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DETERMINATION OF pπ-CONJUGATION ENERGY IN AROMATIC AMINES, ETHERS AND SULFIDES BY COMPLEXING METHOD

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Abstract—On the basis of investigation of the heat effects of formation, dipole moments and UV-spectra of *n*-donors with halides of Group III metals a new method has been developed for the determination of pπ-conjugation energies in aromatic systems containing a heteroatom. The energies of pπ-conjugation of a number of aromatic amines, ethers and sulphides have been determined. The good agreement in the values obtained when using aluminium bromide, aluminium chloride, boron trifluoride and gallium trichloride as acceptors proves the correctness of the concepts which lie at the basis of the above method. The obtained values of pπ-conjugation energies make it possible to draw some conclusions pertaining to the structure of aromatic amines, ethers and sulphides.

AROMATIC amines, ethers and sulphides are characterized by interaction of a lone electron pair of heteroatom (nitrogen, oxygen, sulphur) with π-electrons of the adjacent aromatic system. This interaction designated as pπ-conjugation has influence on a wide variety of properties of the mentioned aromatic compounds. However, a reliable quantitative estimation of this interaction has not yet been made. In the literature rather scant and discrepant information on the values of pπ-conjugation energy (E_c, kcal/mole) are available:

aniline—0[1]; 3[2]; 6[3]; 6·3[4]; 10[5];
diphenylamine—6[1];
anisole—0[7]; 2·7[6]; 11[5];
phenetole—2·7[6]; 5·2[4];
diphenyl ether—0[7]; 5·7[6].

The data on the energies of pπ-conjugation in the aromatic sulphides are found only in the paper by Mackle and Mayrick[8] in which the energies of pπ-conjugation in thioanisole, thiophenetole and diphenylsulphide are stated to be equal to zero. Almost all of these energy values have been obtained from the heats of combustion. However, calculation of the heats of formation of the compounds from the bond energies is not exact.[9] The inaccuracy of this method can be shown by the great difference in E_c values for diphenyl ether (0 and 5·7 kcal/mole) calculated in the papers by Cass *et al.*[6] and Cox[7] on the basis of the same experimental data. Evidently, some other more sensitive method is required for the determination of pπ-conjugation energies. In our opinion, the complexing method is such a one.

The donor properties of amines, ethers and sulphides largely depend on the state of a lone electron pair of a heteroatom. Nitrogen has only one lone electron pair which accounts both for formation of the donor–acceptor bond with the acceptor and for

π-bond with the aromatic system. Sulphur has two lone electron pairs ($3s^2$ and $3p^2$). According to the X-ray analysis of the iodine complex with dibenzylsulphide,[10] $3p^2$ lone pair of sulphur electrons participates in the formation of the donor–acceptor bond, i.e. the same pair which takes part in pπ-conjugation. In case of oxygen the situation is more complicated since the hybridized orbitals of both lone pairs can exhibit substantial s-character. However, in the paper by Romm and Guryanova[11] it has been shown that pπ-conjugation in the aromatic ethers is distorted on complexing with aluminium bromide (detailed information on this will be given shortly). Clearly, in all three cases (amines, ethers, sulphides) the donor–acceptor bond and pπ-conjugation are realized with the participation of one and the same lone electron pair of a heteroatom. Therefore, the characteristics of the complexes and in particular the energetics of the complexing will depend on the state of pπ-conjugation in the donor molecule. This conclusion is well founded when we consider the fact that pπ-conjugation may be treated as a donor–acceptor interaction of a lone electron pair (n-donor) with the aromatic ring (π-acceptor).[12]

In fact, the experimental data obtained in investigation of I_2, $SnCl_4$, $TiCl_4$ complexes show that the donor properties of aromatic amines, ethers and sulphides are sharply weakened as compared to the donor properties of the respective aliphatic compounds.[13, 14] An important regularity was discovered when studying the above systems. It has been shown by Arzamanova and Guryanova[13] and Goldstein *et al.*[15] that in the complexes of the donor–acceptor type (including the systems discussed in the present publication) the degree of charge transfer from the donor to the acceptor (μ_{da}/er) is directly proportional to the heat of formation of the donor–acceptor bond ($-\Delta H_{da}$). Here, μ_{da} is the dipole moment of the donor–acceptor bond, "e" is the electron charge, "r" is the length of the intermolecular bond.

Strong acceptors, such as the halides of III group metals, form high-polar complex compounds with aromatic amines, ethers and sulphides. In these complexes the lone electron pair of a heteroatom of the aromatic donor, being firmly bound with the acceptor, cannot participate in pπ-conjugation at a time. It is possible to determine the values of pπ-conjugation energies from an analysis of the properties of these complexes.

The method developed by us for determination of pπ-conjugation energies is based on the following:

(1) pπ-conjugation is broken when a strong acceptor interacts with an aromatic donor.

(2) The degrees of charge transfer in the complexes of such an acceptor with the aromatic and the respective aliphatic donors are approximately identical. Therefore, the dipole moments of the donor–acceptor bonds in these complexes are rather close. Considering direct proportionality existing between the degree of charge transfer and heat of formation of the donor–acceptor bond, one may expect close values for the heats of formation of the donor–acceptor bonds in these complexes.

(3) The difference in the heats of formation of complexes of a strong acceptor with an aliphatic and aromatic donor corresponds to the consumption of energy for breaking up the pπ-conjugation in an aromatic donor.

The experimental part of this study consisted in measuring the dipole moments of the complexes, measuring the heat effects of complexing reactions, and taking UV spectra.

RESULTS AND DISCUSSION

Breaking of pπ-conjugation in aromatic donors during their interaction with strong acceptors may be proved by use of UV spectroscopy.[11,16]

In the region of 255 mμ benzene exhibits a band with a fine structure (2, Fig. 1). Similar spectrum is exhibited by monosubstituted benzene provided the electrons of the substituent do not interact with the π-electron ring system. The conjugation of a lone electron pair of a heteroatom with the π-electron system substantially changes the spectrum of benzene. For instance, in anisole spectrum (1, Fig. 1) the benzene band is shifted to the long-wave region and its intensity is increased by one order. The formation of a donor–acceptor bond with gallium trichloride causes marked changes in the anisole spectrum. The complex spectrum (3, Fig. 1) shows a band which is close by its position and intensity to the benzene band. A fine structure is reproduced to a certain extent. Hence, pπ-conjugation in the complex has been distorted. A similar picture is observed[11,16] during complexing of aluminium bromide with 2-methoxy-naphthalene (Fig. 2), anisole, phenetole, and diphenyl ether. In aromatic sulphides, complexing with strong acceptors also results in distortion of pπ-conjugation.[16] This has been proved by the study of the spectra of the complexes of gallium trichloride with diphenylsulphide and complexes of aluminium bromide with methyl-β-naphthylsulphide and di-β-naphthylsulphide.

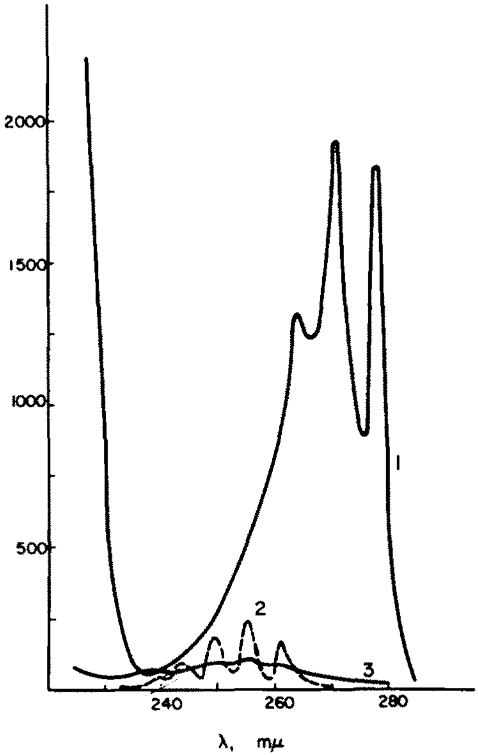


FIG. 1. UV-spectra in cyclohexane solution: 1—anisole; 2—benzene; 3—complex of $GaCl_3$ with anisole.

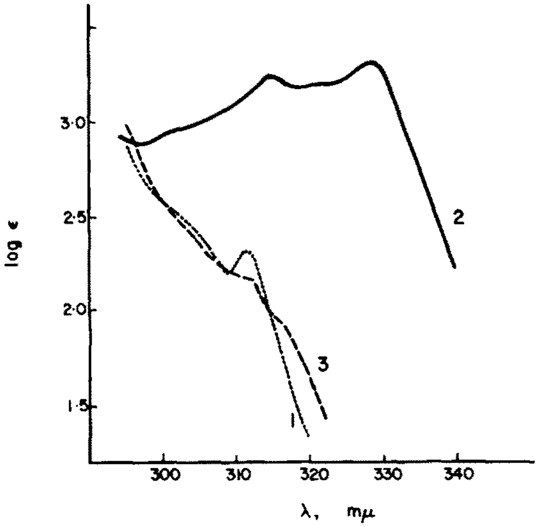


FIG. 2. UV-spectra in benzene solution: 1—naphthalene; 2—2-methoxynaphthalene; 3—complex of $AlBr_3$ with 2-methoxynaphthalene.

Regarding aromatic amines, Khodeev and Terenin[17] have observed that the UV spectrum of aniline adsorbed on aluminium chloride is similar to the benzene spectrum. Analogous changes in the spectra of aniline and N-methylaniline adsorbed on aluminium chloride have been observed in paper.[18]

It has been shown by Perkampus and Kranz[19] that the spectrum of the complex of I-amino-anthracene with aluminium chloride is similar to the anthracene spectrum.

The composition of all the investigated complexes is 1 :1.

The heat effects of the complexing reactions have been determined by calorimetric titration[20] in benzene solution at 25°C. Aluminium bromide is dimerized in benzene. The heat effects of the reaction:

$$\tfrac{1}{2}Al_2Br_6\,(sol) + D\,(sol) = AlBr_3 \cdot D\,(sol)$$

have been determined accurate to ±0·1–0·3 kcal/mole.

The degree of association of gallium trichloride molecules in benzene is not yet clear. The values of heat effects determined accurate to ±0·1–1·0 kcal/mole for the reaction.

$$GaCl_3\,(sol) + D\,(sol) = GaCl_3 \cdot D\,(sol)$$

may be used for comparing the stability of gallium trichloride complexes since the measurements were taken at a constant concentration of the acceptor. Boron trifluoride and aluminium chloride are scantily soluble in benzene. The relative stability of the complexes of these acceptors has been found by measuring (accurate to ±0·1–0·5 kcal/mole) the heat effects of displacement reactions in benzene. The values of the heat effects ($-\Delta H$ kcal/mole) are given in Tables 1 and 2.

The dipole moments of the complexes of aluminium bromide and gallium trichloride were determined by dielectrometric titration.[21] The changes in the dielectric constant

TABLE 1. DIPOLE MOMENTS AND HEAT EFFECTS OF COMPLEXING REACTIONS OF GROUP III HALIDES WITH AMINES, ETHERS AND SULPHIDES IN BENZENE AT 25°C

No.	Donor	P_∞	R_D	μ_k, D	$-\Delta H$ kcal/mole
1	2	3	4	5	6
Aluminium bromide complexes					
1	Diethyl ether	1094·7	67·3	7·05	23·2
2	Dipropyl ether	1165·6	76·6	7·26	22·8
3	Dibutyl ether	1172·2	86·1	7·25	23·2
4	Dioctyl ether	1257·0	122·7	7·41	24·0
5	Anisole	1089·9	77·5	7·00	15·5
6	Phenetole	1117·8	82·1	7·08	16·8
7	Diphenyl ether	1195·8	96·8	7·29	12·0
8	4,4′-dimethyldiphenyl ether	1294·5	106·1	7·58	13·0
9	4,4′-dibromodiphenyl ether	750·5	112·4	5·56	9·5
10	2-methoxynaphthalene	1235·4	94·6	7·44	15·4
11	1-ethoxynaphthalene	—	—	—	16·1
12	Dipropylsulphide	1119·4	32·9	7·08	17·7
13	Dibutylsulphide	1193·2	92·1	7·30	17·6
14	Diisobutylsulphide	1242·9	92·1	7·46	18·2
15	Diamilsulphide	1190·3	101·4	7·26	18·1
16	Diisoheptylsulphide (sec)	1501·2	119·9	8·13	17·1
17	Dioctylsulphide	—	—	—	17·1
18	Diisooctylsulphide (sec)	—	—	—	16·1
19	Dihexadecylsulphide	1439·8	203·0	7·74	—
20	Dicyclohexylsulphide	1507·8	106·2	8·24	16·9
21	Thioanisole	1096·0	85·0	7·00	13·1
22	Thiophenetole	1142·2	89·6	7·14	14·3
23	Diphenylsulphide	1282·9	104·4	7·55	10·2
24	α-naphthylphenylsulphide	1395·3	121·5	7·85	9·8
25	Triethylamine	1658·4	78·9	8·74	31·5
26	Tripopylamine	1614·1	92·7	8·58	33·4
27	Triamylamine	—	—	—	31·5
28	Dimethylcyclohexylamine	1561·2	85·9	8·45	32·7
29	N,N-dimethylaniline	1642·0	84·4	8·68	24·2
30	N-methyldiphenylamine	1428·6	103·7	8·01	17·4
Gallium trichloride complexes					
31	Dibutyl ether	978·6	70·6	6·63	16·0
32	Dioctyl ether	963·6	107·2	6·44	17·4
33	Anisole	833·3	62·0	6·11	10·2
34	Phenetole	—	—	—	11·0
35	Diphenyl ether	902·0	81·3	6·30	5·8
36	Diethylsulphide	1197·0	58·3	7·42	—
37	Dipropylsulphide	—	—	—	19·6
38	Dibutylsulphide	1211·1	76·6	7·41	19·0
39	Diheptylsulphide	1370·6	104·4	7·83	19·2
40	Dicyclohexylsulphide	—	—	—	18·3
41	Thioanisole	1195·8	68·3	7·39	13·9
42	Thiophenetole	—	—	—	15·3
43	Diphenylsulphide	1287·8	87·8	7·62	11·2
44	Triethylamine	1741·6	63·4	9·01	30·2
45	Tripropylamine	—	—	—	35·2

TABLE 1.—*contd.*

46	Triamylamine	1845·2	104·9	9·18	34·9
47	N,N-dimethylaniline	—	—	—	24·5
48	N-methyldiphenylamine	—	—	—	16·4
Aluminium chloride complexes					
49	Dibutylsulphide	1056·7	79·8	6·88	—
50	Diphenylsulphide	1120·6	91·0	7·06	—
Boron Trifluoride Complexes					
51	Diethyl ether	631·9	30·9	5·39	—
52	Dibutyl ether	691·1	49·5	5·57	—
53	Anisole	463·1	40·9	4·52	—
54	Phenetole	502·5	45·5	4·70	—
55	Triethylamine	733·4	42·7	5·78	—
56	Tributylamine	880·8	70·5	6·27	—
57	Triamylamine	893·8	83·8	6·26	
58	Trioctylamine	651·7	123·0	5·06	—
59	N,N-dimethylaniline	679·0	47·8	5·5	—

TABLE 2. HEAT EFFECTS OF DISPLACEMENT REACTIONS $A \cdot D_1$ (sol) + D_2 (sol) = $A \cdot D_2$ (sol) + D_1 (sol) IN BENZENE AT 25°C

No.	D_1	D_2	$-\Delta H$ kcal/mole
1	2	3	4
Boron Trifluoride Complexes			
1	Anisole	Dibutyl ether	8·3
2	Phenetole	Dibutyl ether	8·3
3	Diethyl ether	Pyridine	12·9
4	Diethyl ether	Triethylamine	14·6
5	Diethyl ether	Tripopylamine	14·4
6	Diethyl ether	Triamylamine	12·1
7	Dibutyl ether	Triethylamine	17·2
8	Dibutyl ether	Tripropylamine	16·8
9	Dibutyl ether	Dimethylcyclohexylamine	17·0
10	Dibutyl ether	N,N-dimethylaniline	7·3
Aluminium chloride complexes			
11	N,N-dimethylaniline	Dimethylcyclohexylamine	7·6
12	N-methyldiphenylamine	Dimethylcyclohexylamine	14·8
13	Diphenyl ether	Dibutyl ether	11·2
14	Anisole	Dibutyl ether	7·3
15	Diphenylsulphide	Dibutylsulphide	8·5
16	Diphenyl ether	Dibutylsulphide	6·0
17	Thioanisole	Dibutylsulphide	5·3
18	Thiophenetole	Dibutylsulphide	4·8

and density of acceptor solutions in benzene (at 25°C) were measured[16] with the successive addition of small quantities of donor.

The dipole moments of the aluminium chloride complexes were determined[16] by reverse titration, i.e. by measuring the dielectric constant and the density of donor solutions in benzene (at 25°C) with successive addition of small quantities of aluminium chloride. The dipole moments of liberated boron trifluoride complexes were found by usual method.

The obtained values of molar polarization (P_∞), molar refraction (R_D) and dipole moments (μ_k, D) of the complexes are given in Table 1. The refractions were calculated by the additive rule. The experimental value of polarization equal to 45 cm^3 was taken for aluminium bromide.[22] The dipole moment was calculated from the formula:

$$\mu = 0{\cdot}0128\sqrt{[(P_\infty - R_D)\cdot T]}.$$

The dipole moments and heat effects of the complexing reactions in the solution are likely to be close to the respective values in the gas phase provided that employed solvent is inert to the components of the complexing reaction.[16,23] Only few of the investigated complexes were soluble in the neutral solvents, e.g. in cyclohexane. Therefore, we employed benzene as a solvent. It has been shown by Romm[16] and Romm and Guryanova[24] that the dipole moment of the π-complex of aluminium bromide with benzene equals ~1D, but not 5D as it has been stated in a number of papers.[25] The heat of Al_2Br_6 solution in benzene (ΔH = 5·0 kcal/mole) is close to the heat of solution of the same compound in cyclohexane (ΔH = 5·8 kcal/mole). Consequently, aluminium bromide forms with benzene a weak low-polar π-complex which does not affect the characteristics of the process of complexing of $AlBr_3$ with n-donors. The dipole moments and heat effects of the reactions measured simultaneously in benzene and cyclohexane differ but slightly.[16]

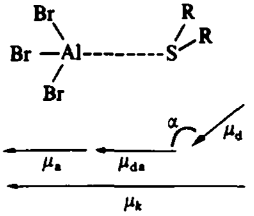
Thus, the heat effects of complexing reactions in benzene ($-\Delta H$) should be close to the heat effects ($-\Delta H$) should be close to the heat effects ($-\Delta H_k$) of the reactions in a gas phase. Therefore, the data obtained in the solution can be analysed with the use of the following equation:

$$\Delta H_k = \Delta H_a + \Delta H_{da} + \Delta H_d \qquad (1)$$

where $-\Delta H_{da}$ is the heat of formation of the donor–acceptor bond, ΔH_a and ΔH_d are the energies of rearrangement of the acceptor and donor during complexing. Since the energies of rearrangement of the investigated acceptors are not known,[16] it is not possible to determine the heats of formation of the donor–acceptor bonds. Therefore, we shall analyse the experimental data by comparing a series of complexes with one and the same acceptor (for instance, aluminium bromide for a number of complexes).

The values of heats of formation of the aluminium bromide and gallium trichloride complexes with aliphatic amines, ethers and sulphides depend very little on the length and branching of the aliphatic radical (1–4, 12–20, 25–28, 31–32, 36–40, 44–46, Table 1). The heats of formation of boron trifluoride complexes depend on the length of the aliphatic radical. From the data given in Table 2 (4, 5, 7, 8) it follows that the stability of $BF_3 \cdot O(C_4H_9)_2$ complex is less approximately by 2·5 kcal/mole than the stability of $BF \cdot O(C_2H_5)_2$ complex. The heats of formation of $BF_3 \cdot R_3N$ complexes also decrease with a slight increase in the length of R radical (4–6, Table 2). Probably, in the complexes of boron trifluoride, as distinguished from the complexes of $AlBr_3$ and $GaCl_3$, the steric factor significantly affects the strength of the donor–acceptor bond. This is in a good conformity with the data cited in paper[26] wherein the role of the steric factor in the boron trifluoride complexes is emphasized.

The total dipole moment μ_k of the complex may be represented in the form of a vector sum according to the diagram:



Here, μ_a is the dipole moment of the acceptor component of the complex, μ_d is the dipole moment of the donor component of the complex, μ_{da} is the dipole moment of the donor–acceptor bond. Since the valency angles of boron, aluminum and gallium in the complexes are tetrahedric, the values of μ_a should be close to the dipole moments of bonds B—F, Al—Br and Ga—Cl. Unfortunately, the dipole moments of these bonds are not known. Therefore, at present it is not possible to determine the values of μ_{da}.

The dipole moments of complexes of BF_3, $AlBr_3$ and $GaCl_3$ with R_3N, R_2S and R_2O, as a rule, increase slightly with a rise in the length and branching of R radicals of the donors. Perhaps this is associated with a certain increase in the contributions of μ_d and μ_a to the dipole moment of the complex. This becomes possible due to some changes in the valency angles of the donor and acceptor molecules in the complex owing to the steric effects.

Now, let us consider in detail the properties of the complexes of aluminium bromide with ethers. As it follows from Table 1, aluminium bromide forms stable complexes with aromatic ethers. The dipole moments of the complexes of $AlBr_3$ with aromatic ethers (5–7, Table 1) are close to the dipole moments of the complexes with aliphatic ethers (1–4, Table 1). The contribution of the dipole moment of the acceptor component (μ_a) to the total dipole moment of the complex and the value of angle α should not strongly change upon a transition from aliphatic ethers to aromatic ones. The dipole moments of the initial aliphatic and aromatic ethers are close to each other and constitute 1·15–1·30D.[25] In the first approximation we may assume that the value of μ_d differs very little from the dipole moments of the initial donor molecules. Therefore the equality of the dipole moments of the aluminium bromide complexes with the aromatic and aliphatic ethers indicates that the dipole moments of the donor–acceptor bonds (μ_{da}) in these complexes are equal. A noticeable difference in the dipole moments of some complexes (8, 9, Table 1) is due to the difference in the dipole moments of the initial ethers.

Although the dipole moments of the complexes of $AlBr_3$ with the aromatic and aliphatic ethers are almost identical, yet the heats of formation of these complexes significantly differ from one another. The heats of formation of the complexes with aliphatic ethers deviate only slightly from an average value of 23·3 kcal/mole, whereas the complexes with the aromatic ethers are characterized by much lower heats of formation (Table 1).

As it has been mentioned earlier, there is a direct proportional relationship between the degree of charge transfer (μ_{da}/er) and heat of formation of the donor–acceptor bond ($-\Delta H_{da}$).[13] In the complexes of aluminum bromide with aliphatic and aromatic ethers the values of μ_{da} are equal. Consequently, the heats of formation of the donor–acceptor bonds in these complexes should also be equal.

Since in a number of complexes of $AlBr_3$ with aromatic and aliphatic ethers the values of ΔH_a and $-\Delta H_{da}$ are constant, it follows from Eq. (1) that the difference in the experimental values of $-\Delta H$ of these complexes (1–11, Table 1) is determined by term ΔH_d, i.e. by the energy of donor rearrangement. The aliphatic donors, probably do not undergo any substantial rearrangement of their structure during complex formation.[27, 28] According to the data given in paper,[27] the energy of donor rearrangement in the aliphatic ethers is of the order of 0·3 kcal/mole. Therefore, the differences in the values of $-\Delta H$ in $AlBr_3$ complexes with aromatic and aliphatic ethers represent the energies of rearrangement of aromatic ethers, i.e. the energies of pπ-conjugation of aromatic ethers. Table 3 gives the heats of formation of the aluminium bromide complexes with aromatic ethers ($-\Delta H$) and energies of pπ-conjugation (E_c) of aromatic ethers. The values of the conjugation energies were obtained by subtracting the respective values of $-\Delta H$ from the mean heat of formation of $AlBr_3$ complexes with aliphatic ethers ($-\Delta H_{mean}$ = 23·3 kcal/mole).

The dipole moments of the $AlBr_3$ complexes with aliphatic amines are close to the dipole moments of the complexes with aromatic amines (25–30, Table 1). The same picture is observed in a number of $AlBr_3$ complexes with sulphides (12–24, Table 1).

The dipole moments of aliphatic and aromatic sulphides are close in their values (about 1·5D).[25] The dipole moments of aliphatic amines (0·7 to 1·0D) are somewhat less than the dipole moments of aromatic amines (~1·5D). Besides, the dipole moments of aromatic amines are directed in the opposite direction (i.e. from nitrogen atom).[5] However, in the complex with aluminium bromide where the mesomeric moment should be absent, the dipole moments of aromatic and aliphatic amines should be much closer to each other. The discussions similar to those for the complexes of $AlBr_3$ with ethers lead to a conclusion that the energies of pπ-conjugation in the aromatic sulphides and amines may be determined by subtracting the respective values of $-\Delta H$ from the mean heats of formation of $AlBr_3$ complexes with aliphatic sulphides ($-\Delta H_{mean}$ = 17·5 kcal/mole) and aliphatic amines ($-\Delta H_{mean}$ = 32·3 kcal/mole). The obtained energies of pπ-conjugation are given in Table 3. The accuracy of determining E_c (±1 kcal/mole) depends on the accuracy of determining the heats of complex formation and on how much properly the values of $-\Delta H_{mean}$ have been estimated.

We shall now consider the other factors (besides the pπ-conjugation) which may decrease the donor properties of a heteroatom of amine, ether or sulphide. As dicyclohexylsulphide (20, Table 1) and dimethylcyclohexylamine (28, Table 1) form with aluminium bromide such complexes whose stability is close to the stability of the complexes of this acceptor with other aliphatic sulphides and amines, evidently the steric factor does not play a significant role.

The inductive effect of the aromatic ring may somewhat reduce the donor ability of a heteroatom, however, the influence of this factor is not substantial because the values of μ_{da} in the complexes of $AlBr_3$ with aromatic and corresponding aliphatic donors are rather close. This is confirmed by the results obtained during the investigation of $AlBr_3$ complex with 2,6-dimethylanisole. The heat of formation of this complex (20·6 kcal/mole) is less only by 2·7 kcal/mole than that of the complexes of $AlBr_3$ with aliphatic ethers. The spectrophotometric analysis has shown that pπ-

TABLE 3. ENERGIES OF pπ-CONJUGATION OF AROMATIC ETHERS, SULPHIDES AND AMINES OBTAINED IN STUDIES ON ALUMINIUM BROMIDE COMPLEXES

	$-\Delta H$, kcal/mole	E_c, kcal/mole	
		Experimental value	Value available in literature
1. Aliphatic ethers	23·3 (mean)	—	
2. Anisole	15·5	7·8	11,[5] 2·7,[6] 0[7]
3. Phenetole	16·8	6·5	5·2,[4] 2·7[6]
4. Diphenyl ether	12·0	11·3	5·7,[6] 0[7]
5. 4,4′-dimethyldiphenyl ether	13·0	10·3	
6. 4,4′-dibromdiphenyl ether	9·5	13·8	
7. 2-methoxynaphthalene	15·4	7·9	
8. 1-ethoxynaphthalene	16·1	7·2	
9. Aliphatic sulphides	17·5 (mean)	—	
10. Thioanisole	13·1	4·4	0[8]
11. Thiophenetole	14·3	3·2	0[8]
12. Diphenylsulphide	10·2	7·3	0[8]
13. α-naphthylphenylsulphide	9·8	7·7	
14. Aliphatic amines	32·3 (mean)	—	
15. N,N-dimethylaniline	24·2	8·1	
16. N-methyldiphenylamine	17·4	14·9	

conjugation in the initial 2,6-dimethylanisole is not completely distorted though it is weakened due to steric factors. The conjugation is completely broken only when $AlBr_3$ molecule is combined with ether. Perhaps the effect of the inductive factor (if there be any) does not exceed the limits of error of E_c determination.

Thus, the basic factor responsible for the reduction in the donor properties of aromatic amines, ethers and sulphides is the presence of pπ-conjugation in the aromatic donor molecules.

The conclusions made on the basis of the data referring to the aluminium bromide complexes are convincingly proved by the extensive experimental data obtained during the investigation of the complexes of three other strong acceptors ($GaCl_3$, $AlCl_3$ and BF_3). Table 4 contains the dipole moments of $AlBr_3$, $AlCl_3$, $GaCl_3$ and BF_3 complexes with aliphatic and aromatic amines, ethers and sulphides. As it follows from the table, the dipole moments of any of these acceptors with aliphatic donors are close to the dipole moments of the same acceptor with the respective aromatic donors. Thus, in the complexes of amines, ethers and sulphides with strong acceptors the degree of charge transfer from the donor to the acceptor is the same irrespective of whether the aromatic or aliphatic radicals are combined with the donor heteroatom. Hence, the calorimetric data obtained during the study of complexes of $GaCl_3$, $AlCl_3$ and BF_3 may be also used to calculate the pπ-conjugation energies.

Table 5 contains the energies of pπ-conjugation of aromatic donors which were obtained by complexing method with four different acceptors. The energies were calculated by subtracting the $-\Delta H$ values of the complexes with aromatic donors

TABLE 4. DIPOLE MOMENTS (D) OF BORON, ALUMINIUM AND GALLIUM HALIDE COMPLEXES WITH ALIPHATIC AND AROMATIC DONORS

No. 1	Donor Acceptor 2	$AlBr_3$ 3	$AlCl_3$ 4	$GaCl_3$ 5	BF_3 6
1	Aliphatic ethers	7·24 (mean)	6·54*	6·54 (mean)	5·10 (mean)
2	Anisole	7·00	6·54*	6·11	4·52
3	Phenetole	7·08			4·70
4	Diphenyl ether	7·29		6·30	
5	2-methoxynaphthalene	7·44			
6	Aliphatic sulphides	7·60 (mean)	6·88	7·55 (mean)	
7	Thioanisole	7·00		7·39	
8	Thiophenetole	7·14			
9	Diphenylsulphide	7·55	7·06	7·62	
10	α-naphthylphenylsulphide	7·85			
11	Aliphatic amines	8·59 (mean)			5·71 (mean)
12	N,N-dimethylaniline	8·68			5·5
13	N-methyldiphenylamine	8·01			

* According to the data available in the literature.[25]

from the $-\Delta H_{mean}$ values of the respective complexes with aliphatic donors. The $-\Delta H_{mean}$ (kcal/mole) values are assumed to be:
$AlBr_3 \cdot R_2O$—23·3; $AlBr_3 \cdot R_2S$—17·5; $AlBr_3 \cdot R_3N$—32·3;
$GaCl_3 \cdot R_2O$—16·7; $GaCl_3 \cdot R_2S$—19·0; $GaCl_3 \cdot R_3N$—33·4. In the case of complexes of aluminium chloride and boron trifluoride, the value of the heat effect of the displacement reaction of the aromatic donor by the respective aliphatic donor (Table 2) was taken to be the value of E_c.

As it follows from Table 5, the energy values of pπ-conjugation determined for one and the same donor by complexing method with four different acceptors are in a good agreement. The discrepancies in the values of E_c depend mainly on the steric factor. The more the effect of the steric factor in the complexes of a given acceptor,

TABLE 5. ENERGIES OF pπ-CONJUGATION (E_c KCAL/MOLE) OF AROMATIC ETHERS, SULPHIDES AND AMINES OBTAINED BY COMPLEXING WITH VARIOUS ACCEPTORS

No.	Donor Acceptor	$AlBr_3$	$AlCl_3$	$GaCl_3$	BF_3
1	Anisole	7·8	7·3	6·5	8·3
2	Phenetole	6·5	—	5·7	8·3
3	Diphenyl ether	11·3	11·2	10·9	—
4	Thioanisole	4·4	5·3	5·2	—
5	Thiophenetole	3·2	4·8	3·8	—
6	Diphenylsulphide	7·3	8·5	7·8	—
7	N,N-dimethylaniline	8·1	7·6	9·0	9·7
8	N-methyldiphenylamine	14·9	14·8	17·0	—

the more is the error in the determination of E_c. From this point of view, boron trifluoride is the least appropriate acceptor since the steric factor plays an important part in its complexes. Evidently, this factor accounts for somewhat reduced values of the heats of formation of BF_3 complexes with phenetole and N,N-dimethylaniline and for the resulting increased values of E_c obtained for these donors by way of their complexing with BF_3.

In our opinion, the most reliable values are the values of E_c obtained by complexing with aluminium bromide. The complexes with this acceptor have been investigated by the authors in detail. The steric factor has a negligible effect on the parameters of the donor–acceptor bonds in the complexes of $AlBr_3$.

Thus, to determine the energies of pπ-conjugation of any aromatic donor by the complexing method, it is necessary:

(1) To select the acceptor whose combination with the donor will distort pπ-conjugation. The distorting of the conjugation may be checked by means of spectroscopy.

(2) To prove that the degree of charge transfer in the complex is the same as in the complex of the selected acceptor with the respective aliphatic donor. The method of dipole moments is a direct and sufficiently accurate method of determining the degree of charge transfer.

(3) To determine the energy of pπ-conjugation as a difference between the heat of complexing of the selected acceptor with the investigated donor and the mean heat of complexing of the same acceptor with the respective aliphatic donors. The heats of complexing may be most easily determined by calorimetric measurements in the solution. When selecting aliphatic donors and acceptor, it is necessary to take into account the effect of the steric factor mentioned elsewhere.

ENERGIES OF pπ-CONJUGATION AND SOME PROBLEMS OF MOLECULE STRUCTURE

The complexing method makes it possible to reliably determine the values of pπ-conjugation energies. The precision of this method makes it possible to recognize the fine peculiarities of molecule structure. As it follows from Table 3, the energies of pπ-conjugation are rather great in all the cases. In the light of this, the results given in the papers by Cox[7] and Mackle and Mayrick[8] are rather doubtful. According to these results, the molecules of aromatic ethers and sulphides have no additional stabilization caused by interaction of π-electrons of the ring with a lone pair of oxygen and sulphur electrons. The presence of pπ-conjugation in aromatic amines, ethers and sulphides is most clearly reflected in the complexing reactions. If the heat of formation of the complex of some acceptor with aliphatic donor is less than or close to the energy required for distorting pπ-conjugation, the complex with the respective aromatic donor is not formed. This phenomenon is observed in the systems of aromatic ethers and sulphides with I_2, $SnCl_4$ and $TiCl_4$. In the case of stronger acceptors such as Group III halides, the heat of formation of the donor–acceptor bond exceeds the heat consumed for rearrangement of the donor and acceptor molecules. If this gain in enthalpy is sufficient to compensate some losses in entropy, the formation of the intermolecular bond becomes energetically advantageous.

The above facts are well illustrated by the complexing of boron trifluoride with aromatic ethers. As it is known, boron trifluoride yields rather stable complexes with anisole and phenetole and fails to form a complex with diphenyl ether.[29] Usually, this is explained by great steric hindrances existing in the complex of boron trifluoride with diphenyl ether.[30] However, it has been recently shown[31] that a complex of boron trichloride with diphenyl ether exists though the steric hindrances in this case should be even greater. In our opinion, these experimental results may be explained by the following: the heat of formation of the complexes of boron trifluoride with aliphatic ethers equals 10–12 kcal/mole. The distorting of pπ-conjugation in anisole and phenetole requires 7–8 kcal/mole which is noticeably less. The distorting of pπ-conjugation in diphenyl ether consumes 11·3 kcal/mole which is close to the heat of formation of BF_3 complexes with aliphatic ethers. Therefore, boron trifluoride yields complexes with anisole and phenetole and forms no complex with diphenyl ether. However, BCl_3 is rather a stronger acceptor than BF_3,[32] consequently the formation of BCl_3 complex with diphenyl ether is accompanied by a certain gain in energy.

The values of energies of pπ-conjugation of aromatic amines, ethers and sulphides given in Table 3 make it possible to draw some conclusions on the structure of these molecules.

The energies of pπ-conjugation of aromatic ethers (2–4, Table 3) are greater than the energies of the respective aromatic sulphides (10–12, Table 3). The energies of pπ-conjugation of the respective aromatic amines are even much greater (15–16, Table 3). Thus, by their ability to form pπ-conjugation with aromatic systems, the investigated heteroatoms may be arranged in the series:

$$N > O > S$$

Introduction of P—CH_3-group into the ring causes a reduction in the energy of pπ-conjugation (4, 5, Table 3), whereas the introduction of bromine into the ring contributes to the conjugation (4, 6, Table 3). The compounds of naphthalene series (7, 8, 13, Table 3) are similar to the respective derivatives of benzene (2, 3, 12, Table 3) with regard to pπ-conjugation energy. Diphenyl derivatives (4, 12, 16, Table 3) exhibit larger energy of pπ-conjugation than the respective monophenyl derivatives (2, 3, 10, 11, 15, Table 3). The question on the conjugation in the molecules of type Ph_2X, where X = O, S, NH is a longstanding unsolved problem. Our data testify to the fact that in diphenyl derivatives both rings participate in the interaction with a lone pair of nitrogen, oxygen or sulphur electrons.

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