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# Full Articles

## Correlation analysis of quantum chemical data and the polarizability effect in H-complexes

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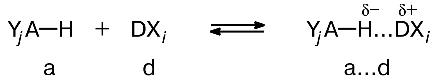
The study is concerned with analysis of the energies of formation ($E$), frequency shifts ($\Delta\nu$) in IR spectra, ionization potentials (IP) of H-complexes, hydrogen bond lengths ($r$), and spin densities (sd) in H-complexes involving radical cations, obtained from quantum chemical calculations for 20 series of H-complexes. It was for the first time established that the $E$, IP, $r$, and sd values and the changes in enthalpy ($\Delta H$) depend not only on the inductive and resonance effects but also on the polarizability effect of the substituents bound to the donor and acceptor centers in the H-complexes. Interrelations between the polarizability effect and the molecular structure of H-complexes are considered.

**Key words:** H-complexes, energy of formation, hydrogen bond length, ionization potential, inductive effect, conjugation, polarizability effect of substituents.

H-Bonded complexes between electron acceptor molecules $Y_jA—H$ (a) and electron donor molecules $DX_i$ (d) are of considerable value in chemistry, biology, and physics.



$$\underset{\text{a}}{Y_jA—H} + \underset{\text{d}}{DX_i} \rightleftarrows \underset{\text{a...d}}{Y_jA—\overset{\delta-}{H}...\overset{\delta+}{D}X_i} \qquad (1)$$

The energy ($E$) and length ($r_{\text{D...H}}$) of the H-bond, the Gibbs free energy ($\Delta G$), and the enthalpy, $\Delta H$, of reaction (1), the frequency shift ($\Delta\nu$) of the stretching vibration $\nu$(A—H) in the IR spectrum on going from isolated molecule to a complex, and some other parameters of H-complexes depend on four variables, namely, the donor (D) and acceptor (A—H) centers and the substituents $X_i$ and $Y_j$.[1—3]

At present, studies of H-complexes provide an approximate idea of the effects of the variables mentioned above on the parameters $E$, $\Delta G$, $\Delta H$, $r$, $\Delta\nu$, *etc*. At the same time elaboration of relevant concepts is important for not only developing the theory of hydrogen bonding but also solving a number of accompanying problems, in particular, establishing the mechanisms of the interaction of the substituents $X_i$ and $Y_j$ with the reaction centers, $D^{\delta+}$ and $A—H^{\delta-}$, bearing a partial positive and negative charge, respectively. It is convenient to study the

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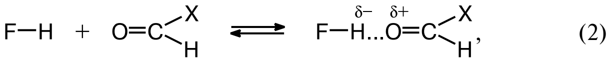
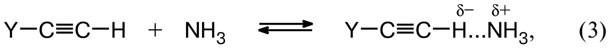
effects of substituents using narrow series of H-complexes, *e.g.*,

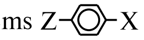


(2)



$$Y{-}C{\equiv}C{-}\overset{\delta-}{H}...\overset{\delta+}{N}H_3 \quad (3)$$

with three of the four variables being fixed.[1–3]

According to Hammett and Taft,[4,5] electronic interactions between the substituent X and the reaction center Z (Z = COOH, $^+CAlk_2$, $NO_2^-$, *etc.*) in "classical" systems  include the inductive effect and conjugation. Usually, they are quantitatively characterized by (i) universal inductive constants $\sigma_I$ and (ii) certain sets of the resonance constants of substituents X ($\sigma_R$, $\sigma_R^+$, and $\sigma_R^-$, depending on the magnitude and sign of the charge on Z). "Non-classical" systems, *e.g.*, those shown in Eqs (2) and (3), differ from the "classical" analogs by shorter distances between X (Y) and Z. As X (Y) approaches the charged center Z, the probability of additional interaction between them (polarizability effect)[4,6] increases. The occurrence of this effect in H-complexes was recently[7] proved in the analysis of experimental $\Delta\nu$ and $\Delta G$ values for a number of narrow series of the type (2).

Nevertheless, comprehensive understanding of how the polarizability effect influences the parameters of H-complexes (and, hence, of the mechanism of the interaction between substituents and the charged reaction centers in "non-classical" systems) requires further studies. Modern quantum chemical studies of H-complexes offer a considerable advantage over experimental investigations. First, it is much easier to carry out quantum chemical calculations of a number of well-known important narrow series of H-complexes than to study them experimentally. Typical examples are provided by the H-complexes involving HF, ions, and radical ions. Second, in order to perform quantum chemical calculations, it is quite easy to compile various series of electron donor molecules $DX_i$ characterized by maximum possible range of changes in the donor-acceptor properties of substituents $X_i$. Experimental studies of such series can be complicated by the problems of the synthesis of compounds and by ambiguity of the results on formation of H-complexes involving $DX_i$ molecules having additional donor centers $X_i$. Third, quantum chemical methods allow any parameter of an H-complex to be calculated. In contrast to this, experimental determination of the distance *r* is a rather complicated task while the energy *E* and the atomic charges can not be determined experimentally.

To date, a considerable body of information on narrow series H-complexes has been accumulated using quantum chemistry methods.[8–14] We believe that it can be efficiently used for extracting information on the intramolecular interactions in "nonclassical" systems.

The aim of this work was to establish correlations between parameters of H-complexes and characteristics of the inductive, resonance, and polarizability effects of the substituents bound to the donor and acceptor centers.

## Calculation Procedure

Using twenty narrow series of H-complexes (Tables 1—5, series **I—XX**), it is possible to consider the effects of substituents X on the parameters *E*, $r_{D-H}$, $\Delta\nu(A-H)$, $\Delta H$, on the ionization potentials (IP) of complexes (series **IV**), and on the spin density (sd) on the O atom of $PhO^{\bullet+}-H$ radical cation in complexes of series **V**. The number of the series, the type of the donor center B, and the computational method (for parameters of H-complexes) are shown below. Series **XXI** is given for comparison.

| Series | Donor center B | Computational method |
|---|---|---|
| **I, II** | Atom N or O | HF/6-31+G(d,p) |
| **III** | Atom N | B3LYP/6-31G(d,p) |
| **IV, V** | Atom N | RMP2/6-311++g**//<br>(U)B3LYP/6-31+g* |
| **VI—X**<br>**XV—XIX** | Atom O | B3LYP/6-311++G(d,p) |
| **XI** | Triple bond | HF/6-311++G** |
| **XII—XIV** | Atom N or O | (U)B3LYP/6-31++g**//<br>(U)B3LYP/6-31++g** |
| **XX** | Atoms N and O | MP2/6-31G(d)//HF/6-31G(d) |
| **XXI** | Atom O | Based on IR spectra[15] |

The energies of formation of hydrogen bonds, *E*, listed in Tables 1—5 represent corrected[8–14] differences between the total energies of the complexes and the reagent molecules.

Taking into account the results obtained in Ref. 7, we can assume that the influence of substituents X in series **I—XXI** is not reduced to the inductive and resonance effects but also includes the polarizability effect. Indeed, in charged systems ($XA-H^{\delta-}$ or $D^{\delta+}X$) the charge *q* polarizes the substituent X, thus inducing a dipole. The energy of electrostatic ion-dipole interaction is given by[6]

$$E_{st} = -q^2\alpha/(2\varepsilon r_q^{\,4}), \qquad (4)$$

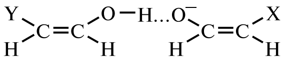
where $\alpha$ is the polarizability of substituent X, $\varepsilon$ is the dielectric constant, and $r_q$ is the distance between the charge *q* and the induced dipole. The energy $E_{st}$ abruptly increases as the distance *r* decreases and therefore plays an important role in the charged "non-classical" systems.

The polarizability effect can be characterized by both the energy $E_{st}$ and universal constants $\sigma_\alpha$ of substituents X.[4] The use of the $\sigma_\alpha$ values, which are tabulated for many X, makes it possible to avoid labor-consuming calculations[6] using expression (4). Besides, the $\sigma_\alpha$ constants are normalized to the inductive ($\sigma_I$) and resonance ($\sigma_R$, $\sigma_R^+$, $\sigma_R^-$) constants of substituents X. This allows linear free energy relationships (LFER) and the assumption of independence and additivity of the effects of substituents X (for more detail, see, *e.g.*, Refs 5 and 16) to be

**Table 1.** Energies of formation ($E$), lengths of hydrogen bonds ($r_{N...H}$ and $r_{O...H}$), and frequency shifts ($\Delta\nu$(F—H) and $\Delta\nu$(O...H)) in the IR spectra of H-complexes (series **I—III**)

| X | F—H...N≡C—X (**I**)[8] | | | F—H...O=CHX (**II**)[8] | | | X—C≡C—H...$NH_3$ (**III**)[9] | | |
|---|---|---|---|---|---|---|---|---|---|
| | $E$ /kcal $mol^{-1}$ | $r_{N...H}$ /Å | $\Delta\nu$(F—H) /$cm^{-1}$ | $E$ /kcal $mol^{-1}$ | $r_{O...H}$ /Å | $\Delta\nu$(F—H) /$cm^{-1}$ | $E$ /kcal $mol^{-1}$ | $r_{N...H}$ /Å | $\Delta\nu$(C—H) /$cm^{-1}$ |
| $NH_2$ | 6.3 | 1.920 | 251 | 7.5 | 1.746 | 392 | — | — | — |
| OH | 5.6 | 1.947 | 214 | 5.4 | 1.820 | 258 | — | — | — |
| OMe | 6.2 | 1.923 | 245 | 6.0 | 1.797 | 290 | — | — | — |
| SH | 4.8 | 1.977 | 190 | 4.8 | 1.840 | 239 | — | — | — |
| Me | 5.8 | 1.937 | 233 | 6.1 | 1.797 | 308 | 2.16 | 2.185 | 193 |
| H | 4.4 | 1.991 | 175 | 4.9 | 1.834 | 252 | 2.88 | 2.156 | 224 |
| F | 4.0 | 2.007 | 154 | 3.5 | 1.911 | 157 | 3.08 | 2.128 | 236 |
| Cl | 4.2 | 2.002 | 162 | 3.3 | 1.920 | 153 | 3.52 | 2.120 | 241 |
| C≡CH | — | — | — | — | — | — | 3.68 | 2.117 | 253 |
| $CF_3$ | 3.0 | 2.059 | 118 | 3.2 | 1.917 | 160 | 4.76 | 2.072 | 281 |
| CN | 2.3 | 2.092 | 96 | 2.8 | 1.939 | 152 | 5.66 | 2.039 | 324 |
| $NO_2$ | 1.9 | 2.122 | 82 | 1.7 | 2.129 | 78 | — | — | — |

**Table 2.** Energies of formation of hydrogen bonds ($E$) in complexes (series **IV—X**), ionization potentials (IP) of complexes (series **IV**), and the spin density (sd) on O atom of phenoxyl radical (series **V**)

| X | PhO—H...$NH_2$C≡CX (series **IV**)[10] | | $PhO^{\bullet +}$—H...$NH_2$C≡CX (series **V**)[10] | |  (series **VI—X**) $E$/kcal $mol^{-1}$ (see Ref. 11) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $E$ /kcal $mol^{-1}$ | IP* /eV | $E$ /kcal $mol^{-1}$ | sd /au | Y = $NH_2$ (**VI**) | Y = H (**VII**) | Y = F (**VIII**) | Y = Cl (**IX**) | Y = CN (**X**) |
| $NH_2$ | — | — | — | — | 27.31 | 29.76 | 33.51 | 36.95 | 48.38 |
| OH | 5.4 | 7.64 | 23.0 | 0.079 | — | — | — | — | — |
| Me | 5.3 | 7.66 | 23.0 | 0.082 | — | — | — | — | — |
| H | 4.9 | 7.81 | 18.3 | 0.076 | 26.74 | 29.42 | 32.97 | 36.24 | 47.48 |
| F | 4.5 | 7.82 | 18.1 | 0.076 | 25.53 | 28.01 | 32.80 | 33.72 | 44.45 |
| Cl | 4.5 | 7.80 | 18.6 | 0.076 | 23.17 | 25.48 | 27.93 | 33.03 | 41.58 |
| CN | — | — | — | — | 19.14 | 21.26 | 23.18 | 26.02 | 34.61 |
| $NO_2$ | 2.9 | 8.11 | 9.9 | 0.065 | — | — | — | — | — |

* Unbound phenol is characterized by IP = 8.41 eV.[10]

**Table 3.** Energies of formation of hydrogen bonds ($E$) in complexes XC≡CX′...HF (**XI**)[12]

| X | X′ | $E$/kcal $mol^{-1}$ |
|---|---|---|
| H | H | 2.69 |
| H | F | 1.53 |
| H | Cl | 1.77 |
| F | F | 0.06 |
| Cl | Cl | 0.66 |

applied to the $\Delta G$ values for narrow series of H-complexes in the form

$$\Delta G = \Delta G_I + \Delta G_R + \Delta G_P, \qquad (5)$$

where $\Delta G_I = b\sigma_I$, $\Delta G_R = c\sigma_R$ ($\sigma_R^+$, $\sigma_R^-$) and $\Delta G_P = d\sigma_\alpha$ are the contributions of the inductive, resonance, and polarizability effects of substituents X to the overall change in $\Delta G$.

Let a change in a characteristic $P$ of a charged "non-classical" system (*e.g.*, $\Delta\nu$ values of H-complexes[7]) caused by the effect of substituents X be a linear function of the change in the free energy $\Delta G$, which is also caused by these substituents. Then, there are grounds to believe that the following equations are valid for $P$

$$P = a + b\sigma_I + c\sigma_R(\sigma_R^+, \sigma_R^-) + d\sigma_\alpha. \qquad (6)$$

Using the results of quantum chemical calculations of the characteristics of H-complexes involving "non-classical" acceptors (donors) (see Tables 1—5), it is possible to check this assumption and thus for the first time establish how the polarizability effect influences the parameters $P = E$, $r$, IP, sd, and $\Delta H$.

Correlation equations were calculated using the "Statgraphics 3.0" program. Data were processed by the least squares method at a confidence level of 95%.

The sets of the $\sigma_I$, $\sigma_R$, $\sigma_R^+$, $\sigma_R^-$, and $\sigma_\alpha$ constants (Table 6) used in this work are the same as those employed earlier.[4,7,16]

**Table 4.** Energies of formation of hydrogen bonds ($E$/kcal mol$^{-1}$) in complexes **XII—XIX**

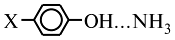
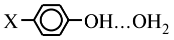
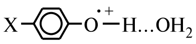
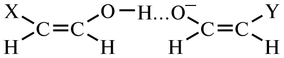
| X |  **(XII)**$^{13}$ |  **(XIII)**$^{13}$ |  **(XIV)**$^{13}$ |  (series **XV—XIX**)$^{11}$ | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Y = $NH_2$ **(XV)** | Y = H **(XVI)** | Y = F **(XVII)** | Y = Cl **(XVIII)** | Y = CN **(XIX)** |
| $NMe_2$ | 5.85 | 3.88 | 13.22 | — | — | — | — | — |
| $NH_2$ | 5.97 | 4.03 | 14.75 | 27.31 | 26.74 | 25.53 | 23.17 | 19.14 |
| OMe | 6.27 | 4.23 | 15.73 | — | — | — | — | — |
| OH | 6.31 | 4.35 | 16.07 | — | — | — | — | — |
| Me | 6.38 | 4.28 | 17.07 | — | — | — | — | — |
| H | 6.63 | 4.49 | 18.49 | 29.76 | 29.42 | 28.01 | 25.48 | 21.26 |
| SMe | 7.10 | 4.48 | 14.57 | — | — | — | — | — |
| F | 7.04 | 4.88 | 18.64 | 33.51 | 32.97 | 32.80 | 27.93 | 23.18 |
| Cl | 7.28 | 5.05 | 17.77 | 36.95 | 36.24 | 33.72 | 33.03 | 26.02 |
| C≡CH | 7.36 | 5.03 | 16.47 | — | — | — | — | — |
| COMe | 7.85 | 5.33 | 17.32 | — | — | — | — | — |
| COOH | 7.91 | 5.40 | 18.80 | — | — | — | — | — |
| $CF_3$ | 7.93 | 5.58 | 19.65 | — | — | — | — | — |
| CN | 8.40 | 5.93 | 19.17 | 48.38 | 47.48 | 44.45 | 41.58 | 34.61 |
| $NO_2$ | 8.89 | 6.25 | 19.83 | — | — | — | — | — |

**Table 5.** Energy of formation ($E$) of complexes series **XX** and changes in enthalpy ($\Delta H$) of hydrogen bonds in complexes (series **XXI**)

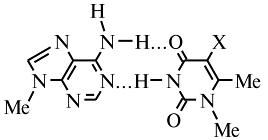
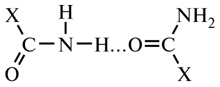
| X |  (series **XX**), $E$ |  (series **XXI**), $-\Delta H$ |
|---|---|---|
| | kcal mol$^{-1}$ | |
| $NH_2$ | 12.12 | — |
| Me | 12.50 | 6.42 |
| Ph | 12.89 | 5.69 |
| H | 12.59 | — |
| F | 12.96 | — |
| $CH_2F$ | — | 4.36 |
| $CHF_2$ | — | 4.02 |
| $CF_3$ | — | 3.90 |
| CN | 13.58 | — |
| $NO_2$ | 13.55 | — |

**Table 6.** Inductive ($\sigma_I$), resonance ($\sigma_R$, $\sigma_R^-$, $\sigma_R^+$), and polarizability ($\sigma_\alpha$) constants of substituents X in series **I—XXI**

| X | $\sigma_I$ | $\sigma_R$ | $\sigma_R^-$ | $\sigma_R^+$ | $\sigma_\alpha$ |
|---|---|---|---|---|---|
| H | 0 | 0 | 0 | 0 | 0 |
| Me | −0.05 | −0.12 | −0.13 | −0.26 | −0.35 |
| Ph | 0.12 | −0.13 | −0.10 | −0.30 | −0.81 |
| C≡CH | 0.22 | 0.01 | 0.31 | −0.04 | −0.60 |
| COOH | 0.34 | 0.11 | 0.43 | 0.08 | −0.34 |
| COMe | 0.33 | 0.17 | 0.51 | 0.14 | −0.55 |
| C≡N | 0.51 | 0.15 | 0.49 | 0.15 | −0.46 |
| $CH_2F$ | 0.15 | −0.04 | — | — | −0.30 |
| $CHF_2$ | 0.29 | 0.03 | — | — | −0.27 |
| $CF_3$ | 0.38 | 0.16 | 0.27 | 0.23 | −0.25 |
| $NH_2$ | 0.08 | −0.74 | −0.23 | −1.38 | −0.16 |
| $NMe_2$ | 0.15 | −0.98 | −0.27 | −1.85 | −0.44 |
| $NO_2$ | 0.65 | 0.13 | 0.62 | 0.14 | −0.26 |
| OH | 0.33 | −0.70 | −0.70 | −1.25 | −0.03 |
| OMe | 0.29 | −0.56 | −0.55 | −1.07 | −0.17 |
| SH | 0.30 | −0.15 | — | −0.33 | −0.55 |
| SMe | 0.23 | −0.23 | −0.17 | −0.83 | −0.68 |
| F | 0.45 | −0.39 | −0.48 | −0.52 | 0.13 |
| Cl | 0.42 | −0.19 | −0.23 | −0.31 | −0.43 |

## Results and Discussion

We began with the following relations:

series **I**

$$E = (0.0260\pm0.0006)\Delta\nu \quad (S_Y = 0.1,\ R = 0.998,\ n = 11), \qquad (7)$$

$$r = (2.199\pm0.010) - (0.00115\pm0.00005)\Delta\nu \quad (S_Y = 0.010,\ R = 0.990,\ n = 11), \qquad (8)$$

series **II**

$$E = (0.28\pm0.17) + (0.0189\pm0.0007)\Delta\nu \quad (S_Y = 0.2,\ R = 0.993,\ n = 11), \qquad (9)$$

$$r = (2.112\pm0.035) - (0.00106\pm0.00011)\Delta\nu \quad (S_Y = 0.042,\ R = 0.922,\ n = 11), \qquad (10)$$

series **III**

$$E = (-3.31\pm0.38) + (0.0279\pm0.0015)\Delta\nu$$

$$(S_Y = 0.16,\ R = 0.993,\ n = 7), \quad (11)$$

$$r = (2.404\pm0.020) - (0.00115\pm0.00008)\Delta\nu$$

$$(S_Y = 0.008,\ R = 0.989,\ n = 7), \quad (12)$$

series **V**

$$\mathrm{sd} = (0.054\pm0.002) + (0.0012\pm0.0001)E$$

$$(S_Y = 0.001,\ R = 0.981,\ n = 6). \quad (13)$$

Validity of the LFER principle for the frequency shifts $\Delta\nu$ [7] and ionization potentials IP [16] and linearity of Eqs (7)—(13) suggest that this principle is also valid for the parameters $E$, $r$, and sd. Therefore, the correlation equation (6) can also be applied to these parameters.

From the data listed in Table 7 it follows that most series do obey Eq. (6), *i.e.*, the polarizability effect does influence the above-mentioned parameters of the H-complexes under study. In some cases the contribution of this effect of substituents X to the overall changes in the corresponding parameters can exceed a value of 25% (Table 8). This does not contradict the fact that the polarizability effect was not found for certain series of H-complexes; the reasons for this will be considered below.

Analysis of the data listed in Tables 7 and 8 makes it possible to draw some general conclusions.

1. Modern quantum chemistry is reliable and useful for calculating parameters of H-complexes, as is, in particular, indicated by high correlation coefficients $R$ in the equations with three unknowns (see Table 7). In this connection it is important that the conclusion about occurrence of the polarizability effect for H-complexes, drawn based on analysis of experimental $\Delta\nu$ values[7] is in excellent agreement with the results obtained in this work (see Tables 7 and 8, series **I—III**).

2. Different parameters of narrow series of H-complexes are in pair related by linear dependences. In addi-

**Table 7.** Coefficients of equations $E(r, \Delta\nu, \mathrm{IP}, \mathrm{sd}, \Delta H) = (a\pm S_a) + (b\pm S_b)\sigma_I + (c\pm S_c)\sigma_R(\sigma_R^-, \sigma_R^+) + (d\pm S_d)\sigma_\alpha$ and their standard errors ($a\pm S_a$, $b\pm S_b$, $c\pm S_c$, $d\pm S_d$), standard errors of approximation ($S_Y$), correlation coefficients ($R$), and sample size ($n$) for series **I—XXI**

| Series | Parameter | $a\pm S_a$ | $b\pm S_b$ | $c\pm S_c$ | $\sigma^a$ | $d\pm S_d$ | $S_Y{}^b$ | $R^b$ | $n$ |
|---|---|---|---|---|---|---|---|---|---|
| **I** | $E$ | 4.5±0.3 | −3.8±0.6 | −3.4±0.4 | $\sigma_R$ | −1.4±0.7 | 0.4 (0.5) | 0.965 (0.950) | 11 |
| | $r_{N...H}$ | 1.99±0.02 | 0.18±0.03 | 0.14±0.02 | $\sigma_R$ | 0.06±0.03 | 0.02 (0.02) | 0.957 (0.948) | 11 |
| | $\Delta\nu$(F—H) | 180±12 | −153±23 | −127±16 | $\sigma_R$ | −60±25 | 15 (19) | 0.966 (0.946) | 11 |
| **II** | $E$ | 5.0±0.2 | −5.2±0.5 | −1.8±0.2 | $\sigma_R{}^+$ | −1.1±0.5 | 0.3 (0.4) | 0.983 (0.975) | 11 |
| | $r_{O...H}$ | 1.83±0.04 | 0.33±0.07 | 0.16±0.05 | $\sigma_R{}^+$ | 0.09±0.08 | 0.04 (0.05) | 0.902 (0.803) | 11 |
| | $\Delta\nu$(F—H) | 256±18 | −288±35 | −89±14 | $\sigma_R{}^+$ | −73±37 | 23 (26) | 0.968 (0.956) | 11 |
| **III** | $E$ | 2.84±0.19 | 3.47±0.42 | 2.64±0.35 | $\sigma_R{}^-$ | 0.74±0.46 | 0.23 (0.27) | 0.981 (0.973) | 7 |
| | $r_{N...H}$ | 2.156±0.005 | −0.164±0.011 | −0.096±0.009 | $\sigma_R{}^-$ | −0.032±0.012 | 0.006 (0.010) | 0.993 (0.980) | 7 |
| | $\Delta\nu$(C—H) | 221±5 | 127±12 | 94±10 | $\sigma_R{}^-$ | 33±13 | 7 (10) | 0.988 (0.973) | 7 |
| **IV** | $E$ | 4.8±0.1 | −2.59±0.27 | −2.11±0.27 | $\sigma_R$ | −0.44±0.36 | 0.16 (0.18) | 0.984 (0.981) | 6 |
| | IP | 7.80±0.05 | 0.42±0.09 | 0.26±0.05 | $\sigma_R{}^+$ | 0.13±0.12 | 0.06 (0.06) | 0.943 (0.941) | 6 |
| **V** | $E$ | 18.6±0.8 | −12.4±1.5 | −12.8±1.5 | $\sigma_R$ | −5.6±2.0 | 0.9 (1.6) | 0.983 (0.940) | 6 |
| | sd | 0.077±0.002 | −0.016±0.004 | −0.013±0.004 | $\sigma_R$ | −0.006±0.005 | 0.002 (0.002) | 0.911 (0.902) | 6 |
| **VI** | $E$ | 26.97±0.38 | −8.98±1.04 | −4.77±0.77 | $\sigma_R{}^-$ | 2.16±1.18 | 0.44 (0.65) | 0.991 (0.981) | 5 |
| **VII** | $E$ | 29.59±0.27 | −9.47±0.76 | −4.85±0.56 | $\sigma_R{}^-$ | 2.56±0.86 | 0.32 (0.71) | 0.996 (0.979) | 5 |
| **VIII** | $E$ | 33.35±0.62 | −9.27±1.73 | −5.83±1.28 | $\sigma_R{}^-$ | 5.92±1.96 | 0.73 (1.64) | 0.987 (0.930) | 5 |
| **IX** | $E$ | 36.13±0.19 | −13.37±0.52 | −7.93±0.38 | $\sigma_R{}^-$ | 1.39±0.59 | 0.22 (0.40) | 0.999 (0.996) | 5 |
| **X** | $E$ | 47.77±0.48 | −16.59±1.34 | −8.02±0.99 | $\sigma_R{}^-$ | 1.91±1.52 | 0.56 (0.64) | 0.995 (0.993) | 5 |
| **XI** | $E$ | 2.76±0.08 | — | 3.66±0.18 | $\sigma_R$ | 0.79±0.11 | 0.10 (0.20) | 0.995 (0.980) | 5 |
| **XII** | $E$ | 6.60±0.14 | 2.61±0.28 | 1.53±0.15 | $\sigma_R$ | −0.39±0.23 | 0.19 (0.20) | 0.978 (0.975) | 15 |
| **XIII** | $E$ | 4.51±0.09 | 2.16±0.24 | 1.17±0.12 | $\sigma_R$ | — | 0.16 | 0.973 | 15 |
| **XIV** | $E$ | 18.60±0.28 | 2.62±0.59 | 2.54±0.17 | $\sigma_R{}^+$ | 3.37±0.46 | 0.39 (0.91) | 0.981 (0.890) | 15 |
| **XV** | $E$ | 29.24±0.61 | 24.62±1.64 | 13.88±1.05 | $\sigma_R{}^-$ | — | 0.76 | 0.996 | 5 |
| **XVI** | $E$ | 28.80±0.67 | 23.98±1.81 | 13.63±1.16 | $\sigma_R{}^-$ | — | 0.84 | 0.995 | 5 |
| **XVII** | $E$ | 27.61±0.66 | 24.22±1.84 | 12.70±1.36 | $\sigma_R{}^-$ | 3.44±2.09 | 0.77 (1.06) | 0.994 (0.989) | 5 |
| **XVIII** | $E$ | 25.03±1.25 | 21.62±3.40 | 12.25±2.17 | $\sigma_R{}^-$ | — | 1.57 | 0.977 | 5 |
| **XIX** | $E$ | 20.84±0.52 | 17.03±1.40 | 10.76±0.89 | $\sigma_R{}^-$ | — | 0.65 | 0.994 | 5 |
| **XX** | $E$ | 12.59±0.06 | 1.37±0.11 | 0.45±0.06 | $\sigma_R{}^+$ | −0.34±0.09 | 0.07 (0.14) | 0.993 (0.968) | 7 |
| **XXI** | $\Delta H$ | −5.8±0.7 | 10.8±4.5 | −9.2±7.5 | $\sigma_R$ | 2.9±1.8 | 0.46 (0.63) | 0.911 (0.826) | 5 |

[a] The type of the resonance parameter in the term $(c\pm S_c)\sigma_R(\sigma_R^-, \sigma_R^+)$.

[b] The values calculated ignoring the polarizability effect are given in parentheses.

**Table 8.** Inductive ($b\sigma_I$), resonance ($c\sigma_R$, $c\sigma_R^-$, or $c\sigma_R^+$), and polarizability ($d\sigma_\alpha$) contributions (%) to overall changes in $E$, $r_{O...H}$, $r_{N...H}$, Δν, IP, sd, and Δ*H* under the action of substituents X

| Series | Parameter | $b\sigma_I$ | $c\sigma_R$, $c\sigma_R^-$ or $c\sigma_R^+$ | $d\sigma_\alpha$ |
|---|---|---|---|---|
| **I** | *E* | 40±6 | 45±5 | 15±7 |
| | $r_{N...H}$ | 43±7 | 43±6 | 14±7 |
| | Δν(F—H) | 41±6 | 43±6 | 16±6 |
| **II** | *E* | 50±5 | 40±4 | 10±5 |
| | $r_{O...H}$ | 53±11 | 33±10 | 14±12 |
| | Δν(F—H) | 51±6 | 36±6 | 13±6 |
| **III** | *E* | 38±5 | 51±7 | 11±7 |
| | $r_{N...H}$ | 44±3 | 45±4 | 11±4 |
| | Δν(C—H) | 38±4 | 49±5 | 13±5 |
| **IV** | *E* | 48±5 | 46±6 | 6±5 |
| | IP | 40±9 | 50±10 | 10±9 |
| **V** | *E* | 39±5 | 47±6 | 14±5 |
| | sd | 44±11 | 44±13 | 12±11 |
| **VI** | *E* | 44±5 | 44±7 | 12±7 |
| **VII** | *E* | 44±4 | 42±5 | 14±5 |
| **VIII** | *E* | 34±6 | 41±9 | 25±8 |
| **IX** | *E* | 45±2 | 50±2 | 5±2 |
| **X** | *E* | 49±4 | 45±6 | 6±5 |
| **XI** | *E* | — | 76±4 | 24±3 |
| **XII** | *E* | 47±5 | 45±4 | 8±5 |
| **XIII** | *E* | 53±6 | 47±5 | — |
| **XIV** | *E* | 18±4 | 54±4 | 28±4 |
| **XV** | *E* | 48±3 | 52±4 | — |
| **XVI** | *E* | 48±4 | 52±4 | — |
| **XVII** | *E* | 46±4 | 46±5 | 8±5 |
| **XVIII** | *E* | 48±8 | 52±9 | — |
| **XIX** | *E* | 45±4 | 55±4 | — |
| **XX** | *E* | 49±4 | 35±5 | 16±4 |
| **XXI** | Δ*H* | 52±22 | 30±24 | 18±11 |

tion to the known[1,7] dependences of Δ*G* and Δ*H* on Δν and to Eqs (7)—(13), the following relations are valid

$$\mathrm{IP} = (8.64\pm0.08) - (0.18\pm0.02)E$$
$$(S_Y = 0.04,\ R = 0.983,\ n = 6), \qquad (14)$$

$$\mathrm{sd} = (0.336\pm0.030) - (0.033\pm0.004)\mathrm{IP}$$
$$(S_Y = 0.001,\ R = 0.975,\ n = 6) \qquad (15)$$

(series **IV**, **V**).

This indicates the applicability of the LFER principle and makes it possible to calculate unknown values of certain parameters of H-complexes.

3. In narrow series of H-complexes with the same electron acceptor molecule a (complexes that form according to Eq. (2), series **I**, **II**, and **IV—XI**) the hydrogen bond energy *E* is affected by the inductive, resonance, and polarizability effects of substituents X. The stronger the electron-donor properties of X, the higher the energy *E*.

In series **I**, **II**, **IV**, **V**, and **XI** we deal with electrically neutral starting electron donor molecules DX. The formation of an H-complex is accompanied by the appearance of a partial positive charge $\delta^+$ on the donor centers in these molecules. Therefore, conjugation in $D^{\delta+}X$ is characterized by the $\sigma_R$ constants (or $\sigma_R^+$ for series **II**). In series **VI—X**, the starting electron donor molecules bear a large negative charge on the donor center $D^-$. This charge only slightly decreases due to partial charge transfer to the electron acceptor in the course of formation of H-complexes. Therefore, conjugation in $D^-X$ is characterized by the $\sigma_R^-$ constants. Our considerations concerning the signs of the resonance constants are unambiguously substantiated by the results of correlation analysis. Namely, this choice of the resonance constants provides the maximum correlation coefficients, *R*, and minimum standard errors of approximation, $S_Y$. This also concerns all other correlation equations (for series **III**, **XII—XXI**) considered below.

In the complexes of series **I**, **II**, and **IV—XI**, passage from typical resonance acceptors (X = $NO_2$, CN) to typical resonance donors (X = $NH_2$, OH) is accompanied by an increase in the hydrogen bond energy *E*. Additionally, the energies *E* of the H-complexes in series **VI—X**, in which the donor center bears a large negative charge (formally, this is similar to the introduction of the strongest resonance donors X into the d), are much higher than in series **I**, **II**, **IV**, **V**, and **XI**.

4. In narrow series with the same electron donor molecules (complexes similar to that shown in Eq. (3), series **III** and **XII—XIX**) the H-bond energy *E* depends, in the general case, on three effects (inductive, resonance, and polarizability effects) of substituents X and increases as the electron acceptor properties of X are enhanced. The resonance properties of substituents X in these series (except series **XIV**) are described by the $\sigma_R^-$ constants owing to the appearance of a partial negative charge δ– on the acceptor center during the formation of an H-complex. In series **XIV**, the starting electron acceptors are radical cations that bear large positive charges on the acceptor centers. This charge only slightly decreases as a result of partial compensation by a small charge δ– transferred from d to a during the formation of the H-complex. Therefore, conjugation in the a-components of H-complexes of series **XIV** is characterized by the $\sigma_R^+$ constants of substituents X.

A salient feature of the H-complexes in series **XIII**, **XV**, **XVI**, **XVIII**, and **XIX** is that no polarizability effect was found for them (see Tables 7 and 8). The reasons are quite understandable if we use relation (4). *para*-Substituted phenols are very similar to the "classical" electron acceptor molecules that are characterized by long distances $r_q$ (see expression (4)). Because of this the polarizability effect in the complexes involving *para*-substituted phenols is determined by the charge on the acceptor center. The complexes of series **XIII** are characterized by relatively weak donor properties of the molecule d ($H_2O$), which leads to a small charge $q$ and the absence of the polarizability effect. The compounds belonging to series **XII** include stronger donors d ($NH_3$). As a consequence, the charge $q$ is larger, the energy $E$ is higher, and the contribution of the polarizability effect is 8% (see Table 8). In the compounds of series **XIV**, a large charge $q$ is responsible for the greatest contribution of the polarizability effect (28%). In contrast to the series **XV**, **XVI**, **XVIII**, and **XIX** characterized by zero contribution of the polarizability effect due to the long distance $r_q$, for related compounds with Y = F (series **XVII**) this contribution is 8%. Note that among the series **VI—X** the greatest contribution of the polarizability effect was also found for Y = F (see Table 8, series **VIII**). According to calculations,[11] the complexes included in series **VIII** and **XVII** (Y = F) are characterized by shorter O...O$^-$ distances in the O—H...O$^-$ fragments compared to their isostructural analogs and, hence, by smaller $r_q$ values in relation (4) and the greatest contribution of the polarizability effect.

Common to the complexes included in series **III** and **XII—XIX** is an increase in the hydrogen bond energy upon enhancement of the acceptor properties of the electron acceptor molecules, *i.e.*, upon an increase in the positive charge of the H atom in the acceptor center C—H (series **III**) or O—H (other series). For instance, a considerable increase in this charge on going from neutral molecules to radical cations (series **XIII** and **XIV**) is followed by an abrupt increase in the energy $E$. Besides, in the series **III** and **XII—XIX** both the positive charge on the H atom of the acceptor centers C—H and O—H and the energy $E$ increase on going from the resonance donors (X = $NMe_2$, $NH_2$, Me) to the resonance acceptors (X = CN, $NO_2$).

5. The N...H and O...H bond lengths are determined by combination of the inductive, resonance, and polarizability effects of the substituents X bound to the donor or acceptor center in the H-complexes (see Table 7). As follows from Table 8, in each series (**I**, **II** and **III**) the contributions of these effects to the overall change in the parameters $r$, $E$, and $\Delta\nu$ under the action of substituents do not differ from one another within the limits of error in determination.

6. The formation of an H-complex is accompanied by transfer of the electron density from the donor to acceptor and by redistribution of the electron density in the latter. This follows from the parameters IP (ionization potential) and sd (spin density on the oxygen atom in H-complexes), which, similarly to the parameters $E$, $r$, and $\Delta\nu$, depend on the inductive, resonance, and polarizability effects of substituents X in the molecules d (see Tables 2, 7, and 8; series **IV** and **V**). On the one hand, the IPs of the complexes PhO—H...$NH_2C{\equiv}CX$ at any X are much lower than the IP of free phenol (8.41 eV according to Ref. 10). On the other hand, they decrease (increase) as the resonance donor (acceptor) properties of substituents X are enhanced. The ionization potentials in question correspond to detachment of an electron from the highest occupied molecular orbital (HOMO), which is mainly localized on the $\pi$-MO of the aromatic ring. Additionally, Eq. (15) shows that the higher the spin density sd on the O atom in the complexes $PhO^{\bullet+}$—H...$NH_2C{\equiv}CX$ (series **V**), the lower the IP values of the H-complexes of neutral PhOH molecule (series **IV**). From this it follows that the aromatic ring is involved in delocalization of the electron density transferred from the donor to acceptor in the formation of an H-complex.

In conclusion we will briefly outline two series, **XX** and **XXI**, in which both components of H-complexes include both electron-donor and electron acceptor centers. Here, the parameters $E$ and $\Delta H$ are also determined by combination of the inductive, resonance, and polarizability effects of substituents X. In series **XX** the energy $E$ relatively weakly depends on the nature of X and seems to be mainly determined by the degree of conjugation in the amide fragment H—N—C=O (its H and O atoms are involved in the formation of H-bonds, N—H...O and N...H—N). Probably, enhancement of the electron acceptor properties of substituents X causes enhancement of the acceptor properties of the H—N group, an increase in the energy of the hydrogen bond N...H—N, and transfer of the electron density from the N atom to the H—N group and then along the amide conjugation chain to the O atom of the C=O group. As a result the energy of the hydrogen bond N—H...O increases from 12.12 (X = $NH_2$) to 13.55 kcal mol$^{-1}$ (X = $NO_2$, see Table 5). This process seems to compete with a decrease in the electron density on the O atom in the C=O group of the O=C—C—X group and with a decrease in the energy of the hydrogen bond N—H...O upon enhancement of the acceptor properties of X. This process can not be significant because it provides no explanation for the major feature of the compounds in series **XX**, namely, the increase in the energy $E$ upon enhancement of the acceptor properties of X.

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