Infrared spectroscopy of hydrogen bond and substituent effects in electron donor molecules

A. N. Egorochkin and O. V. Kuznetsova*

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation. Fax: +7 (831 2) 66 1497. E-mail: egor@imoc.sinn.ru

The frequency shift, $\Delta\nu$, of the O—H stretching mode in the IR spectra of the H-complexes of phenol with electron donor molecules BX_i (B is the n- or π-donor center and X_i are substituents; a total of eight series), the change in the Gibbs free energy, ΔG, due to H-complexation, and the parameter β (a measure of the ability of BX_i molecules to donate an electron pair; two series) are determined by both the electrostatic interaction and charge transfer in the formation of H-complex. The $\Delta\nu$, ΔG, and β values depend not only on the inductive and resonance effects, but also the polarizability of substituents characterized by the σ_α parameters.

Key words: H-complexes, electrostatic interaction, charge transfer, IR spectroscopy, inductive effect, conjugation, polarizability of substituents.

Theoretical concepts of the hydrogen bond

$$Y_jZ{-}H + BX_i \rightleftharpoons Y_jZ^{\delta-}{-}H\ldots{}^{\delta+}BX_i, \quad (1)$$

between an acceptor molecule Y_jZ—H (A) and an electron donor molecule BX_i (D) usually treat the total energy of the interaction between partners in the H-complex (E_{int}) as the sum of five major contributions[1,2]

$$E_{int} = E_{es} + E_{ex} + E_{ct} + E_{in} + E_{disp}, \quad (2)$$

where E_{es} and E_{ex} are the energies of electrostatic and exchange interaction, respectively; E_{ct} is the charge transfer energy; and E_{in} and E_{disp} are the energies of the induction and dispersion interaction, respectively.

It is commonly accepted[1—3] that the exchange interaction is responsible for the repulsion between the components of an H-complex and that the contribution of the dispersion interaction is small. Other terms in expression (2) are listed in order of decreasing contribution to H-bonding. The largest contribution, E_{es}, corresponds to the common opinion of electrostatic nature of hydrogen bond.[1—6]

Using the concept of hard and soft acids and bases (see, *e.g.*, Ref. 4), the total energy of the interaction between two molecules, D and A, separated by a distance r_{DA} in a medium with the dielectric constant ε can be written as the sum

$$E_{int} = -q_D q_A/(r_{DA}\varepsilon) + 2\sum_D\sum_A (C_D^m C_A^n \Delta\beta_{DA})^2/(E_m - E_n), \quad (3)$$

Here, the first term characterizes the electrostatic interaction controlled by the charges on the donor (q_D) and acceptor (q_A) centers of the molecules D and A, respectively, while the second term describes the "orbitally controlled" charge-transfer interactions between these molecules. Strengthening of the latter is favored by (i) increase in the contributions of AOs to the frontier MOs (the C_D^m and C_A^n coefficients) and to the *m* and *n* MOs of isolated molecules D and A, respectively, with energies close to those of the frontier MOs, (ii) change in the resonance integral $\Delta\beta_{DA}$ upon mixing of the *m* and *n* orbitals, and (iii) equalization of the energies E_m and E_n of the orbitals *m* and *n*, respectively.

By keeping three out of the four variables (acceptor Z—H, donor center B, and substituents X_i and Y_j) in Eq. (1) unchanged (*e.g.*, Y_j, Z and B), one can obtain a series of H-complexes; *e.g.*, for phenol we get:

$$PhO{-}H + O{=}P(X_i)_3 \rightleftharpoons PhO^{\delta-}{-}H\ldots{}^{\delta+}O{=}P(X_i)_3. \quad (4)$$

For each series of complexes, valuable information is provided by the frequency shift $\Delta\nu = \nu(OH) - \nu(OH\ldots B)$, where $\nu(OH)$ and $\nu(OH\ldots B)$ are the stretching vibration frequencies of the O—H bond in the IR spectrum of phenol in the absence and in the presence of electron donor BX_i, respectively. This parameter has been studied experimentally.[5—17] For instance, the following correlation is valid for the series of benzene, thiophene, ethylene, and acetylene derivatives[6]

$$\Delta\nu \approx \text{const} \cdot q_D, \quad (5)$$

where q_D is the effective charge on the donor center B (benzene and thiophene ring and the double and triple bond), which is affected by substituents X_i. This is yet

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another confirmation of predominant role of electrostatic interactions in the formation of hydrogen bond.

It is of great importance that for different series of H-complexes the parameter $\Delta\nu$(ZH) is linearly related to the changes in the Gibbs free energy, ΔG, in processes of the type (1)[5,6]

$$\Delta\nu(\mathrm{ZH}) = l + m\Delta G. \qquad (6)$$

where the coefficients l and m depend on the nature of the molecules D and A. This proves that the linear free energy relationship (LFER) can also be applied to H-complexes and allows examination of the effects of substituents X_i on the parameter $\Delta\nu$ (generally, on $\Delta\nu$(ZH)) using the Hammett—Taft correlations. We assumed that this approach will be useful for more detailed studies of changes in the frequency shift due to the inductive and resonance effects and for estimation of the effect of the partial positive charge $\delta+$ on the donor center (see Eqs. (1) and (4)) due to charge transfer in the formation of H-complexes, on $\Delta\nu$, which was left out of consideration so far.

The aim of this work was to elucidate quantitative relationships between the frequency shift, $\Delta\nu$, in the IR spectra of H-complexes of phenol and the inductive, resonance, and polarizability effects of substituents in electron donor molecules of different nature.

Calculation Procedure

We examined the effect of substituents X_i on the frequency shifts, $\Delta\nu$, in the IR spectra of H-complexes of phenol (A) with molecules D: $O{=}As(X_i)_3$ (**I**), $O{=}P(X_i)_3$ (**II**), $O{=}P(C_6H_4X_i\text{-}4)_3$ (**III**), $S{=}P(X_i)_3$ (**IV**), 1,4-$H_2NC_6H_4X$ (**V**), $Me_3SiC{\equiv}CX$ (**VI**), PhX (**VII**), and ClX (**VIII**) (total of eight series of complexes, see Tables 1 and 2). Since the molecules D in series **I**—**VIII** can have several reaction centers possessing the electron donor ability toward phenol, listed in Tables 1 and 2 are only those $\Delta\nu$ values[7—14,17—19] that are adequate to the formulation of the main goal of this study. The numbers of the series and the type of the corresponding donor center B (in parentheses) are as follows: **I**, **II**, and **III** (O atom), **IV** (S atom), **V** (N atom), **VI** (triple bond), **VII** (benzene ring), and **VIII** (Cl atom). Thus the molecules D are the n- (series **I**—**V** and **VIII**) and π-electron donors (series **VI** and **VII**).

The enthalpy change, $-\Delta H$, in the formation of H-complexes (or the strength of the hydrogen bond) is linearly related to the parameter $\Delta\nu$ only for the series corresponding to the reaction equation (4); for arbitrary molecules A and D these parameters are related by a quadratic equation.[20]

Therefore, based on the $\Delta\nu$ values, the strength of H-complexes and probably the degree of charge transfer from the molecules D to phenol[21] regularly decreases on going from series **I** to series **VIII**.

We assumed that regardless the strength of H-complexes, for any series (**I**—**VIII**) the effect of the partial positive charge $\delta+$ appearing on the donor center B as a result of charge trans-

Table 1. Frequency shifts ($\Delta\nu$) in the IR spectra of H-complexes, changes in the Gibbs free energy (ΔG), and the parameters β for series **I**—**IV**

Series	$(X_i)_3$	$\Delta\nu$/cm^{-1}	$-\Delta G$ /kcal mol^{-1}	β
I [a]	Me_3	734	—	—
	Et_3	817	—	—
	$(C_8H_{17})_3$	829	—	—
	Et_2Ph	711	—	—
	$Ph(OEt)_2$	421	—	—
	$Ph(OPr)_2$	429	—	—
	$Ph(OBu)_2$	432	—	—
	$(OEt)_3$	341	—	—
	$(OPr)_3$	353	—	—
II [b]	Me_3	470	4.3	0.98
	Et_3	510	4.5	1.02
	Pr_3	500	4.5	0.99
	Ph_3	430	4.0	0.92
	$H(OMe)_2$	300	2.8	0.74
	$H(OEt)_2$	310	2.9	0.76
	$Me(OEt)_2$	360	3.4	0.82
	$Et(OMe)_2$	355	3.3	0.81
	$Et(OEt)_2$	360	3.4	0.83
	$Pr^i(OEt)_2$	370	3.5	0.82
	$CH_2Cl(OEt)_2$	325	3.1	0.76
	$CHCl_2(OEt)_2$	275	2.8	0.70
	$CCl_3(OEt)_2$	260	2.5	0.65
	$NEt_2(OEt)_2$	395	3.6	0.88
	$(OMe)_3$	315	3.0	0.77
	$(OPh)_3$	230	2.1	0.62
III [c]	H_3	418	—	—
	Me_3	438	—	—
	$(CN)_3$	315	—	—
	$(COOMe)_3$	370	—	—
	$Me_2(NMe_2)$	460	—	—
	$H(OMe)_2$	436	—	—
	$(OMe)_3$	457	—	—
	Cl_3	372	—	—
IV [d]	Et_3	321	—	—
	Ph_3	241	—	—
	$Et(CH_2Ph)_2$	306	—	—
	$Et_2(OEt)$	261	—	—
	$(OEt)_3$	184	—	—
	$Et_2(SEt)$	261	—	—
	$(OEt)_2(SEt)$	191	—	—
	$Et(SEt)_2$	216	—	—
	$(SEt)_3$	191	—	—
	$PhCl_2$	186	—	—
	$(SMe)Cl_2$	96	—	—
	Cl_3	61	—	—

[a] Data taken from Ref. 7.
[b] Data on $\Delta\nu$ and ΔG were taken from Ref. 5. The β values were taken from Refs. 8 and 9.
[c] Data on $\Delta\nu$ were taken from Refs. 10 and 11.
[d] The $\Delta\nu$ values were taken from Refs. 12 and 13.

Table 2. Frequency shifts (Δν) in the IR spectra of H-complexes, changes in the Gibbs free energy (Δ*G*) in the formation of H-complexes, β parameters, and the σ- and R_S-constants of substituents X for series **V—VIII**

X	$-\Delta G$ [a] /kcal mol^{-1}	β [b]	Δν/cm^{-1}				σ_I [c]	σ_R [c]	σ_R^+ [c]	σ_α [c]	R_S [d]
			V [e]	**VI** [f]	**VII** [g]	**VIII** [h]					
H	0.83	0.38	350	83	49	—	0	0	0	0	−0.62
Me	1.03	0.42	380	122	58	—	−0.05	−0.12	−0.26	−0.35	−1.40
Et	—	—	—	—	—	—	−0.05	−0.10	−0.25	−0.49	−1.82
Pr^n	—	—	—	—	—	—	−0.05	−0.10	−0.25	−0.54	−2.01
Pr^i	—	—	—	—	58	—	−0.03	−0.12	−0.25	−0.62	−2.24
Bu^n	—	—	—	—	—	59	−0.05	−0.10	−0.25	−0.57	−2.15
Bu^i	—	—	—	—	—	63	−0.03	−0.10	−0.25	−0.61	−2.36
Bu^t	—	—	—	131	61	74	−0.07	−0.13	−0.19	−0.75	−2.79
C_8H_{17}	—	—	—	—	—	—	−0.05	−0.10	−0.25	−0.59	~−2.3
Ph	—	—	—	106	—	—	0.12	−0.13	−0.30	−0.81	−2.04
COOMe	—	—	—	—	—	—	0.34	0.11	0.14	−0.49	—
CN	—	—	—	—	—	—	0.51	0.15	0.15	−0.46	—
CF_3	—	—	—	—	28	—	0.38	0.16	0.23	−0.25	—
CH_2Cl	—	—	—	80	49	27	0.13	−0.01	−0.14	−0.54	−1.71
$CHCl_2$	—	—	—	—	—	12	0.31	0.01	−0.15	−0.62	−2.01
CCl_3	—	—	—	—	—	0	0.38	0.09	−0.16	−0.70	−2.32
CH_2Br	—	—	—	84	—	—	0.14	0.00	−0.12	−0.61	−1.86
NMe_2	—	—	—	—	—	—	0.15	−0.98	−1.85	−0.44	—
NEt_2	—	—	—	—	83	—	0.01	−0.73	−2.08	−0.56	—
OMe	1.19	0.45	395	144	62	—	0.29	−0.56	−1.07	−0.17	−1.56
OEt	—	—	—	150	—	—	0.26	−0.50	−1.07	−0.23	−1.76
OPr	—	—	—	—	—	—	0.26	−0.51	−1.09	−0.26	−1.91
OBu	—	—	—	—	—	—	0.29	−0.61	−1.09	−0.26	−1.98
OPh	—	—	—	—	—	—	0.37	−0.40	−0.87	−0.38	—
SMe	—	—	—	107	—	—	0.23	−0.23	−0.83	−0.68	−2.24
SEt	—	—	—	109	—	—	0.26	−0.23	−0.83	−0.74	−2.41
F	0.80	0.36	350	—	30	—	0.45	−0.39	−0.52	0.13	−0.68
Cl	0.69	0.34	330	70	35	—	0.42	−0.19	−0.31	−0.43	−1.07
Br	0.69	0.34	335	75	38	—	0.45	−0.22	−0.30	−0.59	−1.22
$SiMe_3$	—	—	—	—	55	—	−0.15	0.05	0.02	−0.72	—
CH_2SiMe_3	—	—	—	—	58	—	−0.05	−0.20	−0.49	−0.66	–

[a] Listed are the values for series **V**.[5]
[b] Listed are the values for series **V**.[8]
[c] The corresponding values were taken from Refs. 4, 14, and 15.
[d] The steric constants R_S were taken from Ref. 16.
[e] See Ref. 17.
[f] See Ref. 14.
[g] See Refs. 4 and 18.
[h] See Ref. 19.

fer in the complexation (Eqs. (1) and (4)) on the parameter Δν can be estimated based on the following considerations.

The contribution E_{es} (first term in expressions (2) and (3)) is the energy of electrostatic interaction between the D and A molecules with undeformed electron shells.[2] This means that the q_D value in relationship (3) represents the charge on the donor center B of isolated molecules BX_i. For the molecules of series **I—VIII** (see Tables 1 and 2) the charge q_D on the same center B is determined by the electronic effects of variable substituents X_i. In particular, for the molecules of the benzene, ethylene, and acetylene series[22] the q_D value is determined by the inductive and resonance effects of substituents X_i, which are quantitatively characterized by the σ_I and σ_R parameters, respectively.[15]

In each series (**I—VIII**), the charge q_A and the medium (CCl_4 was used as solvent) remained unchanged and the r_{DA} distance was also nearly constant. Therefore, the first term in expression (3) depends on the charge q_D. Taking into account relationship (5) and the fact that H-complexes obey the LFER (see above), one can expect that if the H-bond between the molecules D and A is formed only due to electrostatic interactions, the following dependence is valid for each series of complexes studied in this work

$$\Delta\nu = a + b\Sigma\sigma_I + c\Sigma\sigma_R. \qquad (7)$$

The contribution E_{ct} (second term in expression (3)) to the total interaction energy is due to charge transfer from D to A in

the formation of H-bond.[2] The E_{ct} contribution can be obtained from *ab initio* quantum-chemical calculations with extended basis sets that were performed only for the H-complexes of relatively simple molecules.[1–3] In particular, it was unambiguously confirmed that the $E_{es} > E_{ct}$ for the $(H_2O)_2$ and $(HF)_2$ complexes;[1–3] however, these calculations can hardly be carried out for the molecules of series **I**—**VIII**.

Assuming that the Hammett—Taft equations can allow for the effect of charge transfer in the H-complex on the frequency shift $\Delta\nu$, one should introduce the third, polarizability parameter (σ_α) into the two-parameter equation (7)

$$\Delta\nu = a + b\Sigma\sigma_I + c\Sigma\sigma_R + d\Sigma\sigma_\alpha. \quad (8)$$

Indeed, charge transfer described by the E_{ct} contribution to the total energy of H-bonding causes shift of the electron density from the electron donor molecule BX_i to PhOH and the appearance of a partial positive charge $\delta+$ on the donor center B (Eqs. (1) and (4)). Electronic interactions between substituents X_i and the donor center in neutral molecules BX_i and in $B^{\delta+}X_i$ systems should be different.

Previously,[23] these distinctions were considered taking charge-transfer complexes (CTC) of donor molecules with tetracyanoethylene, iodine, *etc*., as examples. The excited state of the CTC represents a radical ion pair, $A^{\bullet-}$, $B^{\bullet+}X_i$, with complete transfer of an electron from BX_i to A. The positive charge of the cationic component, $B^{\bullet+}$, of this pair polarizes the substituents X_i, thus inducing a dipole. The induced charge is stabilized by the cation—dipole electrostatic attraction, which in the Hammett—Taft system is quantitatively characterized by the polarizability constant, σ_α, of substituent X_i.[23] The σ_α values for different substituents can be obtained from quantum-chemical calculations.[15]

The degree of charge transfer (*i.e*., the $\delta+$ value) in H-complexes is known to be lower than in the CTC.[24] Nevertheless, the aforesaid suggests that three above-mentioned effects of substituents X_i toward the donor center $B^{\delta+}$ also act in the H-complexes. Proof of this assumption would be evidence for both the presence of the E_{ct} contribution to H-bonding and the necessity of correction of the current concepts of substituent effects on the frequency shifts $\Delta\nu$ in the IR spectra of H-complexes.

All correlations were obtained using the STATGRAPHICS 3.0 program package on a PC AT-286 clone. Least-squares processing of the data was carried out at a 95% confidence level.

Results and Discussion

The complexes of series **I**—**VIII** are described by two-parameter equations of the type (7) with the correlation coefficients *r* lying between 0.946 and 0.986 (Table 3). Taking into account the aforesaid, this is consistent with the largest contribution of electrostatic interactions (E_{es}) in the formation of H-bonds in the series under study.

Table 3. Coefficients (*a*, *b*, *c*, and *d*) of equations $\Delta\nu(\Delta G,\beta) = a + b\Sigma\sigma_I + c\Sigma\sigma_R$ and $\Delta\nu(\Delta G,\beta) = a + b\Sigma\sigma_I + c\Sigma\sigma_R + d\Sigma\sigma_\alpha$, standard deviations ($S_a$, S_b, S_c and S_d), standard errors of approximation (S_Y), correlation coefficients (*r*), and sample size (*n*) for series **I**—**VIII**

Series	Parameter	*a*	*b*	*c*	*d*	S_a	S_b	S_c	S_d	S_Y	*r*	*n*
I	$\Delta\nu$	749	−394	57	—	57	154	123	—	34	0.986	9
	$\Delta\nu$	404	−720	−266	−135	74	96	85	27	15	0.997	9
II	$\Delta\nu$	452	−230	−22	—	17	26	22	—	27	0.947	16
	$\Delta\nu$	344	−247	−76	−61	15	11	12	8	11	0.991	16
	ΔG	−4.12	1.92	0.18	—	0.15	0.24	0.20	—	0.24	0.939	16
	ΔG	−3.19	2.06	0.64	0.53	0.16	0.12	0.12	0.08	0.12	0.986	16
	β	0.93	−0.34	−0.06	—	0.02	0.04	0.03	—	0.04	0.947	16
	β	0.79	−0.37	−0.13	−0.08	0.03	0.02	0.02	0.01	0.02	0.987	16
III	$\Delta\nu$	417	−48	−43	—	7	7	5	—	11	0.978	8
	$\Delta\nu$	419	−47	−42	3	11	8	6	10	12	0.973	8
IV	$\Delta\nu$	286	−165	−20	—	14	16	20	—	0.23	0.956	12
	$\Delta\nu$	236	−168	−42	−23	42	16	26	19	0.22	0.958	12
V	$\Delta\nu$	354	−117	−133	—	3	11	12	—	5	0.984	6
	$\Delta\nu$	351	−123	−140	−13	2	5	6	4	2	0.996	6
	ΔG	−0.85	0.91	1.05	—	0.03	0.09	0.10	—	0.04	0.983	6
	ΔG	−0.82	0.95	1.10	0.10	0.01	0.04	0.05	0.03	0.02	0.996	6
	β	0.38	−0.21	−0.22	—	0.01	0.02	0.02	—	0.01	0.979	6
	β	0.38	−0.22	−0.23	−0.02	0.01	0.01	0.02	0.01	0.01	0.992	6
VI	$\Delta\nu$	96	−127	−165	—	3	14	13	—	7	0.970	12
	$\Delta\nu$	85	−134	−177	−21	3	8	8	5	4	0.990	12
VII	$\Delta\nu$	51	−55	−40	—	2	6	6	—	5	0.946	13
	$\Delta\nu$	50	−50	−40	−8	3	7	6	6	5	0.952	13
VIII	$\Delta\nu$	39	−71	−194	—	11	53	123	—	6	0.982	6
	$\Delta\nu$	11	−100	−129	−54	10	27	62	16	3	0.996	6

Going from the two-parameter to three-parameter equations of the type (8) is accompanied by an increase in the r values and by a decrease in the standard errors S_Y for series **I**, **II**, and **IV**—**VIII**. Improvement of the statistical characteristics of equations points to statistical significance of the term $d\Sigma\sigma_\alpha$. For each series **I**, **II**, and **IV**—**VIII** the coefficient d is much larger than the corresponding standard deviation S_d.

Therefore, the partial charge δ+ appearing on the donor center B due to the charge-transfer interaction (E_{ct} contribution to the total formation energy of H-complexes $Ph\overset{\delta-}{O}—H...\overset{\delta+}{B}X_i$) favors a specific interaction between the substituents X_i and the $B^{\delta+}$ center, which was ignored so far in studies of substituents effects on the frequency shift, Δν, in the IR spectra of H-complexes. We call this effect "polarizability effect," thus using the same term widely used in the studies of gas-phase ionic reactions[15] and ionization potentials and electronic spectra of CTC (see Ref. 23).

Let us consider some peculiarities of the influence of the polarizability effect on the frequency shift.

The inductive (Ind = $b\Sigma\sigma_I$), resonance (Res = $c\Sigma\sigma_R$), and polarizability (Pol = $d\Sigma\sigma_\alpha$) contributions to the overall frequency shift, Δν, caused by the effect of substituents X_i are determined by the type of the corresponding series (Table 4). As can be seen, the Pol contribution for the series **I**, **II**, and **IV**—**VIII** varies from 6 to 23%. In the foregoing we showed that the strength of H-complexes and the degree of charge transfer from D to A gradually decreases on going from series **I** to series **VIII** and that the Pol contribution changes nonmonotonically.

It is remarkable that the Pol contribution is zero for series **III** and is small (6%) for series **V**. Qualitatively, this can be rationalized using the known expression for the energy of the electrostatic interaction between the charge and a dipole[25]

$$E_{pol} = -q^2\alpha/2\varepsilon r^4, \quad (9)$$

where q is the partial positive charge δ+ on the B atom, α is the polarizability of the substituent X_i, ε is the dielectric constant, and r is the distance between the charge q and the induced dipole moment of the substituent X_i. From Eq. (9) it follows that the energy E_{pol} strongly depends on the distance r. The molecules of series **III** are characterized by the longest r values; therefore, the E_{pol} value seems to be zero so that the polarizability contribution is also zero. In the molecules of series **V**, the distance r is smaller than in series **III**. This causes the appearance of a small Pol contribution. The maximum distinction between the charges q is observed for series **I** and **VIII**; however, both of them have equal Pol contributions (see Table 4). The reason is the shortest distance r in the molecules of series **VIII**.

Let us take a brief look at the influence of polarizability effect on the change in the Gibbs free energy, ΔG, in H-complexation and on the parameter β. The parameter β is widely used[8,9] as measure of the ability of BX_i molecules to accept a proton (donate an electron pair) in the formation of a hydrogen bond with PhOH, 4-FC_6H_4OH, $CHCl_3$, MeOH, *etc*. The β values obtained from thermodynamic (ΔH, ΔG) and spectroscopic (Δν and the chemical shifts in NMR spectra) data are in good agreement.[8,9]

Complete sets of the Δν, ΔG, and β values are available only for the compounds of series **II** and **V** (see Table 1 and 2). As for the frequency shift Δν, three-parameter correlation equations of the type (8) for ΔG and β have better statistical characteristics compared to the two-parameter equations (see Table 3). From the data listed in Table 4 it follows that the Ind, Res, and Pol contributions to the overall change in the parameters Δν, ΔG, and β coincide within the limits of experimental errors.

From the aforesaid it follows that the parameters Δν, ΔG, and β characterize the effect of both electrostatic interactions and charge transfer on the total energy of H-bonding.

Let us briefly outline possible influence of steric effects of substituents X_i on the Δν, ΔG, and β values and dwell on the validity of using the σ_R constants as quantitative measure of conjugation in studies of hydrogen bonding.

For all series of compounds studied in this work the use of four-parameter correlation equations for Δν, ΔG, and β with the fourth parameter R_S (quantitative measure of steric effect of substituents X_i [16]) instead of three-parameter equations of the type (8) deteriorates the sta-

Table 4. Inductive ($b\Sigma\sigma_I$), resonance ($c\Sigma\sigma_R$), and polarizability ($d\Sigma\sigma_\alpha$) contributions to the overall changes in Δν, ΔG, and β caused by the effect of substituents X_i

Series	Parameter	$b\Sigma\sigma_I$	$c\Sigma\sigma_R$	$d\Sigma\sigma_\alpha$
			%	
I	Δν	59±8	28±9	13±2
II	Δν	57±3	20±3	23±2
	ΔG	56±3	20±4	24±4
	β	57±3	23±4	20±3
III	Δν	47±7	53±6	0
IV	Δν	71±7	17±10	12±10
V	Δν	42±2	52±2	6±2
	ΔG	41±2	53±2	6±2
	β	44±2	52±4	4±3
VI	Δν	38±2	53±2	9±2
VII	Δν	41±6	49±7	10±7
VIII	Δν	54±14	33±16	13±4

tistical characteristics of the correlation equations. Hence it follows that in series **I**—**VIII** the substituents X_i bonded to the donor center B produce no steric hindrances to the formation of H-bond between the molecules D and A.

Conjugation in positively charged systems $B^{\delta+}X_i$ (especially in those containing +M-resonance electron donors such as $NAlk_2$, OAlk, F, *etc*. as substituents X_i) is known to be stronger than in neutral molecules BX_i.[6,15,23] In the Hammett—Taft equations, conjugation in BX_i molecules is quantitatively characterized by the σ_R^0 constants,[22] while conjugation in $B^{\delta+}X_i$ systems is characterized by the σ_R parameters (provided that the charge $\delta+$ on B is small)[6] or σ_R^+ constants (if the charge $\delta+$ on B is large).[6,23] The results of our studies of H-complexes (series **I**—**VIII**) are consistent with these general propositions. Indeed, earlier we established that the resonance properties of X_i substituents are characterized by the σ_R constants taking H-complexes of phenol with π-donor molecules BX_i (B is the aromatic ring[4] or multiple bond[14]) as examples.

The molecules of series **I**—**V** (see Table 1 and 2) form stronger complexes with phenol, in which the charge $\delta+$ on the donor center is much larger than in the H-complexes with π-donor molecules. Nevertheless, for all series of complexes studied in this work the resonance properties of substituents X_i should be characterized by the σ_R constants. This was established after replacing the σ_R constants by the σ_R^+ parameters in the correlation equations of the type (8), which in all cases led to deterioration of statistical characteristics. Therefore, even in the strongest complexes (series **I** and **II**) the charge on the donor center is much smaller than in the excited state of CTC where conjugation is characterized by the σ_R^+ constants of X_i substituents.[23]

Summing up, mention may be made of yet another consequence of the influence of the polarizability effect on the frequency shift Δν. Equations of the type (8) allow calculations of the σ_R constants of silicon-, germanium-, and tin-containing substituents, which play an important role in physical organometallic chemistry.[6]

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