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Structural aspects of interatomic charge-transfer bonding

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In the nineteenth century convincing experimental proof was collected of interactions in liquid systems between molecular species generally regarded as chemically "saturated", leading to more or less stable complexes. In several cases stoichiometric solid compounds could even be isolated from such mixtures. The number of intermolecular complexes more or less extensively studied during the last two decades mainly employing spectrophotometric methods is considerable, and it has become possible not only to classify the different types of complexes, but also to predict and subsequently to prepare and study new complexes. The understanding of the processes leading to the formation of intermolecular complexes remained rather incomplete, however, and about the atomic arrangements in the complexes almost nothing was known until direct interferometric experiments were carried out.

The two types of reversibly functioning intermolecular interactions for which a more precise structural picture was available already before the second world war were apparently only those leading to the formation of hydrogen bonding and to "dative covalent bonds" like those formed in the interaction between amine nitrogen atoms and boron atoms belonging to boron trihalide molecules. For both reaction categories it was suggested that an electron transfer from a "donor" to an "acceptor" atom takes place. Quantitative experimental work carried out by spectroscopists during the last two decades has substantiated the belief that the formation of molecular complexes may generally be attributed to a transfer of negative electrical charge from a *donor* molecule (Lewis or Bronsted base) to an *acceptor* molecule (the Lewis acid) and it had become natural to classify the process involved as a "charge-transfer" interaction.

Among the molecules acting as electron donors those which owe their donor properties to the presence of atoms possessing one or more "lone pairs" of electrons - the "*n* donors" - are of particular significance. Other types of donor molecules are also known, like unsaturated hydrocarbons, in particular aromatic hydrocarbons and some of their derivatives, molecules deriving

their donor properties from the presence of comparatively loosely bound π electrons. Molecules exhibiting electron-accepting properties may be of widely differing nature ranging from aromatic molecules with strongly electronegative substituents to molecular species containing an atom which should normally act as an "n donor" but has, in the molecule in question, acquired a certain positive surplus charge.

During the later part of the 1940's the interest in complexes formed by donor and acceptor molecules was stimulated by quantitative spectroscopic work dealing first with solutions of iodine in benzene, later with a considerable number of liquid systems containing different combinations of donor and acceptor molecules dissolved in solvents regarded as "inert" with respect to the interacting species. From the spectroscopic data equilibrium constants and thermodynamic values associated with the formation of 1:1 complexes were evaluated. A quantum mechanical theory of the "complex resonance" was worked out by Mulliken which is of a very general nature and explains spectroscopical observations, but has not yet made possible reliable predictions regarding the atomic arrangements within the complexes.

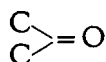
Direct interferometric structure determinations in the vapour phase are regarded virtually impossible in most cases because of the extremely low concentration of the complex which may be expected to be present. X-Ray crystallographic structure determinations have made it possible, however, to draw conclusions regarding atomic arrangements not only in solids, but even in isolated 1:1 complexes, conclusions which should be of value for theoretical workers trying to establish a more elaborate theory of charge-transfer interaction.

Particular importance may be attributed to complexes in which direct bonding exists between one atom belonging to the donor molecule and another atom belonging to the acceptor molecule. Complexes of this kind are above all those formed by donor molecules containing atoms possessing "lone pair electrons" and halogen or halide molecules. A presentation and discussion of the general results obtained by X-ray analysis of solid adducts exhibiting charge-transfer bonding between such atoms might therefore be of some interest.

First, some of the conclusions drawn before direct structure determinations had been carried out, deserve to be recalled.

The considerations were based on the assumption that halogen atoms are directly linked to donor atoms with a bond direction roughly coinciding with

the axes of the orbitals of the lone pairs in the non-complexed donor molecule. The oxygen atom of an ether or ketone molecule was supposed to form bonds with both halogen atoms in an isolated 1 : 1 complex, which would require the halogen molecule axis to run orthogonal to the COC plane in an ether complex, and to be situated in the



plane in a ketone complex. In both cases three-membered rings would then result, containing one oxygen and two halogen atoms. Even in an isolated 1 : 1 complex formed by pyridine both halogen atoms were supposed to be attached to the donor atom, although in different ways: one of them was expected to be situated in the plane of the pyridine molecule on the axis of the nitrogen lone pair orbital, the second (supposed to carry a certain negative surplus charge) outside this plane, under attraction of the (positively charged) nitrogen atom.

Early in the 1950's X-ray crystallographic investigations of halogen adducts were started in Oslo, beginning with the solid 1 : 1 1,4-dioxan-bromine compound. The most striking feature of the resulting crystal structure¹, the endless chains of alternating dioxan and bromine molecules depending on linear O-Br-Br-O arrangements running in a direction roughly equal to the "equatorial" direction in cyclohexane (Fig. 1) was rather unexpected. It proved that both atoms belonging to a particular halogen molecule may simultaneously be bonded to oxygen atoms, although probably not to the same oxygen atom. The existence of halogen molecule bridging between donor atoms contradicts previous assumptions according to which a charge-transfer bond formed by one of the atoms belonging to a particular halogen molecule creates a marked negative charge on the partner atom.

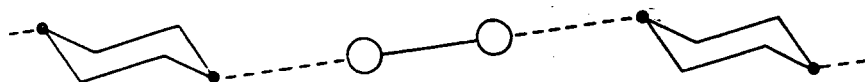


Fig. 1. Chains in the 1 : 1 adduct of 1,4-dioxan and bromine.

The oxygen-bromine distance in the dioxan-bromine adduct is 2.7 Å and thus considerably larger than the sum of the covalent radii of oxygen and bromine, but at the same time definitively shorter than the sum of the corresponding van der Waals radii. The type of "polymerisation" of simple com-

plexes into endless chains observed in the crystalline dioxan-bromine compound has also been observed in the crystalline 1:1 adducts of dioxan and chlorine, resp. iodine. A comparison between the oxygen-halogen separations and of the interhalogen bond lengths in the three 1,4-dioxan adducts leads to the conclusion that the former increases rather slowly from chlorine to iodine, indicating a certain degree of compensation of the effect of larger halogen radius by the increase in charge-transfer bond strength. On the other hand, the halogen-halogen bond length increases, although slowly, from chlorine to iodine compared with that observed in "free" halogen molecules, an observation which must also find its explanation in the stronger charge-transfer interaction between oxygen and halogen.

In the solid 1:2 iodomonochloride 1,4-dioxan adduct, isolated complexes are observed in which iodine is bonded to oxygen in a linear oxygen-iodine-chlorine arrangement, again approximately pointing in the direction of an equatorial bond in cyclohexane. Similar results have been obtained for halogen complexes formed by 1,4-dithiane and 1,4-diselenane, with the exception that in diselenane an (axial, bond direction appears to be more favourable than an equatorial. The increased strength of the charge-transfer bonding is indicated by a more pronounced lengthening of the halogen-halogen bond. The fact that no example of halogen molecule "bridging" between donor atoms has, so far, been observed in dithiane or diselenane compounds also points to a relatively strong donor-acceptor interaction.

From the structures of the crystalline adducts of 1,4-dioxan it became clear that both atoms of a particular halogen molecule are able to form bonds to donor atoms, although apparently not to the same donor atom. The question then arose whether or not a particular donor atom may be involved in more than one bond to halogen. This would appear possible for n donor atoms like oxygen possessing two lone electron pairs. In the crystal structure of the 1 : 1 acetone-bromine adduct it was actually found that each keto oxygen atom is linked in a symmetrical way to two neighbouring bromine atoms, thus serving as a starting point for two bromine molecule bridges, both with a linear O-Br-Br-O arrangement and with an angle between the two bond directions of 110° .

In the case of amine adducts it would not be expected that a nitrogen atom might be capable of forming more than one single bond to halogen. The correctness of this anticipation has been borne out by the results of a considerable number of crystal structure determinations of addition compounds, usually choosing iodine or an iodine monohalide as the acceptor partner. Here again,

the bond direction corresponds to that expected from simple considerations regarding the orbital of the lone electron pair on the amine nitrogen atom in the donor molecule. The nitrogen-halogen-halogen arrangement has always been found to be nearly linear, the bonds between the nitrogen atom and the carbon, resp. the iodine atom are tetrahedrally arranged in the case of aliphatic amines, essentially co-planar if the donor molecule is a heteroaromatic amine. The strength of the charge-transfer bond may be inferred from the short nitrogen-halogen bond distance which is only 2.3 Å in all complexes formed by tertiary amines and iodine or iodine monohalides, a value only about 0.25 Å larger than the sum of the covalent radii of nitrogen and iodine. A lengthening of the interhalogen bond by approximately 0.2 Å observed in these complexes is therefore not surprising. The fact that halogen molecule bridges have never been observed between amino nitrogen atoms also indicates that the nitrogen-halogen bond is rather strong. This does not imply, however, that such bridges can not be stable between other kinds of nitrogen atoms. Thus, in the isolated complex containing two molecules of acetonitrile and one bromine molecule such bridges are present, which appears very natural because nitriles are known from spectroscopical measurements to be weaker donors than are the amines.

The only crystal structure of an amine adduct so far investigated in which a cyanogen halide acts as the acceptor molecule is that formed by pyridine and cyanogen iodide². The complex contains a linear arrangement N-I-C=N which is symmetrically situated in the pyridine plane along the line drawn between the pyridine nitrogen and the γ -carbon atoms. The N-I bond distance is larger than 2.3 Å by about one quarter of an Å unit, in agreement with the spectroscopical finding that cyanogen iodide is a relatively weak acceptor.

Only one single addition compound containing alcohol and halogen molecules has been investigated crystallographically, the 2 : 1 methanol-bromine adducts. Its structure may be, and probably is, characteristic of the type of structure to be generally expected for alcohol-halogen adducts in that oxygen atoms are linked together partly by hydrogen bonds, partly by linear O-Br-Br-O arrangements. Each oxygen atom is actually tetrahedrally surrounded by a methyl group, two hydrogen bonds and one bromine molecule bridge. This structure provides us in any case with a striking example of analogy between intermolecular charge-transfer and hydrogen bonding. Further examples will be presented below.

It would appear natural to search for a closer interdependence between in-

teratomic distances (between donor and acceptor atoms and between the two halogen atoms) and the strength of the charge-transfer bond in crystalline adducts exhibiting the types of linear arrangements of donor and halogen atoms described above. This has, however, not turned out to be an easy task. It is, however, possible to evaluate, with considerable success, overall distances along the linear chains of donor and halogen atoms, either between the donor atom and the second halogen atom or, in the case of halogen molecule bridges, the distance between the two donor atoms. This is done by simple summation of the radii of individual atoms along the chain. Accepted covalent radii of the donor atoms are used, and for halogen atoms radii related to such atoms involved in charge-transfer bonds. For the latter the mean values of the covalent and the Van der Waals radius are chosen. The overall distances thus computed are generally in acceptable agreement with observed distances (Table I). Such predictions of overall distances may no doubt be useful when working out new crystal structures, but considerations which may be expected to yield informations about the strength of the bond between a halogen and a donor atom must evidently involve the shortening of this bond and the lengthening of the adjacent halogen-halogen bond caused by the charge-

Table I
Overall distances in adducts

<i>Substance</i>	<i>Observed distance</i>	<i>Calculated distance</i>
$N(CH_3)_3-I_2$	5.10	5.19
4-Picoline- I_2	5.14	5.19
$N(CH_3)_3-ICI$	4.82	4.85
Pyridine- ICI	4.77	4.85
Pyridine- IBr	4.92	5.00
Pyridine- ICN	4.68	4.63
1,4-Dioxan-2 ICI	4.92	4.81
Benzyl sulphide- I_2	5.60	5.53
1,4-Dithiane- I_2	5.66	5.53
1,4-Diselenane- I_2	5.70	5.66
D—X—X—D distances		
1,4-Dioxan- Cl_2	7.36	7.34
1,4-Dioxan- Br_2	7.73	7.70
1,4-Dioxan- I_2	8.35	8.38
Acetone- Br_2	7.92	7.70
2 Acetonitrile- Br_2	8.00	7.84
2 Methanol- Br_2	7.85	7.70

transfer process. For this reason evaluation of "effective" radii R_1 and R_2 of the centre halogen atom in the two opposite directions, towards the donor and towards the second halogen atom, were carried out simply by subtracting the covalent radii of the donor atom, resp. the second halogen atom from the observed distances. In Fig. 2 the values R_1 and R_2 are plotted against each other for a number of adducts in which iodine is the centre atom. Points representing the individual adducts show a marked tendency to concentrate near a straight line descending from the left to the right according to the equation:

$$R_2 = -1.92 R_1 + 4.59$$

Besides the points representing n donor-IX adducts the figure also contains points giving effective radii of iodine in solids in which trihalide ions are present with iodine as the centre atom and linked to two halogen atoms of the same kind. Such IX_2 ions may be either symmetric or non-symmetrical, in the latter the halogen atom closest to the centre atom is believed to carry a smaller negative charge than the more distant halogen atom. We assume that in the weakest IX complexes like those with oxygen as the donor atom, this atom corresponds to the halogen atom carrying the larger negative charge in

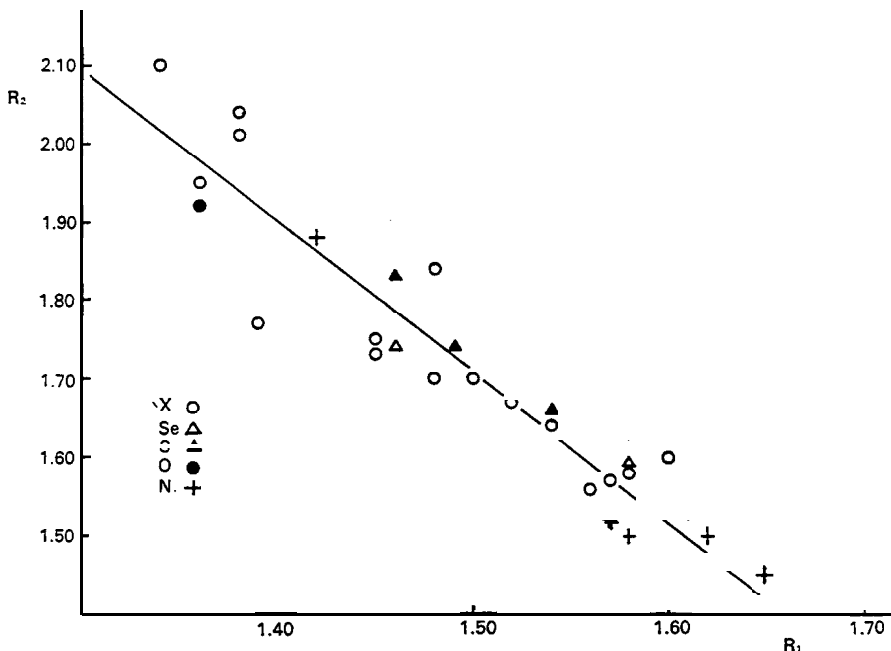


Fig. 2. Plot of "effective" radii R_1 and R_2 of iodine in adducts and in trihalide ions.

non-symmetrical trihalide ions. Further, that the nitrogen atom in the strong IX adducts of tertiary amines takes the place of the other halogen atoms in trihalide ions which has a smaller negative charge and comes closer to the centre atom. The points in Fig. 2 representing the weakest complexes are situated in the upper left part of the diagram, those representing the strongest complexes bottom right. It appears significant that the point corresponding to the relatively weak pyridine-cyanogen iodine complex ($R_1 = 1.42$, $R_2 = 1.88$) is found in the upper middle of the diagram. Theoretically, it is difficult to assess if the relation between R_1 and R_2 should be expected to be strictly linear. It might perhaps be more adequately expressed by another curve, *e.g.* a hyperbola with an angle almost equal to 180° between its asymptotes, than by a straight line.

Turning now to complexes in which halide molecules act as electron acceptors it should be mentioned that the concept of a halogen atom linked to a non-halogen atom but still acting as an electron acceptor emerged at a rather recent date. The conclusion that halides may serve as acceptors in the formation of addition compounds formed with n donor molecules might have been drawn decades ago, but the idea was apparently not put forward until 1959⁵. It had in fact been known for some time that 1:3 adducts of iodoform and of antimony triiodide may exhibit a remarkable (macroscopic) crystallographic similarity and this was now so interpreted that the bonding between the two molecular species present in such adducts depended on bonds linking iodine atoms to n donor atoms. Crystal structure determinations carried out in the following years fully confirmed this suggestion and showed that the atomic arrangement within the complexes is such that the arrangement carbon (antimony)-iodine- n donor atom is linear or at least very nearly so. The crystal structure of a considerable number of other adducts formed by halogenated hydrocarbons and n donor molecules have now been determined with the result that one may be rather confident about the general principles governing the atomic arrangements in such adducts. In particular, a nearly linear arrangement carbon-halogen-donor atom has always been observed.

In most adducts so far investigated both participants contain more than one atom capable of taking part in charge-transfer bonds. When each oxygen, sulphur or selenium atom is linked to only one iodine atom in 1:1 addition compounds of iodoform with 1,4-dioxan or its analogues, structures exhibiting endless chains of alternating donor and acceptor molecules would be anticipated. Such chains are actually present in these adducts, chains analogous to those found in the sulphuric acid-dioxan compound. Figs. 3a and b il-

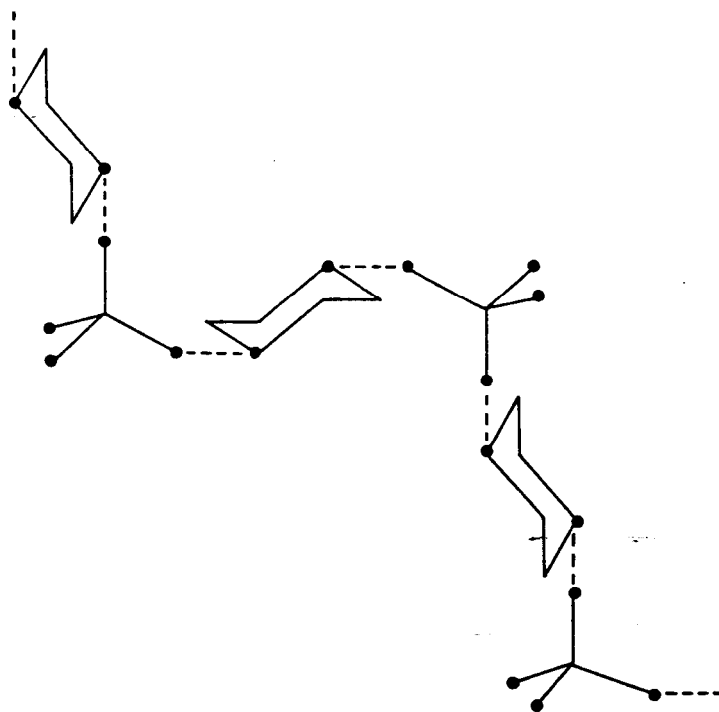


Fig. 3a . Chains of sulphuric acid and dioxan molecule in the 1:1 adduct.

illustrate the shape of the chains observed in the sulphuric acid-dioxan, resp. the iodoform-dithiane compound. The similarity between these chains again affords an example of analogy between hydrogen and charge-transfer bonding.

The possibility that an oxygen, sulphur or selenium atom may be involved in *two* charge-transfer bonds with halogen atoms should always be kept in mind, however, particularly when the acceptor molecule contains a large number of halogen atoms. Thus, in the 1:1 diselenane-etraiodoethylene adduct⁶ every selenium atom is bonded to *two* iodine atoms, the bond directions being roughly equatorial resp. axial and the selenium-iodine bond lengths almost identical. A "cross-linking" of the chains results, all iodine atoms are linked to selenium and each selenium atom to *two* iodine atoms.

In view of the moderate energies apparently involved in bonding between halide halogen atoms and *n* donor atoms it would appear natural to suggest that the Van der Waals interaction energy between acceptor molecules containing a sufficiently large number of the heaviest halogen species may contribute substantially to the lattice energy of a solid addition compound. Crystal

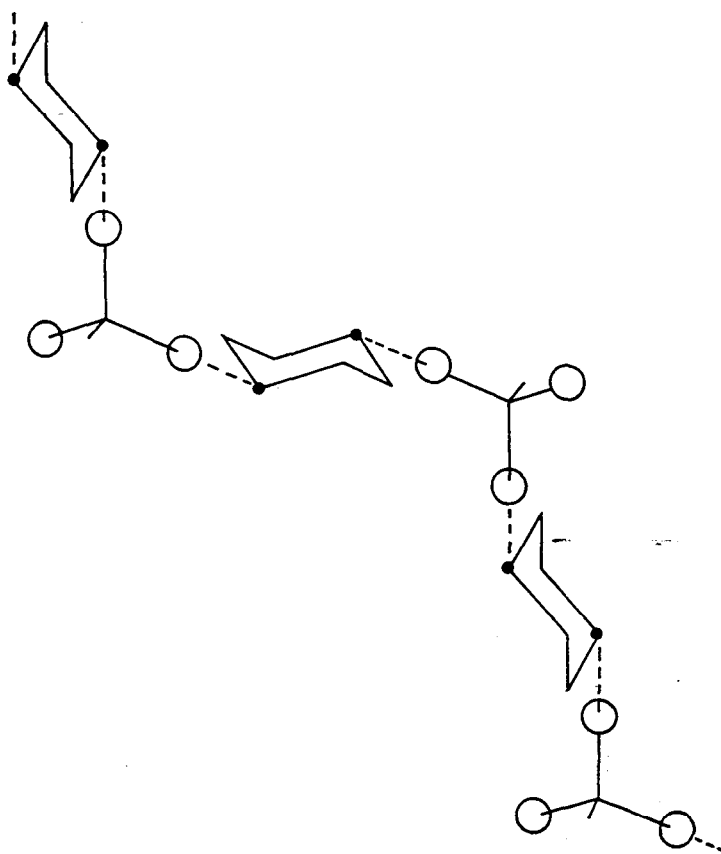


Fig. 3b. Chains of iodoform and dithiane molecules in the 1:1 adduct.

structure determinations of tetrabromo - and tetraiodoethylene and of their 1:1 pyrazine adducts actually give some support to this suggestion. The mutual arrangement of the halide molecules is virtually identical in the tetrahalogenoethylene crystals and in the corresponding crystalline addition compounds. The four crystals all belong to the space group $P2_1/c$ and their unit cells all contain four molecules which are in the tetrahalogenoethylene crystals practically identical in shape, but not crystallographically equivalent. The structures of the 1:1 adduct crystals may formally be derived from those of the tetrahalide crystal by removing one set of equivalent molecules and replacing them by pyrazine molecules. For both adducts this results in the formation of endless chains of alternating donor and acceptor molecules in which each nitrogen atom is bonded to a halogen atom situated near the plane of the pyrazine ring with a nearly linear nitrogen-halogen-carbon arrangement and

a nitrogen-halogen bond about 3 Å long. In the tetrabromoethylene adduct these chains are all parallel, in the tetraiodoethylene adduct, however, the chains are running along two different crystallographic directions⁷.

A phenomenon which has not yet apparently been met with great interest, but should perhaps deserve more attention, is the formation of solid solutions between donor and acceptor molecules. Until recently, the experimental facts favouring the suggestion of mixed crystal formation were somewhat meagre, however, and no attempt of a crystallographic investigation had apparently been made before an X-ray crystallographic investigation of the system hexamethylenetetramine-carbon tetrabromide was carried out⁸. These two substances actually form mixed crystals, containing from zero to about sixty mole per cent of the acceptor partner, which could be examined in the form of single crystals. The crystals are cubic with an over-structure depending on the composition, but with a subcell that corresponds to the true unit cell of the donor component, only slightly decreasing in dimension as the acceptor concentration increases. The experimental findings seem to prove that the tendency towards the formation of solid solutions actually depends on the faculty of the two partners to form nitrogen-bromine charge-transfer bonds. Accurate thermodynamic measurements of this and of certain related binary systems would appear to be of considerable interest.

Solutions containing hexamethylenetetramine and iodoform or bromoform do not show any tendency to deposit mixed crystals when the solvent is evaporated. This may be due to the attraction of the "active" hydrogen atom towards amino nitrogen. A solid 1:1 hexamethylenetetramine-iodoform adduct has been prepared and its crystal structure determined. In this crystal (Fig.4) every acceptor molecule is tetrahedrally linked to four neighbouring donor nitrogen atoms by three I-N bonds (2.94 Å long) and to a fourth nitrogen atom *via* the CH hydrogen atom. The C(H)-N distance is only 3.21 Å and the bond appears therefore to be energetically of some importance. It appears very probable that a 1:1 bromoform adduct of hexamethylenetetramine, isostructural with the iodoform adduct, may exist. In this adduct, the halogen-nitrogen bonds would be expected to be somewhat weaker, the C-H-N bonds, however, somewhat stronger than in the iodoform adduct.

Crystals having the 1:1 composition have so far not been isolated in the hexamethylenetetramine-bromoform system, but another compound, a solid 1:2 compound has been obtained in the form of crystals suitable for X-ray examination. It is obvious that in a solid of this composition all CH

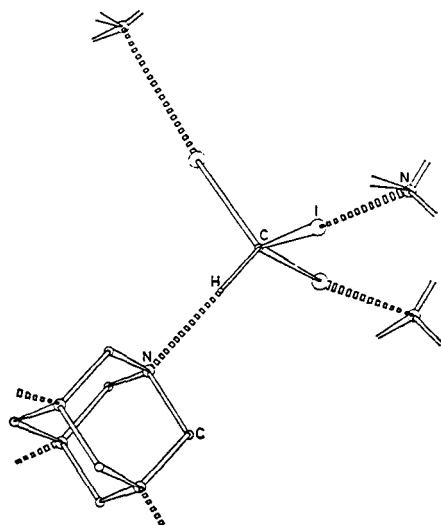


Fig. 4. Tetrahedral arrangement of hexamethylenetetramine molecules around an iodoform molecule in the 1:1 adduct.

groups and all bromine atoms cannot form bonds with nitrogen atoms. This means that a competition between the two kinds of intermolecular bonds may take place, the outcome of which may give indications regarding relative strengths of the bond types. In the crystal structure derived¹⁰ from the X-ray data of the adduct containing hexamethylenetetramine and bromoform molecules in the proportion 1:2 it is obvious that two of the bromine atoms belonging to half the number of acceptor molecules form charge-transfer bonds to nitrogen atoms in neighbouring donor molecules, the other half none. Each donor molecule is tetrahedrally linked to two bromine atoms and to two CH-groups all belonging to neighbouring bromoform molecules. Fig. 5 visualizes the arrangement of bromoform molecules surrounding each hexamethylenetetramine molecule. These results seem to indicate that the CH \cdots N bonds are stronger than are the Br \cdots N bonds between hexamethylenetetramine and bromoform molecules.

The relative stability of C-H \cdots N bonding indicated by the results of X-ray investigations of adducts of hexamethylenetetramine and trihalogenomethanes make it appear possible to carry out chemical separations *via* addition compounds held together by such bonds. It may be suggested for example that the separation into optically active components of racemic haloform - HCFCIBr - can be achieved via adduct formation with a properly chosen optically active amine.

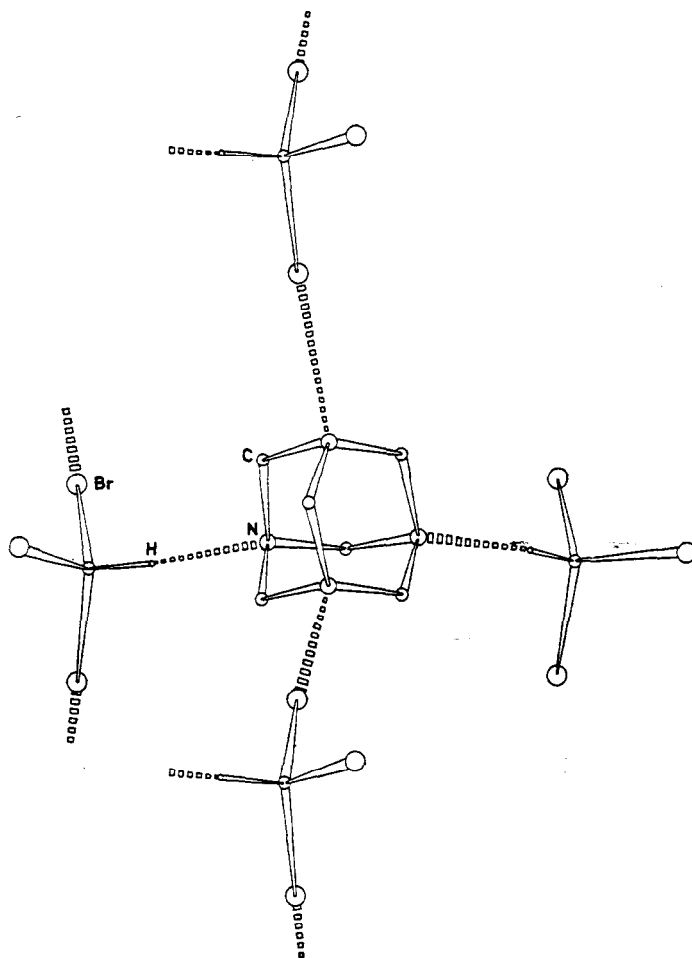


Fig. 5. Bromoform molecules surrounding each hexamethylenetetramine molecule in the 2:1 adduct.

Even in crystals containing only one molecular species intermolecular bonds between n donors and halogen atoms should be expected in particular cases. They were searched for in the crystals of carboxylic acid halides where such bonds between halogen and carbonyl oxygen atoms appeared to be possible since an earlier investigation had proved that oxygen-halogen bonding actually exists in 1:1 adducts formed by oxalyl chloride, resp. oxalyl bromide, and 1,4-dioxan. X-Ray investigations of oxalyl chloride and oxalyl bromide proved that this kind of bonding determines the crystal structure of the bromine compound but are absent in the chlorine compound.

In the former each oxalyl bromide molecule is linked to its four nearest neighbours by $O \cdots Br$ bonds. That the two compounds have quite different crystal structures is not so surprising as the oxygen-chlorine interaction is expected to be considerably weaker than that between oxygen and bromine.

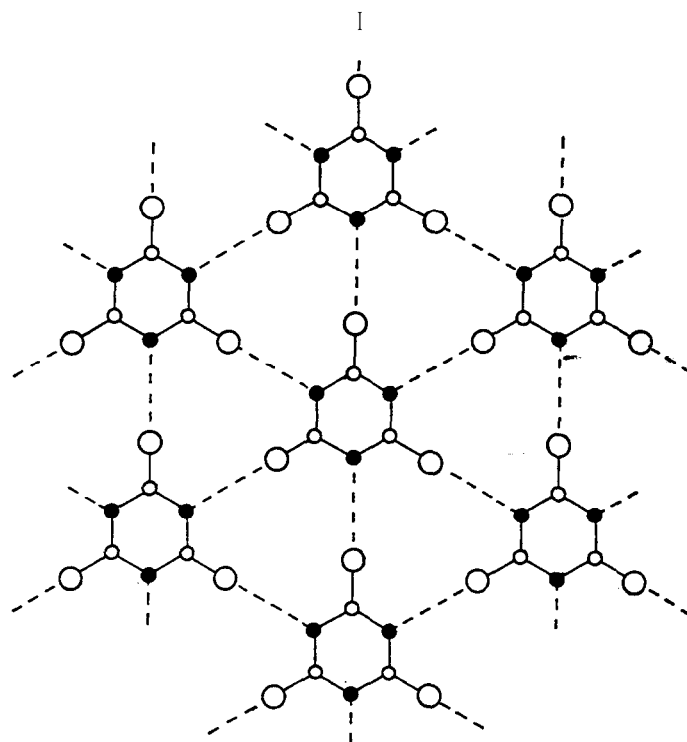


Fig. 6. Planar sheets of cyanuric chloride molecules in the crystal.

A particularly interesting example of charge-transfer interaction between nitrogen and halogen atoms is provided by the structure of solid cyanuric chloride - the trimeric form of cyanogen chloride. According to available X-ray data¹¹ the crystals are built up of planar layers of the type shown in Fig. 6, held together by Van der Waals forces. Within the layers each molecule is linked to six neighbour molecules by nitrogen-chlorine bonds and the C-Cl-N arrangement is probably strictly linear. At the time of publication of this paper no experimental facts about similar charge-transfer bonding were available, and it is not surprising that the authors failed to interpret their results by suggesting bonds between nitrogen and chlorine atoms to be present.

When n donor atoms like oxygen or nitrogen are involved in hydrogen bonds the resulting atomic arrangements are usually similar to those observed in charge-transfer complexes in which the same donor atom is linked to a halogen atom. It is therefore not surprising that a replacement of chlorine in cyanuric chloride by hydroxy groups (cyanuric acid) or amino groups (melamine) leads to crystal structures very similar to that of cyanuric chloride, the aromatic nitrogen atoms being linked to hydroxy resp. amino groups in neighbour molecules by hydrogen bonds.

Complex formation due to charge-transfer interaction between n donor atoms and halogen atoms belonging to halide molecules does not always result in bond distances significantly shorter than those expected for Van der Waals contacts between the two atoms. This may partly be due to the somewhat "diffuse" character of Van der Waals radii, partly also be explained if the bond, in the case of very weak charge-transfer interactions, has an intermediate character. The presence of charge-transfer interaction is indicated by the angle between the halogen-donor atom bond direction and the bond between the halogen atom and the atom in the acceptor molecule which is directly linked to it. This angle tends to be about 180° . It is readily recognized that the charge-transfer contribution to the bond is substantially increased when a lighter halogen atom is replaced by a heavier one. Thus, the nitrogen-halogen distance is actually a little *shorter* in the 1:1 adduct pyrazine-tetraiodoethylene than in the corresponding tetrabromoethylene adduct.

Even in complexes where "active" hydrogen atoms are linked to nitrogen or oxygen atoms bond distances are difficult to predict accurately, and observed values are often insignificantly shorter than those calculated under the assumption of a Van der Waals interaction. In such cases arguments in favour of a weak "hydrogen bond" between donor and acceptor molecule must to some extent be based on the actual geometry of the complex.

X-Ray investigations of solid adducts in which molecules containing oxygen, nitrogen, etc. act as donors, molecules containing halogen atoms or "active" hydrogen atoms as acceptors, have contributed substantially to our present knowledge about atomic arrangements in certain donor-acceptor complexes. Previous suggestions based on spectroscopic observations have in some cases been found incorrect. Simple rules for the arrangements of the bonds (to some extent even bond lengths) have been formulated. Perhaps most striking, and certainly not expected, is the farreaching analogy between atomic arrangements in complexes formed by the same category of donors with the two so

different types of acceptors. It may perhaps be suggested that the results obtained from direct X-ray structure analysis may contribute to the theoretical understanding of both categories of donor-acceptor interaction.

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