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Substituent Effects in Donor–Acceptor Complexes with D→A Coordination Bonds (D = N, O, S; A = B, Al, Ga, Sn, Sb) and Related Systems

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Abstract—The effect of substituent on the enthalpy ΔH^0 and free energy ΔG^0 of complexation, on the dipole moments of complexes μ_C and coordination bonds μ_{DA}, and on the degree of charge transfer Δq was analyzed for 20 series of complexes with D→A coordination bonds (D = N, O, S; A = B, Al, Ga, Sn, Sb), hydrogen bonds, and charge transfer. It was found that ΔH^0, ΔG^0, μ_C, μ_{DA}, and Δq depend not only on the inductive and resonance effects, but also on the polarization effect of substituents; its contribution varies in a wide range and can exceed 50%.

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Donor–acceptor complexes $X_nD \cdot AY_m$ between molecules X_nD and AY_m (electron donors and acceptors, respectively) are actively studied for a long time by experimental and theoretical methods (see, e.g., reviews [1–4]). Let us note some conclusions following from [1–4].

The modern quantum chemistry of donor–acceptor complexes between bases X_nD (donor center D is an atom with lone electron pairs) and acids AY_m (molecule AY_m or acceptor center A has vacant orbitals) considers two contributions to the bonding energy: $\Delta E = \Delta E_{el} + \Delta E_{orb}$, characterizing the electrostatic and orbital interactions between the components. These contributions strongly depend on substituents X and Y. For example, in donor–acceptor complexes $X_3P \cdot AlY_3$ (X = Me, F, Cl, CN; Y = H, F, Cl) the contribution of ΔE_{orb} to ΔE varies from 25 to 75% [4].

As follows from qualitative characteristics, the energy of the D→A coordination bond is very sensitive to the inductive effects of substituents X and Y [3] and to the conjugation in the molecules X_nD and AY_m [1].

There is an analogy between donor–acceptor complexes of Lewis acids and bases $X_nD \cdot AY_m$, charge-transfer complexes, and hydrogen-bonded complexes (H complexes). In particular, all these types of complexes obey relationship (1) [1, 2]:

$$-\Delta H^0 = -0.337\Delta S^0 + 3.1, \quad r\ 0.991,\ n\ 81, \tag{1}$$

where ΔH^0 is the standard enthalpy, and ΔS^0, standard entropy of formation of the complexes.

At the same time, an important aspect of the electronic structure of donor–acceptor complexes remains poorly understood. As will be shown below, satisfactory quantitative description of properties of donor–acceptor complexes in terms of the inductive and resonance effects of substituents is an exception rather than a rule. This fact may be caused by charge transfer in formation of donor–acceptor complexes.

Let us briefly consider narrow series of donor–acceptor complexes in which three of four (X, D, A, Y) constituents are fixed.

$$X_2\overset{q+}{O} \longrightarrow \overset{q-}{AlBr_3}.$$

The charge q^+ arising upon electron density transfer from X_2O to $AlBr_3$ induces a dipole in substituent X. The energy of the ion–dipole interaction (polarization effect) between the charge q and the induced dipole of substituent X is determined by Eq. (2) [5, 6]:

$$E = -q^2\alpha/(2\varepsilon r^4), \tag{2}$$

where α is the polarizability of the substituent; ε, dielectric constant; and r, distance between the charge and induced dipole.

The polarization effect strongly influences the spectroscopic characteristics of charge-transfer [5] and

H complexes [6]. In view of the aforesaid and of the above-noted analogy between donor–acceptor, charge-transfer, and H complexes, this effect should be expected to reveal itself in donor–acceptor complexes also.

Here we report on a comparative study of substituent effects in narrow series of donor–acceptor complexes with D→A coordination bonds (D = N, O, S; A = B, Al, Ga, Sn, Sb), and related systems (H complexes and charge-transfer complexes).

Within narrow series I–XX of complexes (Table 1), we examined the effect of substituents on the following properties: ΔH^0, free energy of complexation ΔG^0, dipole moment of the complex μ_C, dipole moment of the coordination bond μ_{DA}, and degree of charge transfer Δq from X_nD to AY_m. The quantity Δq is determined by Eq. (3) [19]:

$$\Delta q = \mu_{DA}/(er_{DA}), \tag{3}$$

where e is the electron charge, and r_{DA} is the length of the D→A coordination bond.

The substituent effects were studied by correlation analysis based on the linear free energy relationship (see, e.g., [19]). For a specific narrow series with a constant set of substituents X, this relationship can be expressed, e.g., by Eq. (4):

$$\delta_X(P) = \text{const}\cdot\delta_X(\Delta G^0), \tag{4}$$

where the terms $\delta_X(P)$ and $\delta_X(\Delta G^0)$ correspond to the effect of substituents X on a property P and on the free energy ΔG^0 in the given series, respectively. Thus, if in series I–XX the effects of substituents on P and on ΔG^0 are proportional, then the properties P (ΔH^0, μ_C, μ_{DA}, Δq) should obey the linear free energy relationship.

As applied to donor–acceptor complexes, charge-transfer complexes, and H complexes, the proportionality between ΔH^0 and ΔG^0 was not given due attention. At the same time, it directly follows from the Gibbs–Helmholtz equation (5):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \tag{5}$$

Taking into account (1), Eq. (5) can be written in the form

$$\Delta H^0 = \text{const}\cdot\Delta G^0. \tag{6}$$

It is well known [1, 9] that the following relationship is valid for donor–acceptor and charge-transfer complexes:

$$-\Delta H^0 = 35.3\Delta q. \tag{7}$$

For H complexes, linear correlation (8) is observed [2]:

$$-\Delta H^0 = (38.0\pm5.1)\Delta q + (3.9\pm1.4). \tag{8}$$

Equations (6)–(8) indicate that the linear free energy relationship is followed for ΔH^0 and Δq. Assume that in narrow series of complexes the bond length r_{DA} remains approximately constant at variation of substituents X. Then it follows from Eq. (3) that μ_{DA} should also obey the linear free energy relationship.

The above reasonings concerning the linear free energy relationship are confirmed by the experimental data for series IV, XVI, and XX, as indicated by the existence of linear correlations (9)–(11):

$$\Delta H^0(\text{IV}) = (0.9\pm0.1)\Delta G^0 - (3.2\pm0.1), \quad S_Y\ 0.2,\ r\ 0.968,\ n\ 6 \tag{9}$$

(here and hereinafter, the series number is given in parentheses; S_Y is the standard approximation error; r, correlation coefficient; and n, sample size),

$$\Delta H^0(\text{XIX}) = (1.5\pm0.2)\Delta G - (7.5\pm0.9), \quad S_Y\ 1.6,\ r\ 0.961,\ n\ 6, \tag{10}$$

$$\Delta H(\text{XVI}) = -(4.1\pm0.4)\mu_{DA} + (1.9\pm1.1), \quad S_Y\ 1.0,\ r\ 0.988,\ n\ 5. \tag{11}$$

Furthermore, linear correlations (12)–(15) are also observed:

$$\mu_C(\text{II}) = (1.00\pm0.12)\mu_{DA} + (1.35\pm0.80), \quad S_Y\ 0.72,\ r\ 0.977,\ n\ 5, \tag{12}$$

$$\mu_C(\text{III}) = (0.92\pm0.03)\mu_{DA} + (1.78\pm0.11), \quad S_Y\ 0.06,\ r\ 0.997,\ n\ 6, \tag{13}$$

$$\mu_C(\text{XVI}) = (0.96\pm0.01)\mu_{DA} + (3.33\pm0.01), \quad S_Y\ 0.01,\ r\ 0.999,\ n\ 5, \tag{14}$$

$$\mu_C(\text{XVI}) = -(0.23\pm0.02)\Delta H + (3.83\pm0.21), \quad S_Y\ 0.22,\ r\ 0.987,\ n\ 5. \tag{15}$$

The existence of correlations (12)–(15) counts in favor of applicability of the linear free energy relationship to dipole moments of complexes μ_C.

The linear free energy relationship is used in correlation analysis in combination with the postulate that the contributions of inductive, resonance, and other possible effects of substituents to the reaction free energy ΔG^0 are independent and additive, which is expressed by Eq. (16) [19]:

$$\Delta G^0 = \Delta G^0_{Ind} + \Delta G^0_{Res}, \tag{16}$$

Table 1. Standard enthalpies ΔH^0 and free energies ΔG^0 of complexation, dipole moments of complexes μ_D and of coordination bond μ_{DA}, and degree of charge transfer Δq in series of complexes **I–XX**

Series I, $Et_3N\cdots HOOCX$ [7]			Series II, $X_3N\cdot I_2$ [1, 8]				Series III, $X_2S\cdot I_2$ [9]				
X	$-\Delta H^0$, kcal mol^{-1}	μ_C, D	X_3N	$-\Delta H^0$, kcal mol^{-1}	μ_C, D	μ_{DA}, D	X	$-\Delta H^0$, kcal mol^{-1}	μ_C, D	μ_{DA}, D	Δq, e
Me	6.2	3.61	EtH_2N	7.5	–	–	Et	7.8	4.62	3.1	0.23
Ph	8.0	4.43	BuH_2N	–	6.07	4.4	Pr	8.1	4.90	3.4	0.25
CF_3	21.6	7.55	Et_2HN	8.8	–	–	Bu	7.6	5.00	3.6	0.27
CH_2Cl	13.2	6.71	Et_3N	–	10.5	9.7	C_5H_{11}	7.0	5.34	3.8	0.28
$CHCl_2$	16.9	7.28	Pr_3N	12.0	–	–	C_8H_{17}	7.4	–	–	0.26
CCl_3	21.1	7.46	$(C_5H_{11})_3N$	12.1	8.5	7.2	$H_2C{=}CHCH_2$	–	3.64	2.0	–
CH_2Br	12.2	6.84	$(C_8H_{17})_3N$	12.2	8.2	6.0	$PhCH_2$	4.8	3.78	2.2	0.16
CBr_3	18.5	7.56	$(PhCH_2)_3N$	2.3	2.8	2.1	Ph	0.3	–	–	0.03
Ph_3N	1.1	–	–								

Seies IV, $Me_2N(X)C{=}O\cdot I_2$ [1, 10]			Series V, p-$XC_6H_4(Et_2)As{=}S\cdots HOOCCF_3$ [11]		Series VI, p-$XC_6H_4(Et_2)As{=}S\cdot I_2$ [11]		Series VII, $X_3N\cdot BF_3$ [1, 12]		Series VII, $X_3N\cdot AlBF_3$ [13]	
X	$-\Delta H^0$, kcal mol^{-1}	$-\Delta G^0$, kcal mol^{-1}	X	$-\Delta H^0$, kcal mol^{-1}	X	$-\Delta H^0$, kcal mol^{-1}	X_3	$-\Delta H^0$, kcal mol^{-1}	X_3	μ_C, D
H	3.7	0.63	H	8.5	H	11.6	Et_3	26.5	Et_3	8.74
Me	3.9	1.14	Me	9.1	Me	11.8	Pr_3	26.3	Pr_3	8.58
Et	4.0	0.81	Me_2N	–	Me_2N	12.8	$(C_5H_{11})_3$	24.0	$(C_5H_{11})_3$	–
Ph	4.0	0.79	MeO	9.5	MeO	11.8	Me_2Ph	17.5	Me_2Ph	8.68
Me_2N	4.4	–	EtO	9.6	EtO	11.9	HPh_2	–	HPh_2	6.68
$ClCH_2$	3.3	0.15	F	8.5	F	11.2	$MePh_2$	10.0	$MePh_2$	8.01
Cl_3C	2.5	−0.71	Cl	8.0	Cl	10.9				
			Br	8.0	Br	11.0				
			NO_2	7.0	NO_2	10.0				

Series IX, $X_3N\cdot GaCl_3$ [14]		Series X, $X_2O\cdot BF_3$ [1, 15]			Series XI, $X_2O\cdot AlBr_3$ [9]			Series XII, $X_2O\cdot AlI_3$ [16]	
X_3	$-\Delta H^0$, kcal mol^{-1}	X_3	$-\Delta H^0$, kcal mol^{-1}	μ_C, D	X_3	$-\Delta H^0$, kcal mol^{-1}	μ_C, D	X_3	$-\Delta H^0$, kcal mol^{-1}
Et_3	30.2	Me_2	13.5	7.6	Me_2	–	–	Me_2	–
Pr_3	35.2	Et_2	11.2	7.7	Et_2	23.2	7.05	Et_2	35.7
$(C_5H_{11})_3$	34.8	Pr_2	–	–	Pr_2	22.8	7.26	Pr_2	–
Me_2Ph	24.5	i-Pr_2	–	6.9	i-Pr_2	–	–	i-Pr_2	38.4
HPh_2	–	Bu_2	9.6	6.7	Bu_2	23.2	7.25	Bu_2	35.1
$MePh_2$	16.4	$(C_8H_{17})_2$	–	–	$(C_8H_{17})_2$	24.0	7.41	$(C_8H_{17})_2$	35.1
		$(ClCH_2CH_2)_2$	4.8	–	$(ClCH_2CH_2)_2$	–	–	$(ClCH_2CH_2)_2$	–
		Me(Ph)	4.5	5.4	Me(Ph)	15.5	7.00	Me(Ph)	28.3
		Et(Ph)	4.5	5.4	Et(Ph)	16.8	7.08	Et(Ph)	27.6
		Pr(Ph)	–	5.3	Pr(Ph)	–	–	Pr(Ph)	–
		Bu(Ph)	–	5.1	Bu(Ph)	–	–	Bu(Ph)	–
		Ph_2	–	–	Ph_2	12.0	7.29	Ph_2	22.8

Table 1. (Contd.)

Series XIII, $X_2O \cdot GaCl_3$ [9]			Series XIV, $X_2S \cdot AlBr_3$ [9]		Series XV, $X_2O \cdot GaCl_3$ [9]		Series XVI, $X_2S \cdot SnCl_4$ [9]				
X_2	$-\Delta H^0$, kcal mol^{-1}	μ_C, D	X	μ_C, D	X	$-\Delta H^0$, kcal mol^{-1}	X	$-\Delta H^0$, kcal mol^{-1}	μ_C, D	μ_{DA}, D	Δq, e
Me_2	–	–	Pr_2	7.08	Pr_2	19.6	Pr_2	12.9	6.49	3.3	0.27
Et_2	–	–	Bu_2	7.30	Bu_2	19.0	Bu_2	12.6	6.71	3.5	0.28
Pr_2	–	–	i-Bu_2	7.46	i-Bu_2	–	$(C_8H_{17})_2$	11.9	6.79	3.6	0.29
i-Pr_2	–	–	$(C_5H_{11})_2$	7.26	$(C_5H_{11})_2$	–	$(PhCH_2)_2$	3.8	4.77	1.5	0.12
Bu_2	16.0	6.36	$(C_7H_{15})_2$	–	$(C_7H_{15})_2$	19.2	Et(Ph)	2.0	4.20	0.9	0.07
$(C_8H_{17})_2$	17.4	6.44	$(C_8H_{17})_2$	–	$(C_8H_{17})_2$	–					
$(ClCH_2CH_2)_2$	–	–	$(PhCH_2)_2$	–	$(PhCH_2)_2$	–					
Me(Ph)	10.2	6.11	Me(Ph)	7.00	Me(Ph)	13.9					
Et(Ph)	11.0	–	Et(Ph)	7.14	Et(Ph)	15.3					
Pr(Ph)	–	–	Ph_2	7.55	Ph_2	11.2					
Bu(Ph)	–	–									
Ph_2	5.8	6.30									

Series XVII, $X_2C{=}O \cdot AlBr_3$ [17]		Series XVIII, $X_2C{=}O \cdot SnCl_4$ [17]	
X_2	$-\Delta H^0$, kcal mol^{-1}	X_2	$-\Delta H^0$, kcal mol^{-1}
Me(Ph)	37.8	Me(Ph)	7.2
Ph_2	37.8	Ph_2	5.7
$Me(Me_2N)$	47.5	$Me(Me_2N)$	18.2
$Ph(Me_2N)$	47.0	$Ph(Me_2N)$	16.5
Me(EtO)	36.6	Me(EtO)	10.5

Series XIX, $X_2C{=}O \cdot SbCl_5$ [1]					Series XX, $X_2C{=}O \cdot SbCl_5$ [1, 18]	
X_2	$-\Delta H^0$, kcal mol^{-1}	X_2	$-\Delta H^0$, kcal mol^{-1}	$-\Delta G^0$, kcal mol^{-1}	X_2	μ_C, D
i-Pr(t-Bu)	11.6	CF_3(MeO)	2.7	–	Me_2	8.9
$(t\text{-}Bu)_2$	9.6	Et(Cl)	3.3	–	Me(Et)	8.3
$H(Me_2N)$	26.6	Et(EtO)	16.8	6.94	H(Ph)	8.65
Me(HMeN)	29.4	i-Pr(EtO)	16.4	6.21	Me(Ph)	9.02
$Me(Me_2N)$	27.8	t-Bu(EtO)	13.0	2.69	Ph_2	9.1
$(Me_2N)_2$	29.6	$ClCH_2$(EtO)	12.8	2.98		
$CF_3(Me_2N)$	16.6	Cl_2CH(EtO)	9.35	0.41		
$EtO(Me_2N)$	22.4	Cl_3C(EtO)	3.05	−1.60		
$Cl(Me_2N)$	17.2					

where ΔG^0_{Ind} and ΔG^0_{Res} are, respectively, the inductive and resonance contributions to ΔG^0.

All the complexes can be subdivided into so-called classical and nonclassical.

In classical complexes, substituent X and the donor center are at a large distance from each other. Typical examples are H complexes $(p\text{-}XC_6H_4)_3P{=}O\cdots OPh$ (with the P=O oxygen atom as donor center D) [6] and complexes of series V and VI (Table 1). If properties P of classical complexes follow the linear free energy relationships, then correlations of type (17), based on Eq. (16), should be observed for them:

$$P = P_H + a\Sigma\sigma_I + b\Sigma\sigma_R(\sigma_R^+), \qquad (17)$$

Table 2. Inductive (σ_I), resonance (σ_R, σ_R^+), and polarization (σ_α) constants of substituents X[a]

X	σ_I	σ_R	σ_R^+	σ_α
H	0	0	0	0
Me	–0.05	–0.12	–0.26	–0.35
Et	–0.05	–0.10	–0.25	–0.49
Pr	–0.05	–0.10	–0.25	–0.54
i-Pr	–0.03	–0.12	–0.25	–0.62
Bu	–0.05	–0.10	–0.25	–0.57
i-Bu	–0.03	–0.12	–0.25	–0.61
t-Bu	–0.07	–0.13	–0.19	–0.75
C_5H_{11}	–0.05	–0.10	–0.25	–0.58
C_7H_{15}	–0.05	–0.10	–0.25	–0.59
C_8H_{17}	–0.05	–0.10	–0.25	–0.59
Ph	0.12	–0.13	–0.30	–0.81
$PhCH_2$	–0.04	–0.05	–0.45	–0.70
$H_2C{=}CHCH_2$	–0.06	–0.08	–0.16	–0.57
F_3C	0.38	0.16	0.23	–0.25
$ClCH_2CH_2$	0.07	–0.01	–	–0.57
$ClCH_2$	0.13	–0.01	–0.14	–0.54
Cl_2CH	0.31	0.01	–	–0.62
Cl_3C	0.38	0.09	–	–0.70
$BrCH_2$	0.14	0.00	–0.12	–0.61
Br_3C	0.28	0.01	–	–1.12
MeHN	–0.03	–0.73	–1.78	–0.30
Me_2N	0.15	–0.98	–1.85	–0.44
O_2N	0.65	0.13	0.14	–0.26
MeO	0.29	–0.56	–1.07	–0.17
EtO	0.26	–0.50	–1.07	–0.23
F	0.45	–0.39	–0.52	0.13
Cl	0.42	–0.19	–0.31	–0.43
Br	0.45	–0.22	–0.30	–0.59

[a] We used the σ constants applied previously [5, 6, 19, 20].

where P_H is the value of *P* for the unsubstituted donor molecule (X = H); $\Delta\sigma_I$, sum of universal inductive σ_I constants of substituents X; $\Delta\sigma_R$, sum of resonance parameters δ_R characterizing the conjugation of substituents X with center D bearing a small positive charge; and $\Sigma\sigma_R^+$, quantity differing from $\Sigma\sigma_R$ in that center D bears a large positive charge. The traditional system of Hammett–Taft correlation equations was developed mainly for *p*-disubstituted benzenes, i.e., for classical reaction series in which the polarization effect is absent by definition.

Nonclassical complexes are represented by series I–IV and VII–XX (Table 1). In these complexes, the distance *r* between substituents X and donor center D is considerably shorter than in the classical complexes. Therefore, the charge arising on D as a result of formation of nonclassical donor–acceptor complexes, charge-transfer complexes, and H complexes can induce a new kind of intermolecular interaction absent in classical complexes. It was assumed that such an interaction is the polarization effect which, according to Eq. (2), should sharply increase with decreasing distance *r*.

If this assumption is valid, then for nonclassical donor–acceptor complexes Eq. (16) transforms into Eq. (18):

$$\Delta G^0 = \Delta G^0_{\text{Ind}} + \Delta G^0_{Res} + \Delta G^0_{Pol}, \tag{18}$$

where ΔG^0_{Pol} is the polarization contribution to ΔG^0. In turn, relationship (17) transforms into three-parameter correlation equation (19):

$$P = P_H + a\Sigma\sigma_I + b\Sigma\sigma_R(\sigma_R^+) + c\Sigma\sigma_\alpha, \tag{19}$$

where $\Sigma\sigma_\alpha$ is the sum of universal polarization constants σ_α of substituents X. The quantities σ_α are known for a large number of substituents X [20], which simplifies calculations by Eq. (2). The constants σ_I, σ_R, and σ_R^+ (Table 2) are known from the literature [5, 6, 19, 20].

Thus, the correlation analysis seems to be an efficient method for studying the polarization effect. If a property *P* follows the linear free energy relationship, then better statistical characteristics of three-parameter equation (19) compared to two-parameter equation (17) apparently indicates that this effect is significant.

Let us first consider these characteristics in narrow series of H complexes and charge-transfer complexes I–VI. The influence of the polarization effect on the spectroscopic parameters of some H complexes and charge-transfer complexes was established previously [5, 6]. Therefore, series I–VI are model systems of a sort for donor–acceptor complexes VII–XX.

It follows from Table 3 that in series I–IV, in going from relationships of type (17) to three-parameter equations of type (19), the statistical characteristics are considerably improved: The standard approximation errors S_Y decrease and the correlation coefficients *R* increase. This fact convincingly proves the significant contribution of the polarization effect of substituents X to properties *P* (ΔH^0, ΔG^0, μ_C, μ_{DA}, Δq) of charge-transfer complexes and H complexes.

Let us present relationship (19) in the form of Eq. (20):

$$P = P_H + Ind + Res + Pol, \tag{20}$$

where $Ind = a\Sigma\sigma_I$, $Res = b\Sigma\sigma_R$ or $b\Sigma\sigma_R^+$, and $Pol =$

Table 3. Coefficients and their standard deviations ($P_H \pm S_P$, $a \pm S_a$, $b \pm S_b$, $c \pm S_c$) in the equations P (ΔH^0, ΔG^0, μ_C, μ_{DA}, Δq) = ($P_H \pm S_P$) + ($a \pm S_a$)$\Sigma\sigma_I$ + ($b \pm S_b$)$\Sigma\sigma_R(\sigma_R^+)$ + ($c \pm S_c$)$\Sigma\sigma_\alpha$, standard approximation errors S_Y, correlation coefficients R, and sample size n for series I–XX

Series	Property P	$P_H \pm S_P$	$a \pm S_a$	$b \pm S_b$	σ[a]	$c \pm S_c$	S_Y[b]	R[b]	n
I	ΔH^0	–9.4 ± 1.2	–14.2 ± 7.4	–39.0 ± 11.7	σ_R	3.7 ± 2.2	1.1(1.3)	0.982(0.975)	8
	μ_C	4.98 ± 0.60	–	14.94 ± 2.48	σ_R	–2.29 ± 0.89	0.62(0.84)	0.916(0.838)	8
II	ΔH^0	–6.7 ± 0.7	29.2 ± 1.7	–21.0 ± 1.5	σ_R^+	9.8 ± 0.9	0.6(3.3)	0.992(0.709)	7
	μ_C	4.76 ± 0.08	–122 ± 6	4.82 ± 2.00	σ_R	7.56 ± 0.22	0.05(1.25)	0.999(0.904)	5
	μ_{DA}	3.1 ± 0.9	–242 ± 76	44.0 ± 23.7	σ_R	11.1 ± 2.6	0.6(1.9)	0.977(0.752)	5
III	ΔH^0	–11.6 ± 2.2	15.4 ± 3.2	–3.8 ± 1.8	σ_R^+	–3.3 ± 2.3	0.37(0.42)	0.991(0.989)	7
	μ_C	–1.93 ± 1.92	21.41 ± 6.15	–26.67 ± 3.08	σ_R	–3.40 ± 1.00	0.14(0.30)	0.979(0.902)	6
	μ_{DA}	–3.8 ± 1.0	24.9 ± 3.2	–29.0 ± 1.6	σ_R	–3.6 ± 0.5	0.07(0.30)	0.995(0.917)	6
	Δq	0.11 ± 0.06	–0.88 ± 0.09	0.35 ± 0.05	σ_R^+	–0.21 ± 0.06	0.01(0.02)	0.993(0.976)	7
IV	ΔH^0	–3.5 ± 0.2	3.3 ± 0.7	1.2 ± 0.2	σ_R	0.6 ± 0.4	0.22(0.24)	0.938(0.923)	7
	ΔG^0	–0.63 ± 0.01	–0.67 ± 0.14	8.16 ± 0.21	σ_R	–1.21 ± 0.05	0.01(0.15)	0.999(0.973)	6
V	ΔH^0	–8.6 ± 0.1	2.1 ± 0.1	1.5 ± 0.1	σ_R^+	0.2 ± 0.1	0.1(0.1)	0.995(0.994)	8
VI	ΔH^0	–11.6 ± 0.04	2.1 ± 0.1	1.6 ± 0.1	σ_R	–	(0.06)	(0.997)	9
VII	ΔH^0	–127.2 ± 6.0	–	–121.2 ± 9.2	σ_R^+	–6.7 ± 2.3	0.8(1.4)	0.994(0.980)	5
VIII	μ_C	5.37 ± 0.02	–2.56 ± 0.01	–6.01 ± 0.02	σ_R^+	1.04 ± 0.01	0.003(0.18)	1.000(0.978)	5
IX	ΔH^0	0	104.5 ± 39.8	152.0 ± 123.8	σ_R	17.7 ± 10.4	2.0(3.0)	0.968(0.936)	5
X	ΔH^0	–18.3 ± 1.7	25.3 ± 3.5	–6.0 ± 3.5	σ_R	–8.6 ± 1.6	0.6(1.8)	0.989(0.889)	6
	μ_C	22.4 ± 3.0	6.0 ± 3.0	42.4 ± 8.9	σ_R	5.9 ± 0.9	0.1(0.4)	0.994(0.946)	8
XI	ΔH^0	–86.3 ± 3.1	–	–134.3 ± 9.0	σ_R^+	3.8 ± 1.8	0.5(0.6)	0.995(0.993)	7
	μ_C	5.40 ± 0.35	–2.19 ± 0.44	–	–	–1.48 ± 0.29	0.06(0.15)	0.900(0.000)	7
XII	ΔH^0	0	70.0 ± 10.2	107.5 ± 38.5	σ_R	8.2 ± 5.1	1.3(1.5)	0.975(0.964)	7
XIII	ΔH^0	–7.0 ± 3.8	38.8 ± 4.3	–	–	5.1 ± 3.1	0.6(0.7)	0.991(0.988)	5
	μ_C	5.00 ± 0.17	–1.73 ± 0.19	–	–	–1.06 ± 0.14	0.03(0.15)	0.982(0.000)	4
XIV	μ_C	3.41 ± 0.59	–3.14 ± 0.54	–4.64 ± 1.79	σ_R	–2.26 ± 0.29	0.06(0.23)	0.958(0.000)	7
XV	ΔH^0	–44.5 ± 0.8	–	–105.3 ± 4.9	σ_R	–3.7 ± 0.7	0.20(0.25)	0.998(0.997)	6
XVI	ΔH^0	–25.0 ± 3.1	48.4 ± 3.2	–12.8 ± 2.2	σ_R^+	–9.6 ± 3.4	0.2(0.5)	0.999(0.995)	5
	μ_C	4.62 ± 0.41	–15.72 ± 0.42	5.98 ± 0.30	σ_R^+	–3.05 ± 0.46	0.03(0.16)	0.999(0.992)	5
	μ_{DA}	1.5 ± 0.2	–16.3 ± 0.2	6.1 ± 0.2	σ_R^+	–3.0 ± 0.2	0.02(0.15)	0.999(0.993)	5
	Δq	0.16 ± 0.02	–1.29 ± 0.02	0.47 ± 0.02	σ_R^+	–0.20 ± 0.02	0.002(0.010)	0.999(0.995)	5
XVII	ΔH^0	–27.8 ± 0.5	20.6 ± 1.6	14.8 ± 0.3	σ_R	6.7 ± 0.4	0.2(3.2)	0.999(0.809)	5
XVIII	ΔH^0	–4.4 ± 0.2	10.91 ± 0.64	13.32 ± 0.14	σ_R	0.26 ± 0.15	0.10(0.14)	0.9998(0.9996)	5
XIX	ΔH^0[c]	–19.6 ± 3.8	23.8 ± 3.6	7.7 ± 0.8	σ_R^+	–10.4 ± 3.1	2.6(3.5)	0.955(0.916)	15
	ΔH^0[d]	–24.0 ± 2.4	–	49.8 ± 4.2	σ_R	–23.0 ± 3.8	0.8(2.8)	0.987(0.833)	6
	ΔG^0[d]	–12.29 ± 2.94	–	29.33 ± 5.12	σ_R	–17.14 ± 4.64	1.00(2.09)	0.953(0.770)	6
XX	μ_C	8.19 ± 0.04	8.83 ± 0.29	–8.12 ± 0.26	σ_R^+	3.75 ± 0.14	0.02(0.31)	0.999(0.288)	5

[a] Type of the resonance parameter in the term ($b \pm S_b$)$\Sigma\sigma_R(\sigma_R^+)$. [b] In parentheses are the characteristics S_Y and R of the correlation equations P (ΔH^0, ΔG^0, μ_C, μ_{DA}, Δq) = ($P_H \pm S_P$) + ($a \pm S_a$)$\Sigma\sigma_I$ + ($b \pm S_b$)$\Sigma\sigma_R(\sigma_R^+)$ calculated without taking into account the polarization effect. [c] Donor–acceptor complexes with the substituents X = Cl_2CH and Cl_3C, for which the σ_R^+ values are lacking from the literature, were excluded from the sample. [d] Samples for ΔH^0 and ΔG^0 contain identical substituents X.

$c\Sigma\sigma_a$ are, respectively, the inductive, resonance, and polarization contributions to overall changes in properties P under the influence of substituents X. As seen from Table 4, in series I–IV the contribution *Pol* amounts to 15–47%.

According to the above classification, series V and VI complexes are classical. Therefore, in series VI the contribution *Pol* is absent. At first glance, the nonzero contribution *Pol* in series V is incomprehensible. However, a specific feature of H complexes V is a significant transfer of the electron density from donor molecules to a strong acceptor (trifluoroacetic acid molecule). In the process, a large charge q^+ arises on

Table 4. Inductive ($Ind = a\Sigma\sigma_I$), resonance ($Res = b\Sigma\sigma_R$ or $Res = b\Sigma\sigma_R^+$), and polarization ($Pol = c\Sigma\sigma_\alpha$) contributions (%) to the overall changes in properties P (ΔH^0, ΔG^0, μ_C, μ_{DA}, Δq) under the influence of substituents X in series I–XX

Series	Property *P*	*Ind*	*Res*	*Pol*
I	ΔH^0	29±15	55±16	16±9
	μ_C	–	68±11	32±12
II	ΔH^0	26±2	41±3	33±3
	μ_C	49±2	4±2	47±1
	μ_{DA}	48±15	18±10	34±7
III	ΔH^0	59±12	17±8	24±17
	μ_C	17±5	54±6	29±8
	μ_{DA}	18±2	54±3	28±4
	Δq	52±5	24±4	24±4
IV	ΔH^0	45±9	40±7	15±10
	ΔG^0	9±2	59±2	32±1
V	ΔH^0	43±2	53±4	4±2
VI	ΔH^0	57±3	43±3	–
VII	ΔH^0	–	80±6	20±7
VIII	μ_C	32±1	51±1	17±1
IX	ΔH^0	63±24	22±18	15±9
X	ΔH^0	48±7	11±6	41±8
	μ_C	14±7	30±6	56±9
XI	ΔH^0	–	85±6	15±7
	μ_C	44±9	–	56±11
XII	ΔH^0	67±10	18±6	15±9
XIII	ΔH^0	84±9	–	16±10
	μ_C	54±6	–	46±6
XIV	μ_C	42±7	11±4	47±6
XV	ΔH^0	–	76±4	24±4
XVI	ΔH^0	50±3	31±5	19±7
	μ_C	44±1	40±2	16±2
	μ_{DA}	45±1	39±1	16±1
	Δq	46±1	40±2	14±1
XVII	ΔH^0	17±1	54±1	29±2
XVIII	ΔH^0	16±1	82±1	2±1
XIX	ΔH^0	34±5	46±5	20±6
	ΔH^0	–	65±5	35±6
	ΔG^0	–	59±10	41±11
XX	μ_C	34±1	27±1	39±1

the As=S fragment. Partial delocalization of the charge q^+ over the aromatic ring may give rise to a weak polarization effect.

Let us then consider the effect of substituents on properties P (ΔH^0, ΔG^0, μ_C, μ_{DA}, Δq) of donor–acceptor complexes in narrow series VII–XX. The substituent effects have the following specific features.

As in the model systems (charge-transfer complexes and H complexes), the properties of donor–acceptor complexes depend not only on the inductive and resonance effects of substituents X in electron-donor molecules. This is clearly seen, e.g., from zero or approximately zero correlation coefficients R of two-parameter equations of type (17) for $P = \mu_C$ in series XI, XIII, XIV, and XX (Table 3).

In all the series VII–XX, the correlation coefficients R of three-parameter equations of type (19) are larger, and the standard errors S_Y, smaller than in two-parameter equations of type (17) (Table 3). The difference between the R values may be essential (0.982 and 0.000 in series XIII) or insignificant (0.9998 and 0.9996 in series XVIII). This is due to the fact that the contribution of the polarization effect varies from one series to another, as follows from Table 4.

The polarization contribution *Pol* to overall changes in properties P (ΔH^0, ΔG^0, μ_C, μ_{DA}, Δq) under the influence of substituents X in electron-donor molecules of series VII–XX varies from 2 to 56% (Table 4). This is caused by the fact that at least two factors affect *Pol*. First, the contribution *Pol* depends on the charge q^+ is the donor center D of donor–acceptor complexes of a narrow series $\mathrm{X}_n\overset{q^+}{\mathrm{D}}\cdot\overset{q^-}{\mathrm{A}}\mathrm{Y}_m$ (with fixed D, A, and Y). As follows from Eq. (2), the larger q^+, the stronger the polarization effect (the larger *Pol*) under equal other conditions. At the same time, q^+ is determined by the whole set of electronic interactions in donor–acceptor complexes, and estimation of this quantity is difficult. Second, the contribution *Pol* depends on the sample size n, i.e., on the type of substituents X. As the range of variation of polarization constants σ_α of substituents X is made wider, other conditions being equal, the contribution *Pol* increases.

Therefore, on the whole, it is difficult to elucidate the relationship between the polarization effect and the electronic structure of complexes. However, in a particular case the problem is simplified. From series II, III, and XVI we constructed series with a smaller sample size, IIa, IIIa, and XVIa, in which substituents X are alkyl groups (Table 5). For each of the complexes, the contributions *Pol* are calculated by the equations indicated in Table 3 ($P = \mu_{DA}$), and the values of Δq are given (Table 5). For series IIa, the quantities Δq were calculated by Eq. (7) from the enthalpies ΔH^0 (Table 1), and for series IIIa and XVIa they were taken from Table 1.

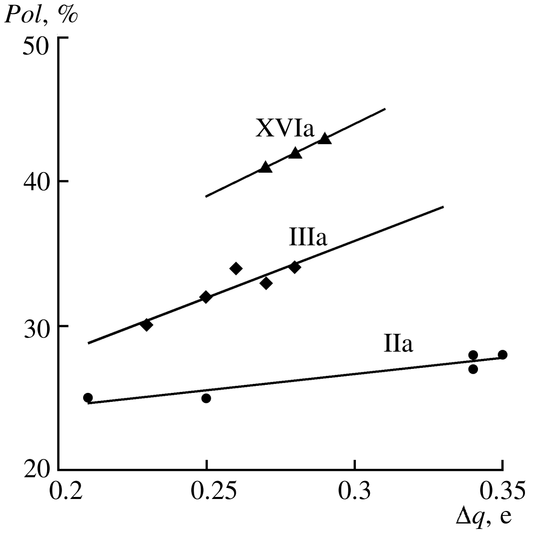
All the alkyl groups are characterized by similar inductive and resonance effects but appreciably differ in the polarization effect. Therefore, on the one hand, in each of the series $\mathrm{Alk}_3\overset{q^+}{\mathrm{N}}\cdot\overset{q^-}{\mathrm{I}}_2$ (IIa), $\mathrm{Alk}_3\overset{q^+}{\mathrm{S}}\cdot\overset{q^-}{\mathrm{I}}_2$ (IIIa),

Table 5. Polarization contribution *Pol* and degree of charge transfer Δq in complexes of series IIa, IIIa, and XVIa

Series	Complex	*Pol*, %	Δq, e
IIa	$EtH_2N \cdot I_2$	25	0.21
	$Et_2HN \cdot I_2$	25	0.25
	$Pr_3N \cdot I_2$	27	0.34
	$(C_5H_{11})_3N \cdot I_2$	28	0.34
	$(C_8H_{17})_3N \cdot I_2$	28	0.35
IIIa	$Et_2S \cdot I_2$	30	0.23
	$Pr_2S \cdot I_2$	32	0.25
	$Bu_2S \cdot I_2$	33	0.27
	$(C_5H_{11})_2S \cdot I_2$	34	0.28
	$(C_8H_{17})_2S \cdot I_2$	34	0.26
XVIa	$Pr_2S \cdot SnCl_4$	41	0.27
	$Bu_2S \cdot SnCl_4$	42	0.28
	$(C_8H_{17})_2S \cdot SnCl_4$	43	0.29

and $\overset{q^+}{Alk_3S} \cdot \overset{q^-}{SnCl_4}$ (XVIa), the charge q^+ on the donor center (N or S atom), controlled by the inductive and resonance effects, is approximately constant.

On the other hand, in each of series IIa, IIIa, and XVIa the charge q^+ slightly varies. This follows directly from the degrees of charge transfer Δq, somewhat varying within each series in going from one complex to another (Table 5). The variation of q^+, according to Eq. (2), results in that each complex is characterized by its specific value of *Pol* even within the same series (IIa, IIIa, XVIa, Table 5).



Correlation between the polarization contribution *Pol* and degree of charge transfer Δq in complexes of series IIa, IIIa, and XVIa.

These facts suggest a close correlation between *Pol* and Δq. Indeed, these quantities show linear correlations (see figure).

Thus, adequate description of substituent effects on the properties of complexes (charge-transfer complexes, H complexes, donor–acceptor complexes) is possible only if the polarization effect is taken into account.

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