found in the crystal. In any case the bond between nitrogen and halogen should probably, both in these crystals and in the crystal of the cyanuric chloride, be classified as a charge-transfer bond.

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[53] Townes and Dailey, *J. Chem. Phys.*, 1952, **20**, 35.

Conclusions

The empirical results obtained from structural investigations of solids in which charge-transfer bonds are present linking together electron-donating molecules or parts of molecules and electron acceptors like halogen molecules or halide molecules may be summarised as follows:

If the acceptor is a halogen (or interhalogen) molecule and the donor possesses a lone-pair atom, a charge-transfer bond between the latter and one of the halogen atoms may be formed resulting in a linear or at least nearly linear arrangement: donor atom–halogen–halogen. If the charge-transfer bond is comparatively weak like the bonds formed by oxygen atoms of an ether or a ketone both halogen atoms of a particular halogen molecule may simultaneously be involved and an intermolecular "halogen molecule bridge" between two oxygen atoms result. In this case the arrangement oxygen–halogen–halogen–oxygen is at least nearly linear. The charge-transfer bond between a tertiary nitrogen atom and halogen is obviously much stronger than the bonds formed by oxygen, and this probably explains the fact that halogen molecule bridges between such nitrogen atoms have so far not been observed. There are reasons to believe that the bond to halogen formed by a nitrogen atom of a nitrile group is considerably weaker and that further examples of halogen molecule bridges between nitrile groups may be found.

The direction of a bond linking a lone-pair donor atom to a halogen atom is roughly that to be expected from the orientation of the orbitals of the non-bonding electron pairs in the donor atom before the charge-transfer bond formation. In the case that two lone pairs of the donor atom are involved in bond formation the resulting atomic arrangement appears to be in accord with this simple picture (acetone–bromine, p. 7).

The weakness of the bond between a benzene and a halogen molecule in the 1:1 complex makes it appear natural that halogen molecule bridges between benzene molecules are possible in the solid state with a halogen–halogen distance practically identical with that of the free halogen molecule.

When a halogen atom belonging to a halide molecule forms a bond to a donor atom (O,N,S) of a neighbour molecule similar rather simple considerations appear to be of some value for the prediction of the resulting atomic arrangement. Thus, the angle between the line joining the halogen atom and the (carbon) atom to which it is attached and the direction of the charge-transfer bond does not deviate much from 180°. The length of the charge-transfer bond apparently never exceeds the value expected for a van der Waals separation but approaches it for particularly weak bonds like those formed by ether or keto-oxygen. If oxygen is replaced by sulphur or amine nitrogen a significantly shorter donor–acceptor distance results. The distribution of the bonds around the donor atom appears to conform to that observed in halogen addition compounds. So far no exceptions to these simple rules are known even for crystalline substances with identical molecules containing both halogen and electron-donating atoms.

Unfortunately, a satisfactory theoretical interpretation of the observed geometry of the atomic arrangements associated with charge-transfer bonding is still lacking. Even the apparently simpler question regarding the linearity of the trihalide ion and the influence of surrounding ions determining whether or not the Hal_3^- ion is centrosymmetrical, are still somewhat obscure. It has been thought for a long time that the orbitals occupied by the electrons of the central atom are of the $sp^3d_{z^2}$ type, a suggestion which is in agreement with the linearity of the ion. Recent results of quadrupole magnetic resonance measurements,[54] however, seem to indicate that the surplus negative charge of the ion is mainly concentrated on the two outer rather than on the central halogen atom. It also appears questionable to what extent *d*-orbitals are at all of importance for the actual distribution of the valency electrons within the ion. Further experimental work appears most desirable which might contribute to the establishment of the electron distribution in the ions just discussed and *a fortiori* in carefully selected substances exhibiting charge-transfer bonds.

[54] Cornwell and Yamasaki, *J. Chem. Phys.*, 1957, **27**, 1060.