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Formation of Donor-Acceptor Complexes

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Results are summarised for the main principles governing the formation of complexes of type σn, νn (of halogens, metal halides, and organometallic compounds with various amines, ethers, and sulphides). The dipole moments and the heats of formation of the complexes are examined as the most important parameters characterising the properties of donor-acceptor bonds. Methods of determining these parameters are analysed.
Special attention is paid to the character of the relation between the degree of charge transfer and the energy of intermolecular bonds.
Two aspects of the problem of the donor properties of amines, ethers, and sulphides—the effect of molecular structure on the donor properties of the heteroatom, and the conditions for overlap of orbitals involved in the formation of donor-acceptor bonds—are discussed.
A method for determining the energy of p_π-conjugation in aromatic compounds containing a heteroatom is briefly described.
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1. INTRODUCTION

The nature of the intermolecular bonds in compounds of donor–acceptor type has remained a matter of controversy. The interpretation of π-complexes as charge-transfer complexes[1] is open to doubt[2]. It is supposed that the relatively low bond energies in π-complexes may be due to van der Waals forces, dipole–dipole interaction, and polarisation forces, and are not associated with charge transfer. A large number of molecular compounds are known whose formation is accompanied by a considerable change in dipole moments, which indicates a displacement of electron density or a transfer of charge from one component to the other on complex formation.

Within the very wide range of properties of intermolecular bonds it is impossible to draw a sharp distinction between strong and weak complexes. It is probable that the formation of intermolecular bonds between two valency-saturated molecules involves the maximum development of all possible forces—including polarisation, dipole–dipole, and van der Waals forces—and use is also made of the valency expansion possibilities of atoms and molecules responsible for donor–acceptor interaction. Each factor makes its contribution to the overall effect of formation of a molecular compound. Specific properties of molecular compounds and of intermolecular bonds will appear depending on how large a particular contribution is, the latter being determined by the composition and structure of the initial molecules.

The present Review will survey molecular compounds in which the transfer of charge predominates over other forces: i.e. compounds will be examined to which there is every justification for applying the term "charge-transfer complexes". Complexes formed by metal halides with various amines, ethers, sulphides, and also with certain aromatic compounds will be considered. It is supposed that the formation of intermolecular bonds in compounds of this type is accomplished mainly by partial transfer of an electron (or displacement of electron density) from the donor molecule to the acceptor molecule.

A necessary condition for the formation of an additional bond between two valency-saturated molecules is the presence of an occupied orbital of sufficiently high energy in the donor molecule and the presence of a sufficiently low unoccupied molecular orbital in the acceptor molecule. If electron transfer from a high filled orbital of one molecule to a lower free orbital of another is energetically favourable, a donor–acceptor bond is formed.

From the point of view of the theory of localised pairs, such an intermolecular bond is similar to an ordinary chemical bond produced by a pair of electrons in the field of two nuclei. The fundamental difference is that each atom supplies one electron to the formation of an ordinary chemical bond, whereas here one molecule—the donor—supplies the pair of electrons, while the second molecule—the acceptor—provides the vacant molecular orbital. Consequently, the properties of intermolecular bonds have many features in common with those of ordinary chemical bonds, as will be shown later, but they also exhibit their own specific characteristics.

Thus intermolecular bonds are formed by interaction between quite definite molecular orbitals in electron-donor and electron-acceptor molecules. The properties and the stereochemistry of such complexes will depend to a considerable extent on which orbitals are involved in forming the bond.

The existing classification[3] of molecular compounds of donor–acceptor type is based on the type of orbitals involved in bond formation. According to this, all molecules capable of developing donor properties, i.e. of donating an electron on interaction with other molecules, can be divided by means of the structural criterion into three groups—n, σ, and π—in the first of which the energetically highest orbital is the lone pair of n-electrons of the heteroatom (R_2O, R_2S, R_3N, etc.), in the second the pair of electrons of the σ-bond (R–Hal), and in the third a pair of π-

electrons of unsaturated and aromatic compounds having a sufficiently low ionisation potential.

Acceptor molecules can also be divided structurally into three groups—v, σ, and π—the lowest molecular orbital in the first being the vacant v-valency orbital of the metal atom (metal halides, certain organometallic compounds), in the second the non-bonding σ-orbital (I_2, ICl, Br_2, etc.), and in the third the system of π-bonds (aromatic and unsaturated compounds containing electron-acceptor substituents). In principle any donor is able to form a compound with any acceptor. It is all determined by the energetics of these processes. The same atom or molecule can act sometimes as a donor, sometimes as an acceptor, depending on its partner.

Donor–acceptor complexes can be classified as follows:

nv ($R_2O \cdot BX_3$)	σv ($RX \cdot BX_3$)	πv ($Ar \cdot BX_3$)
$n\pi$ ($R_2O \cdot Ar$)	$\sigma\sigma$ ($RX \cdot I_2$)	$\pi\sigma$ ($Ar \cdot I_2$)
$n\sigma$ ($R_2O \cdot I_2$)	$\sigma\pi$ ($RX \cdot Ar$)	$\pi\pi$ ($Ar \cdot Ar$).

The largest number of investigations have been concerned with complexes of types $\pi\pi$ and $\pi\sigma$. Comprehensive monographs[4,5] and reviews[6-8] have been published. Complexes with σ-donors have been least studied. As already stated, the present Review will survey mainly the results of our investigations on complexes of types nv, $n\sigma$, and partly πv.

From general ideas on donor–acceptor interaction it may be supposed that the most important parameter, on which the properties of intermolecular bonds and of the complexes largely depend, is the magnitude of the charge transferred from donor to acceptor.

One way to test experimentally the concept of intermolecular bonds as charge-transfer bonds is to investigate the type of relation between the degree of charge transfer and the stability of the resulting bonds. The degree of charge transfer can be assessed from the dipole moment of the intermolecular bond, and the stability from the heat of formation of the complexes. These two parameters will be examined later as the most important for characterising a donor–acceptor bond. The dipole moments of complexes have been investigated quite widely[9], but considerably fewer data are available on their heats of formation[10,11].

2. DETERMINATION OF DIPOLE MOMENTS AND HEATS OF FORMATION OF MOLECULAR COMPOUNDS

The usual method for determining the dipole moments of molecules in dilute solution is not very suitable for the investigation of molecular compounds, owing to possible dissociation into their components[12-15]. In several investigations attempts were made to overcome this difficulty by allowing for the dissociation constant of the complex, which was found by some other method; this necessitated additional experiments, and did not always yield the desired results.

More accurate results can be obtained by a method[16-19] in which the molecular polarisation of the complexes is determined by measuring the dielectric constant and the density (or refractive index) of a series of isomolar solutions. The experimental values of the polarisation for a range in which one component is present in excess, i.e. a range in which dissociation of the complex is suppressed, are extrapolated to infinite dilution. However, this method is extremely laborious, and exhibits the general defects associated with the extrapolation of experimental values of molecular polarisation to infinite dilution.

Dielectrometric titration must be acknowledged as experimentally the simplest method, giving the most accurate results for the dipole moments of molecular compounds[20-22]. It consists essentially in measuring the dielectric constant ϵ and the density d of solutions of the component A in an inert solvent ($C_A \simeq 0.05$–0.1 M) with successive addition of small portions of the component D.

The experiment is conducted in a measuring cell with stirring of the solution, which enables ϵ–C_D and d–C_D curves to be obtained (the latter by a float method) over a wide range of concentrations C_D for the same initial solution of component A. The design of the measuring cell enables experiments to be conducted in an atmosphere of a dry inert gas.

If the components A and D do not interact, linear ϵ–C_D and d–C_D relations are observed. In such case all that is required is to determine the dipole moment of the added substance D in a solvent containing a small quantity of substance A.

If a complex having a different dipole moment from that of the added component D is formed in the system, the dielectrometric titration curve for 1 : 1 complexes of moderate stability usually has the form mnl (Fig. 1). Extrapolation (by Hedestrand's method) of the initial portions of the ϵ–C_D and d–C_D curves gives the dipole moment of the compound AD when dissociation is suppressed. Extrapolation of the second portions of the curves (following the inflection) gives the dipole moment of the added substance D.

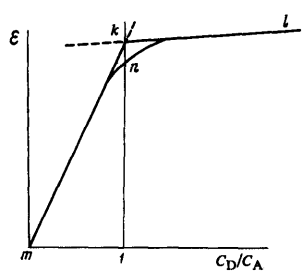


Figure 1. General form of dielectrometric titration curves for systems of the type A + D ⇌ A.D.

The parameters α and β in Hedestrand's equation are determined from the relations

$$\alpha = \frac{\varepsilon_s - \varepsilon_b}{C_{AD}}, \quad \beta = \frac{d_s - d_b}{C_{AD}},$$

where ϵ_s and d_s are the extrapolated values of the dielectric constant and the density of the solution at the point k (Fig.1), and ϵ_b and d_b are the dielectric constant and the density of benzene.

The departure of the experimental curve mnl from the extrapolated mkl is due to dissociation of the complex into its components. The magnitude of this deviation enables the equilibrium constant of the complexing reactions to be determined, and the thermodynamic parameters of the complex from the temperature dependence of the equilibrium constant[23,24].

In the case of complexes which are only slightly dissociated in solution the $\epsilon-C_D$ curves have the form *mkl* (Fig. 1), and dielectrometric titration gives values for the dipole moment which are close to those obtained by the usual method. With complexes which are dissociated the two methods show very substantial differences, the usual method giving incorrect results for the dipole moments in such systems.

Dielectrometric titration will give valuable information on complex formation in more complicated systems than 1 : 1 complexes. For example, investigation of the complexes formed by tin and titanium tetrachlorides with ethers and sulphides revealed that the processes took place in stages. Fig. 2 shows $\epsilon-C_D$ curves for the complexes of tin(IV) chloride with certain sulphides[25]. It is clearly evident that a 1 : 1 complex having a large dipole moment is formed initially when a sulphide is added to a solution of the tin chloride in benzene; this is followed by addition of a second molecule of the sulphide, accompanied by a decrease in the overall dipole moment of the complex. The process is complete with formation of a 1 : 2 complex, and the slope of the straight line following this ratio of the components corresponds to the dipole moment of the added sulphide.

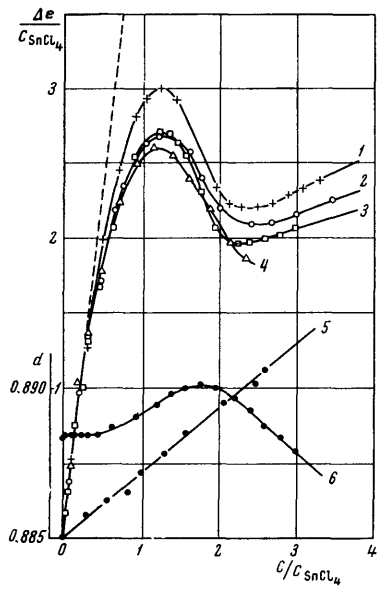


Figure 2. Curves for the dielectrometric titration of 0.05–0.15 M $SnCl_4$ in benzene with:
1) dibutyl sulphide; *2*) dinonyl sulphide; *3*) dioctyl sulphide; *4*) dihexadecyl sulphide; *5*) diphenyl sulphide; *6*) density of solutions of $SnCl_4 + (C_8H_{17})_2S$.

Valuable information on complexing processes has been obtained where more than one donor atom is present. Forward and back titration, e.g. in the aluminium bromide–dioxan system, has enabled the composition, structure, and mutual convertibility of 1 : 1 and 2 : 1 complexes to be established[26]. This procedure may be extremely useful for investigating complex formation by polymer molecules.

Thus dielectrometric titration enables the process of complex formation to be followed, the composition of the resulting complexes to be determined, and their dipole moments to be measured under conditions such that dissociation is suppressed. It is possible by this method to determine the equilibrium constants of the complexing reactions, and from their temperature dependence to find the thermodynamic parameters of the complexes[23,24].

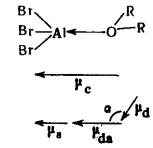
Investigation of the aluminium bromide–benzene system by dielectrometric titration[27] has led to the conclusion that the large dipole moment (exceeding 5 D), usually attributed to a complex of aluminium bromide with benzene, is due to water present as impurity in the benzene and the formation of a highly polar ternary complex $Al_2Br_6.HBr.nC_6H_6$. The true dipole moment of the complex of aluminium bromide with benzene proved to be ~ 1.0 D.

The heat of complex formation in the gas phase, with the energy of rearrangement of donor and acceptor molecules accompanying complex formation taken into account, is a direct measure[10] of the energy of the donor–acceptor bond. Among several methods[5,10] for determining heats of complex formation the most convenient—both experimentally and in the wide range of varied systems covered—is their measurement in solution. However, the effect of the solvent must then be allowed for. Several workers have shown[28–30] that heats of complex formation in inert solvents are close to the values in the gas phase.

Calorimetric titration is the most convenient method for obtaining actual data on heats of formation of molecular compounds which dissociate in solution[31]. Valuable information on the state of the compounds in solution is provided by cryoscopic titration[32]. Correlation of the results obtained by dielectrometry and calorimetry with the results of this method enables more unambiguous answers to be given to the questions of what complex and what state the measured parameters relate to.

3. STRUCTURE OF COMPLEXES OF DONOR–ACCEPTOR TYPE

The overall dipole moment of a complex μ_c can be written as the sum of three terms: $\mu_c = \mu_d + \mu_a + \mu_{da}$, where the right-hand side represents the dipole moments of the donor portion of the complex, the acceptor portion of the complex, and the donor–acceptor bond respectively. With the complex of aluminium bromide and ether, for example, resolution of the overall dipole moments μ_c into its components can be represented by the scheme



Hence, in order to evaluate μ_{da} from the experimental value of μ_c, it is necessary to know the magnitude and the relative orientation of μ_d and μ_a. Since complex formation involves in several cases rearrangement of both acceptor and donor molecules, the experimental data can be analysed provided that the structure of the molecular compounds is known. Structural investigations of complexes also provide information on the type of molecular orbitals involved in the formation of intermolecular bonds.

Extensive X-ray investigations[33–37] of complexes formed by halogens X_2 (Cl_2, Br_2, I_2, ICl) with aromatic hydrocarbons and with compounds containing oxygen, nitrogen, and

sulphur have shown that roughly the same kind of changes in the molecules accompany complex formation in all these systems.

In all X_2.D complexes the donor–acceptor bond X← D is located in line with the X–X bond: X–X←D has an XXD angle of 178–180°. Thus the two halogen atoms in the complex are not equivalent. The length of the X–X bond increases on complex formation, the elongation being greater the more stable the complex. Thus in the comparatively stable complexes formed by iodine with dibenzyl sulphide and with trimethylamine the increase in length of the iodine–iodine bond is 0.15 and 0.20 Å respectively. In the less stable complexes formed by chlorine and by bromine with benzene the X–X bonds are of practically the same length as in the free molecules. The lengths of the intermolecular bonds X–D are also associated with the stability of the complexes.

The orientation of donor molecules relative to the donor–acceptor bond differs with amines, ethers and sulphides.

The complex of dibenzyl sulphide with iodine[34] has an angular configuration (Fig. 3). The mirror plane of the molecule passes through the I–I←S line between the benzyl groups. The interatomic distances and angles in the sulphide molecule remain practically unchanged on complex formation. An analogous angular configuration has been found[35,36] in the complex of iodine with dithian. The angular configuration of the complexes formed by iodine with sulphides can be regarded as evidence that the donor pair of electrons in the sulphide molecule is the $3p^2$ lone pair of the sulphur atom.

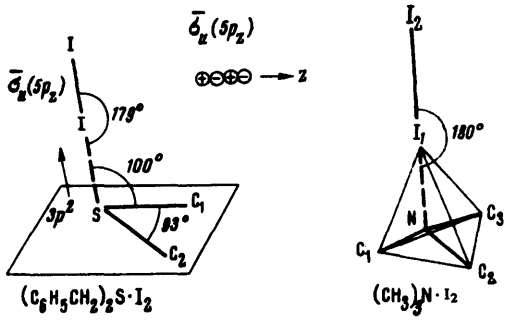


Figure 3. Structure of the complexes $(C_6H_5CH_2)_2S.I_2$ and $(CH_3)_3N.I_2$.

The trimethylamine molecule has a tetrahedral configuration[37] ($\alpha = 180°$) in its complex with iodine (Fig. 3). This indicates that the lone pair of electrons of the nitrogen atom takes part in the intermolecular bond in the sp^3 state.

The valency angle of oxygen in its complexes with halogens is not reliably known. X-Ray examination of the complex of dioxan with iodine chloride yields[38] 178° for the OICl angle, and a value of 160° has been found[39] from examination of the complex of dioxan with iodine.

X-Ray and electron-diffraction investigations of the complexes formed by boron trifluoride with amines[40–42] and with diethyl ether and by aluminium bromide with hydrogen sulphide[43] have shown that the acceptor portion of these complexes has a tetrahedral conformation. The amine molecules undergo no fundamental rearrangement on complex formation with boron trifluoride. Thus the angles at the nitrogen in the complexes formed by this halide with ammonia, methylamine, and trimethylamine are close to the tetrahedral angles (107–114°), while the length of the carbon–nitrogen bond in trimethylamine is 1.50 Å,[41] these being close to the parameters in free trimethylamine. The lengths of the boron–nitrogen, boron–oxygen, and aluminium–sulphur donor–acceptor bonds (1.53–1.60,[41,42] 1.52,[40] and 2.40 [43] Å) are close to or slightly exceed the sum of the covalent radii (1.58, 1.54, and 2.30 Å respectively).

Little work has been done on establishing the structure of the complexes formed by tetrahalides of Group IV metals. Tin and titanium tetrahalides give with oxygen and sulphur compounds complexes of two types—MX_4.D with five-coordination of the metal atom, and MX_4.2D with six-coordination of the metal—the process of complex formation taking place in stages[22,35,44,45].

It has been established by means of dipole moments that $TiCl_4.R_2S$ complexes[46] have the tetragonal pyramidal conformation *I* (Fig. 4), and $SnCl_4.R_2S$ complexes the trigonal bipyramidal conformation *II*. A bipyramidal structure has been found also by X-ray analysis for the 1 : 1 complex of trimethyltin chloride with pyridine[47].

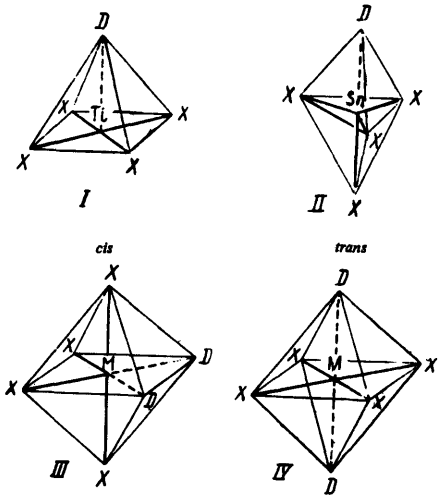


Figure 4. Conformation of complexes of tin and titanium tetrahalides.

For compounds having the composition MX_4.2D an octahedral conformation is the most probable, two isomers being possible here, with the donor molecules in *cis*- and *trans*-positions in the octahedron (*III* and *IV*, Fig. 4). An octahedral structure with *cis*-arrangement of the donor molecules has been established by X-ray examination for the complex $SnCl_4.2POCl_3$.[48] The same structure has been found for the complexes $SnCl_4.2SeOCl_2$ [49] and $TiCl_4.2POCl_3$.[50] A *cis*-octahedral structure has been established also for the dimeric compounds $SnCl_3OCH_3.CH_3OH$ and $SnBr_3OCH_3.CH_3OH$.[51] In contrast to this, a *trans*-octahedral conformation has been found[52] for the complex of tin tetrachloride with tetrahydrothiophen $SnCl_4.2C_4H_8S$.

The first use has been reported[53] of nuclear quadrupole resonance (n.q.r. of halogen atoms) for solving problems of *cis–trans*-isomerism in octahedral complexes. It has been established by the method of molecular orbitals that the n.q.r. frequency shifts and the character of the n.q.r. splittings differ for *cis*- and *trans*-isomers of octahedral complexes of Group IV metal halides with *n*-donors. Fig. 5 illustrates the relation between the structure of the isomers and the corresponding form of n.q.r. spectra. Fig. 5 includes also a suggested scheme of splitting for the bipyramidal complex $MX_4.D$, in which the coordination number of the metal is 5. The large splitting in the spectrum of the *cis*-isomer has been found to be due to the chemical non-equivalence of axial and equatorial halogen atoms.

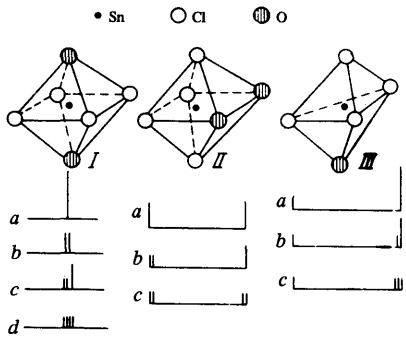


Figure 5. Splitting of nuclear quadrupole resonance spectra of complexes formed by tetrahalides of Group IV metals with *n*-donors.

The structure of several complexes of tin(IV) chloride has been established from the character of the splitting in the n.q.r. spectra: n.q.r. data[53] show that the complexes $SnCl_4.2POCl_3$ and $SnCl_4.2C_2H_5OH$ have the *cis*-structure *III* (Fig. 4), the complex $SnCl_4.2(C_2H_5)_2O$ has the *trans*-structure *IV* (Fig. 4), and the complexes $SnCl_4.CH_3O[CH_2]_2OCH_3$ and $SnCl_4.CH_3O[CH_2]_4OCH_3$ have a *trans*-chain structure (Fig. 6).

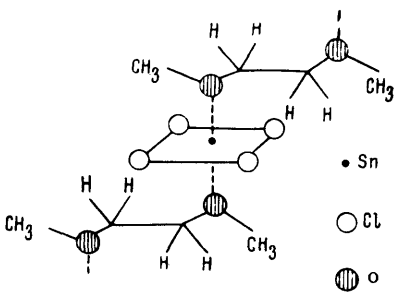


Figure 6. Structure of the complex $SnCl_4.CH_3O[CH_2]_2OCH_3$ in the solid state.

It may be noted that data on the structure of complexes obtained by X-ray examination and from nuclear quadrupole resonance, as well as most of the published data obtained by infrared spectroscopy[54–58], relate to the crystalline solid state. The method of dipole moments enables an assessment to be made of the state of complexes in solution.

A detailed investigation of the complexes formed by titanium tetrachloride with various sulphides led to the conclusion[45] that, in solution, the octahedral complexes $TiCl_4.2R_2S$ consist of a mixture of *cis*- and *trans*-isomers (*III* and *IV*, Fig. 4), with an approximately random distribution of donor molecules among the apices of the octahedron.

The dipole moments suggest that the complexes $SnCl_4.2R_2S$ are also present in solution (in benzene) as a mixture of *cis*- and *trans*-isomers[46]. On crystallisation the equilibrium may be displaced towards formation of either form. Such a situation is observed, for example, in the tin(IV) chloride–thiolan system: in benzene the complex $SnCl_4.2C_4H_8S$ is a mixture of isomers (dipole moment 5.0 [44]), but in the solid state it has the *trans*-structure[52].

Extremely interesting results have been obtained from an investigation of the complexes $SnCl_4.RO[CH_2]_2OR$ in benzene (dipole moments) and in the solid state (n.q.r.). Compounds of the type $RO[CH_2]_nOR$ or $RS[CH_2]_nSR$, whose molecules contain two donor atoms, enable octahedral complexes of definitely *cis*-structure to be obtained with titanium and tin tetrachlorides at values of $n = 2, 3$. The dipole moments of such complexes reach 9–10 D.[45,46,59] It was found that in benzene the complex $SnCl_4.RO[CH_2]_2OR$ was monomeric and had the *cis*-structure, and in the crystalline state it had a *trans*-chain structure[53].

Thus all the results obtained indicate unambiguously that the structure of octahedral complexes formed by tetrahalides of Group IV metals with *n*-donors may change on passing from one state to another. The character of the changes differs in different systems. This fact was further taken into account when considering the experimental dipole moments of the complexes.

4. DEGREE OF CHARGE TRANSFER AND STABILITY OF INTERMOLECULAR BONDS

Examination of the dipole moments and heats of formation of complexes formed by iodine with organic sulphides varying in structure has led[24,60] to the establishment of direct proportionality between the dipole moments of intermolecular bonds (μ_{da}) and the heats of formation of the complexes ($-\Delta H$). A similar $\mu_{da}-\Delta H$ relationship has been found in complexes formed by tin tetrachloride with organic sulphides[46]. It has been confirmed[61] for the complexes formed by iodine with amines and with ethers.

The value of μ_{da} is in general a complicated function of several parameters. Besides the displacement of electron density from donor to acceptor, a dipole moment may appear here, as in ordinary chemical bonds, as a result of a difference in size of the atoms, of a state of hybridisation. Contributions due to the difference in size of the atoms forming the bond (homopolar dipole) and to the change in hybridisation of the *n*-donors (atomic dipole) are probably small, especially as the molecules of donors (amines, ethers, sulphides) do not undergo any substantial changes on complex formation. Hence it may be assumed to a first approximation that the main contribution to the value of μ_{da} is made by the displacement of electron density from donor to acceptor, or the degree of charge transfer. The latter can be determined from the experimental values of μ_{da} and the interatomic distances r as the ratio μ_{da}/er, where e is the charge on the electron.

An attempt has been made[62] to ascertain whether a linear relation between μ_{da}/er and ΔH is characteristic of

narrow series of analogous complexes or whether it is general for the complexes under discussion. The range of materials investigated was therefore considerably extended, by determining the dipole moments and heats of formation of the complexes formed by tin and titanium tetrachlorides and tetrabromides with sulphides, ethers, and nitriles. Published data on the dipole moments and the heats of formation of the complexes were surveyed.

Table 1. Dipole moments, degrees of charge transfer, and heats of formation of donor–acceptor bonds in complexes[62].

No.	Complex	μ_c	μ_d	μ_{da}	r	$\frac{\mu_{da}}{er}$	ΔH
1	$I_2 \cdot (C_2H_5)_2O$	1.9	1.21	1.4	2.60	0.11	4.3
2	$I_2 \cdot C_5H_{10}O$	2.82	1.63	1.8	2.60	0.14	4.9
3	$I_2 \cdot C_4H_8O$	3.00	1.70	2.0	2.60	0.16	5.3
4	$I_2 \cdot (C_2H_5)_2S$	1.99	1.56	0.4	2.78	0.03	0.3
5	$I_2 \cdot (C_2H_5)_2S$	3.64	1.44	2.0	2.78	0.15	4.6
6	$I_2 \cdot (C_6H_5CH_2)_2S$	3.78	1.38	2.2	2.78	0.16	4.8
7	$I_2 \cdot (i\text{-}C_8H_{17})_2S$	4.72	1.63	3.1	2.78	0.23	7.4
8	$I_2 \cdot (i\text{-}C_7H_{15})_2S$	4.90	1.63	3.4	2.78	0.25	8.1
9	$I_2 \cdot (C_2H_5)_2S$	4.62	1.60	3.1	2.78	0.23	7.8
10	$I_2 \cdot (C_3H_7)_2S$	4.90	1.55	3.4	2.78	0.25	8.1
11	$I_2 \cdot (C_4H_9)_2S$	5.0	1.57	3.6	2.78	0.27	7.6
12	$I_2 \cdot (C_6H_{11})_2S$	5.34	1.58	3.8	2.78	0.28	7.0
13	$I_2 \cdot (C_{16}H_{17})_2S$	5.07	1.58	3.5	2.78	0.26	7.4
14	$I_2 \cdot C_4H_8S$	5.49	1.87	3.9	2.78	0.29	10.0
15	$I_2 \cdot (C_4H_{11})_2S$	5.44		4.0	2.78	0.30	10.5
16	$I_2 \cdot (C_6H_5CH_2)_3N$	2.80	0.65	1.1	2.30	0.10	2.3
17	$I_2 \cdot C_5H_5N$	5.70	2.02	2.7	2.30	0.24	7.5
18	$I_2 \cdot C_9H_7N$	5.70	2.25	2.5	2.30	0.23	7.1
19	$I_2 \cdot C_6H_5NH_2$	6.07	1.4	3.4	2.30	0.31	8.4
20	$SnCl_4 \cdot C_2H_5O(CH_2)_4OC_2H_5$	6.63	1.65	1.7	2.27	0.16	6.7
21	$SnCl_4 \cdot CH_3O(CH_2)_2O(CH_2)_2OCH_3$	8.15	1.91	2.8	2.27	0.26	10.7
22	$SnCl_4 \cdot C_2H_5O(CH_2)_2OC_2H_5$	9.24	1.63	3.5	2.27	0.32	10.9
23	$SnCl_4 \cdot C_2H_5O(CH_2)_2OC_2H_5$	8.82	1.65	3.2	2.27	0.29	11.9
24	$SnCl_4 \cdot C_4H_9O(CH_2)_2OC_4H_9$	9.18	1.60	3.5	2.30	0.32	11.5
25	$SnCl_4 \cdot C_6H_5SC_2H_5$	4.20	1.48	0.9	2.56	0.07	2.0
26	$SnCl_4 \cdot (C_6H_5CH_2)_2S$	4.77	1.38	1.5	2.56	0.12	3.8
27	$SnCl_4 \cdot (C_3H_7)_2S$	6.49	1.55	3.3	2.56	0.27	12.9
28	$SnCl_4 \cdot (C_4H_9)_2S$	6.71	1.57	3.5	2.56	0.28	12.6
29	$SnCl_4 (C_8H_{17})_2S$	6.79	1.58	3.6	2.56	0.29	11.9
30	$SnCl_4 (i\text{-}C_8H_{17})_2S$	3.76	1.63	0.4	2.56	0.03	0.4
31	$SnCl_4 \cdot C_4H_9SCH_2SC_4H_9$	8.42	1.34	2.7	2.56	0.22	7.3
32	$SnCl_4 \cdot C_4H_9S(CH_2)_2SC_4H_9$	9.96	2.02	3.9	2.56	0.32	12.6
33	$SnCl_4 \cdot C_4H_9S(CH_2)_3SC_4H_9$	10.82	1.89	4.4	2.56	0.36	13.7
34	$SnCl_4 \cdot CH_3CN$	7.63	3.40	1.2	2.20	0.11	7.0
35	$SnCl_4 \cdot C_6H_5CN$	8.40	3.90	1.5	2.20	0.14	6.1
36	$TiCl_4 \cdot C_6H_5CN$	7.08	3.90	3.1	2.13	0.30	11.5
37	$TiCl_4 \cdot (C_6H_5)_2O$	3.67	1.22	2.5	2.18	0.24	6.0
38	$TiCl_4 \cdot (C_6H_{17})_2O$	3.83	1.22	2.6	2.18	0.25	6.3
39	$TiCl_4 \cdot C_5H_{10}O$	4.52	1.87	3.1	2.18	0.30	12.0
40	$TiCl_4 \cdot C_2H_5O(CH_2)_2OC_2H_5$	7.77	1.65	3.3	2.18	0.31	11.9
41	$TiCl_4 \cdot C_4H_9O(CH_2)_2OC_4H_9$	8.23	1.60	3.6	2.18	0.34	12.9
42	$TiCl_4 \cdot C_2H_5O(CH_2)_2OC_2H_5$	8.16	1.63	3.6	2.18	0.34	11.6
43	$TiCl_4 \cdot C_4H_8S$	4.54	1.71	4.1	2.47	0.34	12.0
44	$TiCl_4 \cdot (C_4H_9)_2S$	4.66	1.58	4.3	2.47	0.36	11.5
45	$TiCl_4 \cdot C_4H_9S(CH_2)_2SC_4H_9$	8.78	1.89	4.1	2.47	0.34	12.6
46	$TiCl_4 \cdot C_4H_9S(CH_2)_2SC_4H_9$	8.31	2.02	3.7	2.47	0.31	11.0
47	$SnBr_4 \cdot C_4H_9S(CH_2)_2SC_4H_9$	10.25	1.89	4.2	2.56	0.34	10.0
48	$TiBr_4 \cdot C_4H_9S(CH_2)_2SC_4H_9$	8.42	2.02	3.9	2.47	0.33	10.3
49	$TiBr_4 \cdot C_2H_5O(CH_2)_2OC_2H_5$	7.70	1.65	3.4	2.18	0.32	10.6
50	$BF_3 \cdot (CH_3)_2O$	4.35	1.25	2.8	1.54	0.38	13.7
51	$BF_3 \cdot C_4H_8O$	5.68	1.70	3.4	1.54	0.46	16.8
52	$B(CH_3)_3 \cdot NH_3$	4.15	1.30	2.6	1.58	0.34	13.8
53	$B(CH_3)_3 \cdot N(CH_3)_3$	3.92	0.75	2.9	1.58	0.38	17.6

Since the relationship proved to be general in character, it appears desirable to examine the results of this work in greater detail. Table 1 gives the formulae of the complexes, the values of μ_c, μ_d, μ_{da}, and r, and also the parameters μ_{da}/er and the heats of formation ΔH per donor–acceptor bond. In the determination of μ_{da} (see scheme at beginning of Section 3) from the experimental values of μ_c, account was taken of the structure of the complex and the values of μ_d and μ_a. The molecules of amines, ethers, sulphides, and nitriles give donor–acceptor bonds involving the lone pair of the corresponding heteroatom. It can be assumed to a first approximation that μ_d in the complex is equal to the dipole moment of the initial molecule. With regard to the relative arrangement of the μ_d and μ_{da} vectors, it follows from what has been said above that the angle α between them can be taken to be 100° in the sulphide complexes, 150–160° in the ether complexes, and 180° in the complexes with amines and nitriles.

The dipole moments of the acceptor part of the complexes μ_a were determined in conformity with the structure of the complex and the moments of the M–Hal bonds. The conformation of a tetragonal pyramid (*I*, Fig. 4) was adopted for the five-coordinate complexes $TiX_4.D$, a trigonal bipyramid (*II*) for the five-coordinate complexes $SnCl_4.D$, and an octahedral conformation for the six-coordinate complexes $MX_4.2D$. For the third group, only data relating to complexes of definitely *cis*-structure (*III*, Fig. 4) have been considered. The dipole moments of the M–X bonds were taken to be as follows[65]: Sn–Cl 3.0 D, Sn–Br 2.9 D, Ti–Cl 2.2 D, and Ti–Br 2.1 D.

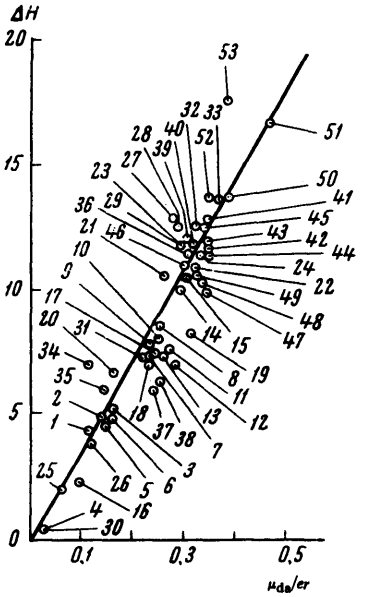


Figure 7. Dependence of ΔH on μ_{da}/er for complexes of I_2, $SnCl_4$, $SnBr_4$, $TiCl_4$, $TiBr_4$, $(CH_3)_3B$, and BF_3 with amines, ethers, and sulphides (numbering of points corresponds to Table 1.).

A tetrahedral structure was adopted[40] for the complexes formed by boron trifluoride with dimethyl ether and with tetrahydrofuran and by trimethylboron with ammonia and with trimethylamine, the bond dipole moments being 1.6 D for the boron–fluorine bond[64,65] and 0.3 D for the boron–methyl bond[65].

The data in Table 1 show that a definite relation exists between the parameters μ_{da}/er and the heats of formation of the coordinate bonds $-\Delta H$: the greater the degree of charge transfer, the larger the heat of formation, and hence the more stable the intermolecular bond. This is especially clearly evident from Fig. 7.

The equation to the straight line, found by the method of least squares, is

$$\Delta H = 35.3 \frac{\mu_{da}}{er} \qquad (1)$$

The results in Table 1 cover more than fifty diverse systems. From this it may be concluded that the relation established between the degree of charge transfer and the stability of the intermolecular bond is general for donor–acceptor complexes of type $n\nu$, $n\sigma$.

The direct proportionality between the degree of charge transfer and the energy of formation of a coordinate bond can be regarded as quantitative evidence of the correctness of the view that intermolecular bonds of this type are charge-transfer bonds.

A theoretical basis for the experimental relation (1) can be obtained from Mulliken's theory of charge-transfer complexes[1,3]. The wave function of the ground state of a complex A.D is written to a first approximation in the form

$$\psi = a\psi_0(\mathrm{A, D}) + b\psi_1(\mathrm{A^- — D^+}) \qquad (2)$$

in which ψ_0 is the wave function of the "bondless" structure and ψ_1 the wave function corresponding to the structure with transfer of charge. Solution of this equation for the case in which $a > b$ gave relations[1] between certain parameters of the complexes.

On the basis of these relations the equation

$$\Delta H = \frac{h\nu}{a^2\left(1+\frac{a}{b}S_{01}\right)\left(1+\frac{b^2}{a^2}+\frac{b^{*2}}{a^{*2}}\right)} \cdot \frac{\mu_{da}}{er} \qquad (3)$$

has been deduced[24,61], linking the degree of charge transfer μ_{da}/er with the energy of formation of the complex ΔH. Here $h\nu$ is the energy of the electronic transition corresponding to the charge-transfer band, a and b are the coefficients in Eqn. (2), a^* and b^* are the coefficients in the analogous equation describing the excited state, and $S_{01} = S\psi_1\psi_0 d\tau$ is the overlap integral of the functions ψ_0 and ψ_1 (Eqn. 2).

The large majority of investigations[4–6] on charge-transfer complexes have involved studying the corresponding ultraviolet or visible absorption bands. Equation (3) shows how the position of the charge-transfer band is related to the degree of charge transfer and the energy of the intermolecular bond. It enables experimental values of μ_{da}/er and ΔH to be used to predict the position of the corresponding bands. This is of great value, especially in view of the fact that hardly any work has been done on charge-transfer bands for complexes of type $n\nu$.

The necessary and sufficient condition for a linear relation between μ_{da}/er and ΔH is that the coefficient

$$\frac{h\nu}{a^2\left(1+\frac{a}{b}S_{01}\right)\left(1+\frac{b^2}{a^2}+\frac{b^{*2}}{a^{*2}}\right)} = K \qquad (4)$$

should be constant for different complexes. The problem of the constancy of K (Eqns. 3 and 4) for different complexes, and how close it is to the slope (35.5 kcal or 1.5 eV) of the experimental straight line (1), can be approached in various ways.

We can use the charge-transfer bands $h\nu$ known for certain complexes to calculate K (Eqn. (4) and compare the result with the experimental value (1). Or, if the charge-transfer bands are unknown, we can start with experimental values of ΔH and μ_{da}/er, predict the position of the bands by means of Eqn. (3), and verify the result experimentally.

Corresponding calculations of K using values of $h\nu$ for a series of iodine complexes have shown[62] entirely satisfactory agreement with the experimental value of K. In addition, experimental values of μ_{da}/er and ΔH have been used to predict and to find previously unknown charge-transfer bands in a series of complexes of tin and titanium tetrachlorides with ethers and sulphides.

It has been shown that the experimentally established linear relation between degree of charge transfer and energy of the donor–acceptor bond can be described by Eqn. (3), obtained on the basis of Mulliken's theory.

The presence of direct proportionality between values of ΔH and μ_{da} for the same acceptor with a group of similar donors can be used to estimate values of μ_a. In this way dipole moments have been determined[62] for the iodine molecule in complexes with sulphides and amines (0.8–1.0 D). These values have been taken into account in determining μ_{da} in the corresponding complexes. An analogous estimate[62] of the dipole moment of the tin–chlorine bond in five-coordinate complexes of tin(IV) chloride with organic sulphides gives 3.0 D, practically identical with the dipole moment of this bond in the tin tetrachloride molecule[63].

5. DONOR PROPERTIES OF AMINES, ETHERS, AND SULPHIDES

Two aspects of the problem of the donor properties of molecules containing a heteroatom—the influence of the structure of the molecule on the donor properties of the heteroatom and the comparative donor properties of amines, ethers, and sulphides of similar structure—will be considered. The effect of molecular structure on donor properties is revealed most clearly in sterically unhindered complexes. The complexes formed by iodine with amines, ethers, and sulphides meet these requirements most closely.

Table 2. Dipole moments and dissociation constants of complexes of iodine with sulphides.

Complex	μ	$10^{-3}K$	Complex	μ	$10^{-3}K$
$(C_2H_5)_2S\cdot I_2$	4.62	4.0	$(C_3H_5)_2S\cdot I_2$	3.64	2.0
$(C_3H_7)_2S\cdot I_2$	4.90	3.4	$C_4H_8S\cdot I_2$	5.49	1.2
$(C_4H_9)_2S\cdot I_2$	5.00	2.7	$2.5(CH_3)_2C_4H_8S\cdot I_2$	5.76	1.4
$(C_5H_{11})_2S\cdot I_2$	5.37	3.1	$(C_6H_5CH_2)_2S\cdot I_2$	3.78	2.3
$(C_8H_{17})_2S\cdot I_2$	5.07	1.6	$(C_6H_{11})_2S\cdot I_2$	5.44	2.3
$(C_9H_{19})_2S\cdot I_2$	5.23	1.9	$C_4H_4S+I_2$	0.42*	—
$(C_{10}H_{21})_2S\cdot I_2$	4.78	0.8	$(C_6H_5)_2S+I_2$	1.99*	—
$(C_{16}H_{33})_2S\cdot I_2$	4.35	0.3	$C_6H_5SCH_3+I_2$	1.88*	—
$(i\text{-}C_4H_9)_2S\cdot I_2$	5.15	4.7	$C_6H_5SC_2H_5+I_2$	2.63*	—
$(i\text{-}C_5H_{11})_2S\cdot I_2$	5.06	1.9	$C_6H_5SC_{10}H_7+I_2$	1.75*	—
$(i\text{-}C_5H_{11})SC_4H_9\cdot I_2$	5.12	1.4	$(C_2H_5)_2S_2+I_2$	2.48*	—
$(s\text{-}C_7H_{15})_2S.I_2$	4.90	1.4	$(C_2H_5)_2S_3+I_2$	2.24*	—
$(s\text{-}C_8H_{17})_2S.I_2$	4.72	1.0	$C_2H_5S(CH_2)_2SC_2H_5\cdot 2I_2$	5.50	—

* Dipole moments of the sulphides in the presence of iodine (~0.04 M).

Table 2 gives[66] dipole moments and dissociation constants for complexes of iodine with sulphides of different structures. Various dialkyl sulphides (C_2–C_{16}) both straight-chain and iso-structures, form with iodine complexes of almost identical stability, their dipole moments being 4.6–5.6 D.

In contrast, aromatic and $\alpha\beta$-unsaturated sulphides exhibit very weak donor properties towards iodine. The dipole moments of diphenyl sulphide and thiophen, measured in the presence of iodine (0.05–0.1 M), are close to the values in the pure solvent. Proof that the diminution in donor properties in this case is not due to steric hindrance is provided by the fact that the saturated analogues—dicyclohexyl sulphide and thiolan—form with iodine under

the same conditions stable compounds having dipole moments and dissociation constants close to the corresponding values for complexes of iodine with dialkyl sulphides.

If the C=C double bond or the aromatic ring is moved away from the sulphur atom, as occurs in $\beta\gamma$-unsaturated compounds, the sulphur atom is able to form a donor–acceptor bond with iodine. Dibenzyl sulphide and diallyl sulphide behave towards iodine in a fundamentally similar manner to dialkyl sulphides, but the dipole moments of the complexes are considerably smaller.

The differences in the behaviour of $\alpha\beta$- and $\beta\gamma$-unsaturated compounds of sulphur compared with saturated compounds is probably explained by a greater or smaller degree of interaction of the lone pair of electrons of the sulphur atom, responsible for complex formation, with the π-electrons of the unsaturated systems.

Table 3. Dipole moments and thermodynamic constants of complexes I_2.D of iodine with amines, sulphides, and ethers.

Donor	μ_c	μ_{da}	$-\Delta H$	$-\Delta S$	$-\Delta F_{298°}$	$K_{298°}$
Triethylamine	10.50	9.7	—			
Tripentylamine	8.50	7.2	12.3			
Trioctylamine	8.20	6.0	12.2			
Butylamine	6.07	4.4	8.4			
Pyridine	5.70	3.7	6.0	9.4	3.2	222
Quinoline	5.70	3.5	5.6	7.4	3.4	300
Tribenzylamine	2.80	2.1	2.3			
Triphenylamine	—	—	1.1			
Thiophan **	5.49	4.7	10.0			
Dicyclohexyl sulphide	5.44	4.8	10.5	23.1	3.6	435
Diethyl sulphide	4.62	3.9	7.8	15.9	3.4	310
Dipropyl sulphide	4.90	4.2	8.1	15.8	3.4	294
Dibutyl sulphide	5.00	4.4	7.6	13.6	3.6	385
Dipentyl sulphide	5.34	4.6	7.0	11.7	3.5	360
Dioctyl sulphide	5.07	4.3	7.4	11.6	3.9	746
Di-s-heptyl sulphide	4.90	4.2	8.1	14.0	3.9	714
Di-s-octyl sulphide	4.72	3.9	7.4	11.0	4.1	1000
Dibenzyl sulphide	3.78	3.0	4.8	3.3	3.8	614
Diallyl sulphide	3.64	2.8	4.6	3.0	3.7	500
Thiophen	0.42*	0	0.4			
Diphenyl sulphide	1.99*	0.4	0.3			
Tetrahydrofuran	3.00	2.0	5.3			
Tetrahydropyran	2.82	1.8	4.9			
Diethyl ether	1.9	1.4	4.3			
Phenetole	—	—	0.5			

* Dipole moments of the sulphides measured in the presence of iodine.

** It is not clear whether thiophen or tetrahydrothiophen is intended here (Ed. of Translation).

Analysis of experimental data on the effect of the structure of the radicals on the donor properties of the heteroatom has shown that the Hammett–Taft rule is satisfied in sterically unhindered complexes. For complexes of iodine with sulphides the equation[25,26] is $-\Delta H = 7.7 - 6.7\,\Sigma\sigma^*$. The large value (6.7) of the coefficient indicates that the complexing reactions are very sensitive to change in the electron density on the heteroatom. An analogous effect of molecular structure on the donor properties of the heteroatom is observed in complexes of iodine with amines and with ethers[24,61,67], as is well illustrated by the data in Table 3.

Complexes with other acceptors, however, begin to exhibit the effect of the steric factor, which makes corrections necessary. The length and the branching of the aliphatic radicals R in ethers ROR have been shown[59] to have an immense influence on their complexing power towards tin(IV) chloride. In the analogous but more stable complexes of the latter with sulphides[22,25,46] the effect of the steric factor is less important, the size of the heteroatom also being of significance.

With aluminium tribromide and also with gallium trichloride aliphatic amines, ethers, and sulphides, independently of the length or degree of branching of the radicals, form complexes having approximately the same degree of charge transfer and stability of their intermolecular bonds[21,68,69].

The donor (or basic) properties of ethers and amines are often assessed from the displacement of the γ_{OD} band in the infrared spectrum of deuteriomethanol on interaction of the latter with the donor (Gordy's method). It is clear from the above that the basicity sequences obtained by this method may be completely different when other acceptors are used. This must be borne in mind in interpreting experimental data in terms of donor–acceptor interaction.

Let us compare the donor properties of amines, ethers, and sulphides of analogous structure. From the ionisation potentials of amines, sulphides, and ethers of similar composition (Table 4) it may be expected that, according to the degree of charge transfer and the stability of the intermolecular bonds with the same acceptor, the sequence of the compounds will be amines > sulphides > ethers. Such a sequence of donor properties is actually observed in the complexes with iodine[61] and tin(IV) chloride[62] and bromide[62].

Table 4. Ionisation potentials (eV) of some amines, sulphides, and ethers[70,71].

Amines	I	Sulphides	I	Ethers	I
$(CH_3)_3N$	7.82	$(CH_3)_2S$	8.68	$(CH_3)_2O$	10.0
$(C_2H_5)_3N$	7 50	$C_2H_5SCH_3$	8.55	$C_2H_5OCH_3$	9.81
$(C_3H_7)_3N$	7.23	$(C_2H_5)_2S$	8.48	$(C_2H_5)_2O$	9.53

In the complexes with titanium(IV) chloride and bromide[62] ethers and sulphides have closely similar donor properties, but in the complexes with aluminium tribromide and trichloride the sequence changes, ethers proving to be stronger donors than are sulphides. According to the degree of charge transfer and the stability of the intermolecular bonds the complexes are arranged in the sequence[68,69]

$$AlBr_3 \cdot R_3N > AlBr_3 \cdot R_2O > AlBr_3 \cdot R_2S\ .$$

The same sequence is observed in the complexes with boron trifluoride[68].

The question arises why ethers, which have a higher ionisation potential than have sulphides, are more active donors towards aluminium and boron halides than are the corresponding sulphides. A possible explanation, that this is due to the specific character of halides of Group III elements, in particular their strength as acceptors, is untenable, since in the complexes with gallium trichloride the strength of the donor–acceptor bonds and the degree of charge transfer vary in the sequence[21,68]

$$GaCl_3 \cdot R_3N > GaCl_3 \cdot R_2S > GaCl_3 \cdot R_2O\ .$$

Sulphides are more active donors than are ethers towards gallium trichloride. A similar sequence[72] of variation in donor properties is found in the gallium tribromide and tri-iodide complexes.

An extremely important factor in the formation of ordinary chemical bonds, by means of a pair of electrons in the

field of two nuclei, is the degree of overlap of the corresponding orbitals. This factor has been found to play a quite important part also in the formation of donor–acceptor bonds. Table 5 gives the overlap integrals of the corresponding orbitals involved in the formation of intermolecular bonds, calculated by the Slater approximation[73].

Table 5. Overlap integrals of intermolecular bonds.

Acceptor	Donor				Experimental sequences	Ref.
	N($2sp^3$)	S($3p$)	O($2sp^3$)	O($2sp^3$)		
I ($5p$)	0.29	0.23	0.14	0.14	I—N>I—S>I—O	24.61
Sn ($5d^2sp^3$)	0.42	0.36	0.28	—	Sn—N>Sn—S>Sn—O	62
Ti ($3d^24sp^3$)	—	0.36	0.38	—	Ti—S≃Ti—O	62
Ga ($4sp^3$)	0.49	0.41	0.41	0.43	Ga—N>Ga—S—Ga—O	68
Al ($3sp^3$)	0.48	0.38	0.42	0.40	Al—N>Al—O>Al—S	68.69
B ($2sp^3$)	0.60	0.47	0.54	0.52	B—N>B—O>B—S	68
O—H($1s$)	0.48	0.36	0.42	0.43	O—H...N>OH···O>OH...S	

In the complexes of amines, sulphides, and ethers with iodine and with tin tetrahalides the overlap integrals vary in the same sequence as do the ionisation potentials of the corresponding donors. These two factors operate in the same direction, ensuring the sequence—amines > sulphides > ethers—for the donor properties. In the complexes of titanium tetrahalides the overlap integrals are closely similar with ethers and with sulphides. This is probably the main reason for the almost identical stability of the intermolecular bonds in complexes of titanium(IV) chloride and bromide with ethers and with sulphides.

Gallium–sulphur and gallium–oxygen intermolecular bonds have equal overlap integrals. Here the sequence of donor properties—amines > sulphides > ethers—corresponds to the differences in the ionisation potentials.

In the complexes of boron and aluminium halides the overlap integrals of the aluminium–oxygen intermolecular bonds are larger than those of the aluminium–sulphur bonds. This fact obviously plays a decisive part and is responsible for the greater stability of the bonds in ether than in sulphide complexes, in spite of the opposite relationship of the ionisation potentials. It is interesting that the same sequence of donor properties—amines > ethers > sulphides—is observed also with hydrogen bonds. Preliminary calculations of the overlap integrals of the corresponding orbitals (Table 5) confirm this sequence.

Comparison of data (Table 5) relating to aluminium and boron halides with those for systems containing hydrogen bonds shows that the observed relationship of the donor properties of ethers and sulphides is not linked with the strength of the acceptor, as would appear at first glance, but is actually determined by the degree of overlap of the corresponding orbitals.

Thus the results which have been cited show that the conditions of overlap of the orbitals involved in the formation of intermolecular bonds are of paramount significance in the formation of donor–acceptor bonds, and in considerable measure determine the properties of the latter.

When the donor properties of various compounds containing a heteroatom are to be compared, account must be taken of the whole set of parameters governing the formation of intermolecular donor–acceptor bonds.

6. DETERMINATION OF ENERGY OF P_π-CONJUGATION IN AROMATIC COMPOUNDS CONTAINING A HETEROATOM BY THE METHOD OF COMPLEX FORMATION

Investigation of the donor power of amines, ethers, and sulphides towards iodine, and of ethers and sulphides towards tin and titanium tetrahalides, has shown that aromatic compounds, unlike aliphatic compounds, do not give with these acceptors complexes which are stable in solution. The chief reason for the marked weakening of the donor properties of aromatic compared with aliphatic compounds is, as mentioned above, interaction of the lone pair of electrons of the heteroatom responsible for complex formation with the system of π-electrons of the aromatic radicals (p_π-conjugation).

In contrast to the above, relatively weak acceptors—the halides of aluminium, gallium, and also boron—yield with aromatic amines, ethers, and sulphides stable complexes, whose dipole moments are close to those of the corresponding complexes with aliphatic donors.

Detailed investigation of the properties of the complexes formed by aluminium tribromide and gallium trichloride with aromatic compounds has shown[68,74–76] that the formation of intermolecular bonds is accompanied by the breakdown of p_π-conjugation. This is clearly demonstrated, for example, on comparing the ultraviolet spectra of anisole and its complex with aluminium tribromide. The spectrum of anisole changes abruptly on complex formation, and approaches that of benzene. The absorption bands in the region of 219 and 270 nm, attributed[77–80] to conjugation of the lone pair of electrons of the oxygen atom with the system of π-electrons of the ring, disappear on complex formation.

Analogous changes in spectra, indicating breakdown of p_π-conjugation in heteroaromatic compounds on complex formation with aluminium tribromide and with gallium trichloride, have been observed[68] in systems containing phenetole, diphenyl ether, 2-methoxynaphthalene, and their sulphur analogues.

Table 6. Dipole moments μ_c and heats of formation ($-\Delta H$) of complexes in benzene.

Complex	μ_c	$-\Delta H$	Complex	μ_c	$-\Delta H$
$AlBr_3$.D, where D =			$(C_3H_7)_3N$	8.58	33.4
$(C_2H_5)_2O$	7.05	23.2	$(C_5H_{11})_3N$	—	31.5
$(C_3H_7)_2O$	7.26	22.8	$(CH_3)_2NC_6H_{11}$	8.45	32.7
$(C_4H_9)_2O$	7.25	23.2	$C_6H_5N(CH_3)_2$	8.68	24.2
$(C_8H_{17})_2O$	7.41	24.0	$(C_6H_5)_2NCH_3$	8.01	17.2
$C_6H_5OCH_3$	7.00	15.5	C_5H_5N	9.00	31.4
$C_6H_5OC_2H_5$	7.08	16.8	C_9H_7N	9.89	30.1
$(C_6H_5)_2O$	7.29	12.0			
$(p\text{-}CH_3C_6H_5)_2O$	7.58	13.0			
$(p\text{-}BrC_6H_5)_2O$	5.56	9.5	$GaCl_3$.D, where D =		
$\beta\text{-}C_{10}H_7OCH_3$	7.44	15.4	$(C_4H_9)_2O$	6.36	16.0
$\alpha\text{-}C_{10}H_7OC_2H_5$	—	16.1	$(C_8H_{17})_2O$	6.44	17.4
$C_4H_8O_2$	5.40	20.9	$C_6H_5OCH_3$	6.11	10.2
C_4H_8O	7.14	29.4	$C_6H_5OC_2H_5$	—	11.0
$C_5H_{10}O$	7.18	25.6	$(C_6H_5)_2O$	6.30	5.8
$(C_3H_7)_2S$	7.08	17.7	$(C_6H_5)_2S$	7.42	—
$(C_4H_9)_2S$	7.30	17.6	$(C_8H_7)_2S$	—	19.6
$(i\text{-}C_4H_9)_2S$	7.46	18.2	$(C_4H_9)_2S$	7.41	19.0
$(C_5H_{11})_2S$	7.26	18.1	$(C_7H_{15})_2S$	7.83	19.2
$(i\text{-}C_7H_{15})_2S$	8.13	17.1	$(C_9H_{11})_2S$	—	18.3
$(C_8H_{17})_2S$	—	17.1	$C_6H_5SCH_3$	7.39	13.9
$(i\text{-}C_8H_{17})_2S$	—	16.1	$C_6H_5SC_2H_5$	—	15.3
$(C_{16}H_{33})_2S$	7.74	—	$(C_6H_5)_2S$	7.62	11.2
$(C_6H_{11})_2S$	8.24	16.9	C_4H_8S	7.54	18.7
$C_6H_5SCH_3$	7.00	13.1	$(C_3H_7)_3N$	9.01	30.2
$C_6H_5SC_2H_5$	7.14	14.3	$(C_5H_{11})_3N$	—	35.2
$(C_6H_5)_2S$	7.55	10.2	$(C_6H_{13})_3N$	9.18	34.9
$C_{10}H_7SC_6H_5$	7.85	9.8	$C_6H_5N(CH_3)_2$	—	24.5
C_4H_8S	—	18.4	$(C_6H_5)_2NCH_3$	—	16.4
$(C_5H_5)_3N$	8.74	31.5			

The destruction of p_π-conjugation in aromatic compounds accompanying complex formation should, of course, be evident in the energetics of the complexing reactions.

Table 6 shows that corresponding complexes with aliphatic and aromatic ethers have closely similar dipole moments. Taking the complexes of aluminium bromide with ethers as example, we can examine the contributions made by the acceptor molecule μ_a and the donor molecule μ_d to the overall dipole moment of the complex μ_c (see scheme at beginning of Section 3). If a tetrahedral conformation is assumed for the bonds about the aluminium atom in the complex, μ_a will be close to the dipole moment of the aluminium–bromine bond. Unfortunately, this quantity is unknown, but it can obviously be assumed, to an adequate degree of approximation, to be the same in all complexes of aluminium bromide with ethers.

The dipole moments of aliphatic and aromatic (unsubstituted) ethers are closely similar at 1.15–1.30 D.[9] The angle α can also be regarded as the same in all these complexes. It therefore follows from the equality of μ_c for complexes of aluminium bromide with aliphatic and with aromatic ethers that the dipole moments of the donor–acceptor bonds μ_{da} are also equal in these complexes.

It has been shown above that there is direct proportionality between μ_{da}/er and ΔH for complexes of donor–acceptor type. Consequently the equality of values of μ_{da} in complexes formed by aluminium tribromide with aliphatic and with aromatic ethers should imply equality of the formation enthalpies of the intermolecular bonds in these complexes.

The total heat of complex formation in an inert solvent can be represented by three components:

$$\Delta H = \Delta H_{da} + \Delta H_a + \Delta H_d$$

where ΔH_{da} is the heat of formation of the donor–acceptor bond and ΔH_d and ΔH_a are the energies or rearrangement of donor and acceptor molecules on complex formation. In the complexes of aluminium bromide with ethers the term ΔH_a can be regarded as constant. Hence in the series of complexes of aluminium bromide with aromatic and aliphatic ethers the quantity $\Delta H_{da} + \Delta H_a$ is the same, and differences in the experimental heats of complex formation ΔH are determined by the term ΔH_d, the energy of rearrangement of the donor molecule. No substantial quantity of heat—of the order of 0.3 kcal mole^{-1} [40]—is required for the molecular rearrangement of aliphatic ethers on complex formation. Therefore the differences in the values of ΔH for complexes of aluminium bromide with aliphatic and aromatic ethers (Table 6) can be ascribed to the energy of rearrangement of the corresponding aromatic ethers.

It has been established spectroscopically[68,74,76] that the rearrangement of aromatic ethers accompanying complex formation consists in the disruption of p_π-conjugation, so that the energy of rearrangement of an aromatic donor is the p_π-conjugation energy. The latter has been determined[68,75] as the difference between the mean value of ΔH for complexes of aluminium bromide with aliphatic ethers (23.3 kcal mole^{-1}) and the corresponding values of ΔH for its complexes with aromatic ethers.

An analogous analysis of the ultraviolet spectra, dipole moments, and heats of formation of complexes with sulphides and amines, as well as of the aluminium chloride, gallium chloride, and boron fluoride complexes with aliphatic and aromatic amines, ethers, and sulphides, has enabled the energies of conjugation E_j in the corresponding molecules to be determined. The accuracy of the determination is 0.8–1.0 kcal mole^{-1}.

Table 7 gives values of E_j found[68] by the method of complex formation with various acceptors. It is seen that closely similar values of the p_π-conjugation energy are obtained for the same donor by complex formation with four different acceptors. The slight discrepancy of 1–1.5 kcal mole^{-1} is primarily due to the steric factor. Among the acceptors investigated the steric effect is least in the aluminium bromide complexes, and greatest in the complexes of boron trifluoride. The most reliable values of E_j are those obtained in the aluminium bromide complexes.

Table 7. Energies of p_π-conjugation (E_j, kcal mole^{-1}) in aromatic ethers, sulphides, and amines obtained by complex formation with various acceptors.

Donor	Acceptor			
	$AlBr_3$	$AlCl_3$	$GaCl_3$	BF_3
$C_6H_5OCH_3$	7.8	7.3	6.5	8.3
$C_6H_5OC_2H_5$	6.5	—	5.7	8.3
$(C_6H_5)_2O$	11.3	11.2	10.9	—
$(p\text{-}CH_3C_6H_4)_2O$	10.3	—	—	—
$(p\text{-}BrC_6H_4)_2O$	13.8	—	—	—
$\beta\text{-}C_{10}H_7OCH_3$	7.9	—	—	—
$\alpha\text{-}C_{10}H_7OC_2H_5$	7.2	—	—	—
$C_6H_5SCH_3$	4.4	5.3	5.2	—
$C_6H_5SC_2H_5$	3.2	4.8	3.8	—
$(C_6H_5)_2S$	7.3	8.5	7.8	—
$\alpha\text{-}C_{10}H_7SC_6H_5$	7.7	—	—	—
$C_6H_5N(CH_3)_2$	8.1	7.6	9.0	9.7
$(C_6H_5)_2NCH_3$	14.9	14.8	17.0	—

The identical values of E_j obtained in complexes with different acceptors confirm the correctness of the initial premises, and indicate that the direct proportionality established between the degree of charge transfer and the energy of the intermolecular bond is applicable to complexes of halides of Group III elements: i.e. it is actually a general characteristic of donor–acceptor bonds.

Published information on the energy of p_π-conjugation is extremely scanty and contradictory[68]. Values have usually been obtained from the heats of combustion of the compounds. Comparison of E_j for a number of amines, ethers, and sulphides indicates that the heteroatoms are arranged in the sequence—N > O > S—according to their capacity for p_π-conjugation with aromatic systems.

The values found for E_j provide a quantitative explanation of why certain aromatic donors form complexes with some acceptors and not with others (with similar values of the steric factor). It is obvious that, if the energy of formation of an intermolecular bond by a donor with a particular acceptor is less than or similar to the p_π-conjugation energy, no complex is formed.

An excellent illustration of the above is provided by complex formation between boron trifluoride and aromatic ethers. The heat of reaction of boron trifluoride with aliphatic ethers is 10–12 kcal mole^{-1}. The destruction of p_π-conjugation in anisole and phenetole requires 7–8 kcal mole^{-1}, and in diphenyl ether ~ 11 kcal mole^{-1}: with this last compound the heat of reaction should be close to zero. Hence boron trifluoride will give quite stable complexes with anisole and with phenetole, but will not form complexes with diphenyl ether.

This also explains the absence of complexes of type $n\sigma$ between iodine and aromatic amines, ethers, and sulphides, as well as of complexes of tin and titanium tetrachlorides with certain aromatic ethers and sulphides.

This method of determining the energy of p_π-conjugation can probably be applied not only to nitrogen, oxygen, and sulphur compounds but also to aromatic compounds of other elements, as well as for estimating the energy of p_π–d_π bonding in organometallic compounds[81].

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Organomagnesium Compounds and Their Complexes as Polymerisation Initiators

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This the first review devoted specifically to polymerisation processes initiated by organomagnesium compounds. Attention is concentrated mainly on the anionic polymerisation of unsaturated monomers (hydrocarbons, acrylates, nitriles, vinylpyridines, halogeno-derivatives, etc.). The review also includes short sections on the anionic polymerisation of carbonyl derivatives and cyclic monomers, on cationic polymerisation, and on initiating systems of the Ziegler-Natta type. The bibliography contains 215 references.

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I. INTRODUCTION

Until quite recently organomagnesium derivatives occupied a very modest position among the organometallic compounds used as initiators for anionic polymerisation. This was due to their relatively low reactivity towards non-polar unsaturated monomers (i.e. hydrocarbons of the vinyl and diene types), on which most of the research on anionic polymerisation was concentrated for a long time. With studies on the anionic polymerisation of polar monomers, organomagnesium initiators have begun to attract substantially more attention, since in these cases they are quite comparable in efficiency with many organic derivatives of the alkali metals. The considerable experimental data which have now accumulated on polymerisations initiated by organomagnesium compounds have not yet been reviewed and we have therefore attempted to fill this gap. Modern ideas on the composition and structure of organomagnesium compounds have been discussed in detail in the recently published reviews by Wakefield[1] and by Ashby[2].

II. ANIONIC POLYMERISATION OF UNSATURATED MONOMERS

Among studies of the polymerisation of anionic systems by organomagnesium compounds and their complexes, investigations on various polar unsaturated monomers are of the greatest interest. These processes are often highly efficient and stereospecific. Non-polar and low-polarity monomers exhibit a very limited tendency to polymerisation in such systems.

1. Hydrocarbons

Gilman[3-5] and Kinney[6] showed that unsaturated hydrocarbons of the ethylene and diene series do not react with organomagnesium compounds under ordinary conditions. Instances of the addition of alkylmagnesium halides to unsaturated hydrocarbons were established by Fuson[7-10] for compounds of the fluorene and fulvene series containing highly reactive double bonds—dibiphenylylene-ethylene, tetraphenylfulvene, etc.

The first results on the polymerisation of unsaturated hydrocarbons in the presence of organomagnesium compounds were obtained by Ziegler[11], who found that solid polymers were formed in C_2H_4–RMgX(or R_2Mg) systems at 100–150°C and pressures from 100 to 1000 atm. Raising the temperature enables several other hydrocarbon monomers to be polymerised with the same initiators. Wang Fo-sung, Dolgoplosk, Erusalimskii, et al.[12-14] have shown that polymerisation of various diene hydrocarbons with initiators of the above type at 90°C and above is feasible, but even under these conditions the rate of polymerisation is low. When isoprene is bulk-polymerised at 90°C with an initiator concentration of about 0.003 M, the rate does not exceed 1% h^{-1}. Still lower rates characterise the polymerisation of butadiene and 2,3-dimethylbutadiene. Kinetic data on the consumption of the initiator have established