

Polarization Effect in Radical Cations and H-Complexes

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Abstract—The effect of substituents X on the ionization potentials IP (process $DX + h\nu \rightarrow D^+X + e$) and shifts in vibration frequencies $\Delta\nu$ of $\nu(\text{OH})$ in the IR spectra of phenol complexes $\text{PhO-H} + \text{DX} \rightleftharpoons \text{PhO}^{\delta-}\text{-H}\cdots\text{D}^{\delta+}\text{X}$ for nine series of DX molecules were studied. On compiling with three conditions (a constant donor center D; the electron density donation only from D and not from X; a constant sampling size within each series) it was possible to compare the polarization effect in D^+X and $D^{\delta+}X$. In the radical cations D^+X the polarization effect is on the average 2.2 times larger than in the systems $D^{\delta+}X$. The systems D^+X and $D^{\delta+}X$ are virtually indistinguishable with respect to the external delocalization of the positive charge.

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The intramolecular interactions between D and X (inorganic, organic, organometallic substituents) essentially differ in neutral molecules DX compared with the electron-deficient systems with a partial $D^{\delta+}X$ or total D^+X positive charge on the reaction center D [1]. These interactions in the DX molecules consist in inductive and resonance effects, and in the systems $D^{\delta+}X$ and D^+X include also the so-called polarization effect. The latter is revealed not only in the ionic gas-phase reactions with formation of cations of D^+X kind where it has been discovered for the first time (see [2, 3] for more details). We recently established the large influence of the polarization effect on the spectral characteristics both in the gas phase (first vertical ionization potentials in the photoelectron spectra [4–7]) and in solution (energy of the charge transfer bands in the UV spectra of the charge-transfer complexes [8], shifts of the stretching vibration frequencies $\Delta\nu$ of the O–H bond in phenol in the IR spectra of its H-complexes containing a hydrogen bond with electron donors [9]).

The polarization effect in the electron-deficient systems D^+X and $D^{\delta+}X$ originates from the charge q on the center D. The charge q polarizes the substituent X inducing a dipole therein. In the classic electrostatics the energy of the polarization interaction charge–induced dipole that stabilizes the charge q is described by the expression (1) [7–9].

$$E_{es} = -q^2\alpha/2\epsilon r^4, \quad (1)$$

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

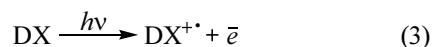
In the molecular electrostatics the medium dividing the charge and the dipole induced by it in the substituent X is the internal space of the molecule. It is well known [10] that in this case the efficient dielectric constant of the medium is virtually equal in various molecules ($\epsilon \approx 2$). Therefore the expression (1) may be rewritten as (2).

$$E_{es} = -q^2\alpha/4r^4 \quad (2)$$

It follows from equation (2) that all the other conditions being equal the larger is the charge q on the reaction center D, the greater should be the polarization effect. The results of our first spectroscopic studies are in general consistent with this statement [8, 9]. At the same time the complexity of the problem under consideration is *a priori* clear. It will suffice to mention that the polarization effect: (a) is interconnected with the inductive and resonance effect, and therefore should be strictly isolated from the overall intramolecular interactions; (b) can be dependent on the charge q delocalization over the reaction center D and therefore depend on the D nature; (c) depends on the polarizability α and consequently in the series $D^{\delta+}X$, D^+X , D^+X changes as a function of the sampling size of substituents X, i.e., of the number and type of X. Therefore the relationship between the polarization effect and the charge on the reaction center requires further experimental investigation.

The goal of the present study is a comprehensive investigation of the polarization effect in radical cations and H-complexes depending on the character of the reaction center and the positive charge delocalization.

One of the possible ways to achieve the target is application of the correlation analysis procedure. In this case the study of the polarization effect in radical cations (CR) D^+X can be conveniently based on the gas-phase photoionization reaction (3) of neutral DX molecules that is used in the photoelectron spectroscopy for the measurement of the ionization potentials.



We shall consider below, firstly, DX molecules whose highest occupied molecular orbital (HOMO) is mainly localized on D and not on X, and, secondly, the first vertical ionization potentials IP corresponding to electron detachment from the HOMO of the DX molecules. The exceptions will be mentioned separately.

The ionization potential $IP(DX)$ is by definition [7] the standard enthalpy $\Delta_r H^\circ(T)$ of reaction (3) at temperature T [equation (4)].

$$IP = \Delta_r H^\circ(T) \quad (4)$$

In a wide temperature range (0–500 K) the entropy contribution $T\Delta_r S^\circ(T)$ to the standard Gibbs free energy $\Delta_r G^\circ(T)$ of reaction (3) does not exceed 5%. Therefore the Gibbs–Helmholtz equation (5) for the process (3) may be well approximated by expression (6) [7].

$$\Delta_r G^\circ(T) = \Delta_r H^\circ(T) - T\Delta_r S^\circ(T) \quad (5)$$

$$\Delta_r G^\circ(T) = IP \quad (6)$$

From expression (6) follows a conclusion that the influence of substituents X on IP may be treated based on the principle of the linear dependence of the differences in the free energy which is conventionally applied in the form of the correlation Hammett–Taft equations [1].

The above proves the validity and high accuracy of equations of type (7).

$$IP = IP_H + a\sigma_I + b\sigma_R^+ + c\sigma_a \quad (7)$$

Here IP_H is the IP value at $X = H$; a , b , and c are coefficients.

Equations (7) were considered in detail in [4–7]. Here we will give only short remarks.

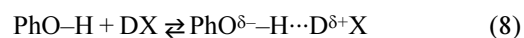
The universal and invariant with respect to D type constants σ_I characterize the inductive effect of substituents X [1].

The resonance effect of substituents X cannot in the general case be described with a universal set of the resonance constants. Depending on the value and the sign of the charge on the reaction center at least four sets of parameters are applied: σ_R^\ominus , σ_R , σ_R^+ , and σ_R^- . In our case the use of σ_R^+ values is quite reasonable. The parameter σ_R^+ characterizes the conjugation of the substituent X with any electron-deficient reaction center which is formed either in transition or in final state of the chemical reaction [11]. In reaction (3) under consideration the positively charged center is a cation-radical. Therefore the ionization potentials IP of DX molecules contain the information of the conjugation in the radical cations D^+X [4–7].

The universal constants σ_α characterize the polarization effect of substituents X [2–10]. The σ_α values calculated by procedures of quantum chemistry and known for a large number of substituents [2, 3] permit avoiding laborious calculations by formula (2).

From equation (7) it is possible to calculate the inductive $Ind(CR) = \alpha\sigma_I$, resonance $Res(CR) = b\sigma_R^+$, and polarization $Pol(CR) = c\sigma_\alpha$ contribution into the overall change of IP under the influence of substituents.

Let us consider now the approach to the polarization study in the systems $D^{\delta+}X$ based on the analysis of the IIR spectra of the H-complexes (H-C) of phenol CCl_4 solutions.



The electron density donation from the electron-donor molecules DX to the electron-acceptor molecule PhOH at formation of the H-complex results in generation of a partial positive charge δ^+ on the donor center D. An informative characteristic of the complexes with a hydrogen bond is the frequency shift $\Delta\nu = \nu(OH) - \nu(OH\cdots DX)$ { $\nu(OH)$ and $\nu(OH\cdots DX)$ are frequencies of the stretching vibrations of the O–H bond in phenol in the absence and in the presence of DX respectively [9, 12]}. It was experimentally found [1, 9, 12], that within the narrow series of H-complexes (when the donor center D remains constant) the parameter $\Delta\nu$ is linearly related to the standard free energy $\Delta_r G^\circ(T)$ of process (8). The validity of principle of the linear dependence of the differences in the free energy appears also in correctness of equations of type (8) for the narrow series of H-complexes.

$$\Delta\nu = \Delta\nu_H + k\sigma_I + l\sigma_R + m\sigma_a \quad (9)$$

Here Δv_H is the Δv value at $X = H$; k , l , and m are coefficients. The parameters σ_I and σ_a are the same as in equation (7).

The resonance effect of substituents X in the system $D^{\delta+}X$ is characterized by parameters σ_R . The reason of application of parameters σ_R instead of σ_R^{\ddagger} used in equation (7) is the lower value of the positive charge in the systems $D^{\delta+}X$ bearing only a partial charge δ^+ than in the radical cations D^+X (see [1, 9] for more details). From equation (9) it is possible to calculate the inductive $Ind(C-H) = k\sigma_I$, resonance $Res(C-H) = l\sigma_R$, and polarization $Pol(C-H) = m\sigma_a$ contribution into the overall change in the Δv values effected by substituents.

Taking into account the above reasoning, the following conditions should be fulfilled for comparative investigation of the polarization effect in radical cations D^+X and the systems $D^{\delta+}X$.

(1) In the series (narrow series) of radical cations D^+X and H-complexes $PhO^{\delta-}-H\cdots D^{\delta+}X$ the donor center D should be kept constant. Therewith in the processes (3) and (8) should be involved the same atom (or fragment) of the donor center D . For instance, in the series of nitriles $NC-X$ the H-complexes with PhOH form at the nitrogen atom possessing a local effective negative charge [9]. At the same time the unshared electron pair of the nitrogen in $N\equiv C-X$ makes the largest contribution not into the HOMO, but into the next orbital HOMO-1, and the electron detachment from the latter corresponds to the second ionization potential (IP_2) in the photoelectron spectrum [13]. Therefore in studying the contribution $Pol(CR)$ in radical cations $N^+\equiv C-X$ the data on IP_2 should be used.

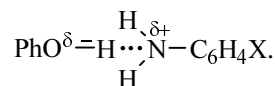
(2) In each series of DX ($D = \text{const}$) both the electron detachments at radical cations D^+X formation and the electron density donation in the H-complexes $PhO^{\delta-}-H\cdots D^{\delta+}X$ should occur only from the donor center D and not from the substituent X . For instance, in the series $O=PX_3$ the oxygen may be selected as the donor center, for on its n orbital the HOMO is prevailingly localized [6]. The H-complex also involves the oxygen atom [9]. The molecule $O=P(CH=CH_2)F_2$ whose HOMO is mostly localized on the atoms of the fragment $CH=CH_2$ should be excluded from this series. Thus the careful choice of substituents X should prevent the transmission of the electron-donor center from D to X in all series DX under study.

(3) Every series DX ($D = \text{const}$) applied to the comparison of the polarization contributions $Pol(CR)$ and

$Pol(C-H)$ should be of a constant sampling size (n) with respect to substituents X . In other words, in the series DX at $D = \text{const}$ the number and type of substituents X should remain unchanged in the study both of the radical cations D^+X and the H-complexes $PhO^{\delta-}-H\cdots D^{\delta+}X$. The necessity of the standard sampling size n is caused by the changes as a rule in the range of values σ_I , σ_R^{\ddagger} (or σ_R), and σ_a of substituents X at varying the n . The latter leads to the changes in the relative contributions Ind , Res and Pol (see [7] for more detail).

From the numerous DX systems we succeeded to select in agreement with the conditions (1–3) only series **I–IX** (Table 1). For each series in Table 1 the chosen by us atom of the center D is indicated playing the role of the electron-donor in formation of the complexes with a hydrogen bond with PhOH along equation (8). According to the above requirements (1) and (2) in each series this atom of the center D should make the dominant contribution into the molecular orbital whose electron loss corresponds to the ionization potentials considered in this series.

For instance, in series **II** the H-complexes involve the nitrogen atom:



Therefore the reasonable comparison of the polarization effects in the complexes with the hydrogen bond and in the radical cations of series **II** only the radical cations $p-H_2N^+C_6H_4X$ should be taken into consideration. Radical cations of this type form on electron detachment from an orbital with the prevailing contribution from the unshared electron pair of the nitrogen which corresponds to the third ionization potential [IP (II) in Table 1] in the photoelectron spectrum of the molecules $p-H_2NC_6H_4X$.

As has been discussed above, in the series **I** the H-complexes also form at the nitrogen atom, and the generation of radical cations of $N^+\equiv C-X$ type occurs by electron elimination from the molecular orbital corresponding to the second ionization potential [IP (I) in Table 1] in the photoelectron spectrum of the molecules NCX .

Ionization potentials $IP(\text{III})-IP(\text{IX})$ of series **III–IX** correspond to the electron detachment from HOMO. The prevailing contribution into HOMO of the molecules in series **III–VIII** make the atoms involved in formation of the H-complexes: unshared electron pairs of the oxygen (series **III–V**), the sulfur (series **VI** and **VII**), and chlorine

Table 1. Values of ionization potentials *IP* (eV) and frequency shifts $\Delta\nu$ (cm⁻¹) in the spectra of compounds of series I–IX

I^a NCX ^b N≡C ^c Atom N ^d		
X	<i>IP</i> (I) [13, 14]	$\Delta\nu$ (I) [15]
H	14.01	140
Me	13.17	159
Et	12.83	165
Pr	12.87	167
<i>i</i> -Pr	12.51	166
Br	13.58	102
II^a <i>p</i> -H ₂ NC ₆ H ₄ X ^b H ₂ NC ₆ H ₄ ^c Atom N ^d		
X	<i>IP</i> (II) [13]	$\Delta\nu$ (II) [9]
H	10.84	350
Me	10.50	380
OMe	10.00	395
F	10.91	350
Cl	10.70	330
III^a O=CX ₂ ^b O=C ^c Atom O ^d		
X ₂	<i>IP</i> (III) [13, 16, 17]	$\Delta\nu$ (III) [12, 18]
Me ₂	9.71	193
MeEt	9.56	202
MePr	9.38	210
MePr- <i>i</i>	9.29	200
MeBu- <i>t</i>	9.11	200
<i>t</i> -Bu ₂	8.67	195
Me(CH ₂ Cl)	9.88	142
Me(OEt)	10.45	173
CH ₂ Cl(OMe)	10.70	125
(OMe) ₂	11.00	136
Me(SET)	9.65	150
IV^a O=PX ₃ ^b O=P ^c Atom O ^d		
X ₃	<i>IP</i> (IV) [6]	$\Delta\nu$ (IV) [19–22]
Me ₃	9.90	461
Et ₂ (CH=CH ₂)	9.66	450
H(OMe) ₂	11.10	314
H(OEt) ₂	10.86	320
(OMe) ₃	10.81	326
(OEt) ₃	10.51	338
(CH=CH ₂)Cl ₂	11.24	110
Cl ₃	11.89	110
Br ₃	11.02	115

Table 1. (Contd.)

V^a O=SX ₂ ^b O=S ^c Atom O ^d		
X ₂	<i>IP</i> (V) [23]	$\Delta\nu$ (V) [12]
Me ₂	9.01	350
<i>i</i> -Pr ₂	8.46	360
Me(CH=CH ₂)	9.02	315
Ph ₂	8.58	294
(OEt) ₂	10.25	154
VI^a SX ₂ ^b S ^c Atom S ^d		
X ₂	<i>IP</i> (VI) [5]	$\Delta\nu$ (VI) [24, 25]
Me ₂	8.67	230
Et ₂	8.44	245
Pr ₂	8.34	245
<i>i</i> -Pr ₂	8.26	256
Bu ₂	8.22	250
<i>t</i> -Bu ₂	8.07	275
Et(CH ₂ CH=CH ₂)	8.51	227
(CH ₂ CH=CH ₂) ₂	8.55	216
Me(CH=CH ₂)	8.45	164
Et(CH=CH ₂)	8.50	175
Pr(CH=CH ₂)	8.34	173
<i>t</i> -Bu(CH=CH ₂)	8.33	202
(CH=CH ₂) ₂	8.44	123
Me(Ph)	8.12	172
Et(Ph)	8.01	180
CH ₂ CH=CH ₂ (Ph)	8.13	176
CH=CH ₂ (Ph)	8.18	140
Ph ₂	7.88	122
VII^a S=PX ₃ ^b S=P ^c Atom S ^d		
X ₃	<i>IP</i> (VII) [6]	$\Delta\nu$ (VII) [9]
Et ₃	8.34	321
Et(CH ₂ Ph) ₂	8.06	306
(OEt) ₃	8.96	184
(SMe)Cl ₂	9.61	96
Cl ₃	10.61	61

Table 1. (Contd.)

VIII ^a CIX ^b Cl ^c Atom Cl ^d		
X	IP(VIII) [7]	$\Delta\nu$ (VIII) [9, 26]
Bu	10.84	59
<i>i</i> -Bu	10.66	63
<i>t</i> -Bu	10.61	74
CH ₂ Cl	11.40	27
SiMe ₃	10.84	54
GeMe ₃	10.35	90
SnMe ₃	10.16	113
IX ^a C ₆ H ₅ X ^b C ₆ H ₅ ^c One of atoms C ^d		
X	IP(IX) [4]	Dn(IX) [9]
H	9.24	49
Me	8.72	58
<i>i</i> -Pr	8.73	58
<i>t</i> -Bu	8.74	61
CF ₃	9.86	28
CH ₂ Cl	9.27	49
NEt ₂	7.20	83
OMe	8.42	62
F	9.20	30
Cl	9.07	35
Br	9.04	38
SiMe ₃	8.94	55
CH ₂ SiMe ₃	8.42	58

^a Series number.^b Series.^c Donor center D.^d Atom of D center involved in the process (8).

(series VIII). The HOMO of molecules C₆H₅X (series IX) is the e_{1g} orbital of benzene perturbed by the interactions with substituents X.

Obviously the cause of the variation of the values *IP* and $\Delta\nu$ in each series I–IX originates from the interaction of the donor center D with substituents X, and we have studied these interactions with the use of the correlation analysis.

The correlation equations were calculated by standard programs Statgraphics 3.0 on a PC AT-286. The treatment by the least-squares method was carried out to the confidence level 95%. The standard values of inductive, resonance, polarization, and sterical parameters of the substituents are given in Table 2.

Table 2. Inductive σ_I , resonance σ_R and σ_R^+ , polarization σ_a , and sterical E_s' parameters of substituents X in compounds of series I–IX

Substituent	σ_I^a	σ_R^a	σ_R^{+a}	σ_a^a	$E_s'^b$
H	0	0	0	0	1.12
Me	-0.05	-0.12	-0.26	-0.35	0
Et	-0.05	-0.10	-0.25	-0.49	-0.08
Pr	-0.05	-0.10	-0.25	-0.54	-0.31
<i>i</i> -Pr	-0.03	-0.12	-0.25	-0.62	-0.48
Bu	-0.05	-0.10	-0.25	-0.57	-0.31
<i>i</i> -Bu	-0.03	-0.10	-0.25	-0.61	-0.93
<i>t</i> -Bu	-0.07	-0.13	-0.19	-0.75	-1.43
CH=CH ₂	0.13	-0.17	-0.29	-0.50	-2.07
Ph	0.12	-0.13	-0.30	-0.81	-2.31
CH ₂ CH=CH ₂	-0.06	-0.08	-0.16	-0.57	-0.31
CH ₂ Ph	-0.04	-0.05	-0.45	-0.70	-0.39
CF ₃	0.38	0.16	0.23	-0.25	-0.78
CH ₂ Cl	0.13	-0.01	-0.14	-0.54	-0.18
NEt ₂	0.01	-0.73	-2.08	-0.56	–
OMe	0.29	-0.56	-1.07	-0.17	0.20
OEt	0.26	-0.50	-1.07	-0.23	-0.07
SMe	0.23	-0.23	-0.83	-0.68	-0.72
SEt	0.26	-0.23	-0.83	-0.74	-0.96
F	0.45	-0.39	-0.52	0.13	0.57
Cl	0.42	-0.19	-0.31	-0.43	-0.02
Br	0.45	-0.22	-0.30	-0.59	-0.22
SiMe ₃	-0.15	0.05 ^c , -0.05 ^d	0.02 ^c , 0.05 ^e	-0.72	-1.79
GeMe ₃	-0.11	-0.19 ^d	-0.47 ^e	-0.60	–
SnMe ₃	-0.13	-0.27 ^d	-0.58 ^e	-0.60	–
CH ₂ SiMe ₃	-0.05	-0.20 ^c	-0.49 ^c	-0.66	–

^a The standard set of parameters σ_I , σ_R , σ_R^+ , σ_a of substituents used was already applied before [3–9].^b The values of the sterical parameters E_s' of substituents were taken from [27, 28].^c The values σ_R and σ_R^+ for X = SiMe₃, CH₂SiMe₃ in C₆H₅X (series IX) are taken from [1, 4].^d The values σ_R for X = SiMe₃, GeMe₃, SnMe₃ in CIX (series VIII) were calculated by a method described earlier [9] proceeding from the $\Delta\nu$ value.^e The values σ_R^+ in CIX (series VIII) are taken from [7].

The ionization potentials *IP* of the molecules from the series I–IX fit to the equations of (7) type, and the parameters $\Delta\nu$ in the IR spectra of the H-complexes for the majority of the series (except for III and VI) fit to the equations of (9) type (Table 3). Introducing into the three-parameter equations (7) of the fourth parameter E_s' , the quantitative characteristic of the sterical effect

Table 3. Coefficients in equations $IP = IP_H + a\Sigma\sigma_I + b\Sigma\sigma_R + c\Sigma\sigma_\alpha$ and $\Delta v = \Delta v_H + k\Sigma\sigma_I + l\Sigma\sigma_R + m\Sigma\sigma_\alpha$, standard approximation errors S_Y , correlation factors r , and sampling size n

Series no. ^a	$IP (\Delta v)$	$IP_H (\Delta v_H)$	$a (k)$	$b (l)$	$c (m)$	S_Y	r	n
I	$IP (\mathbf{I})$	14.02 ± 0.09	1.88 ± 0.22	–	2.19 ± 0.19	0.091	0.9860.999	6
	$\Delta v (\mathbf{I})$	140 ± 1	-132 ± 1	–	-37 ± 1			
Ia	$IP (\mathbf{Ia})$	14.00 ± 0.07	1.78 ± 0.18	–	2.06 ± 0.17	0.071	0.9890.999	5
	$\Delta v (\mathbf{Ia})$	140 ± 1	-133 ± 1	–	-38 ± 1			
II	$IP (\mathbf{II})$	10.90 ± 0.10	0.83 ± 0.30	0.95 ± 0.17	0.54 ± 0.26	0.123	0.9430.995	5
	$\Delta v (\mathbf{II})$	351 ± 2	-125 ± 7	-141 ± 8	-11 ± 6			
III	$IP (\mathbf{III})$	11.00 ± 0.21	2.35 ± 0.37	0.38 ± 0.17	1.26 ± 0.16	0.116	0.9880.978	11
	$\Delta v (\mathbf{III})$	84 ± 42	-246 ± 23	-146 ± 31	-78 ± 44			
IIIa	$IP (\mathbf{IIIa})$	10.89 ± 0.15	2.19 ± 0.25	0.16 ± 0.13	1.29 ± 0.10	0.075	0.9930.988	10
	$\Delta v (\mathbf{IIIa})$	55 ± 32	-263 ± 18	-189 ± 28	-100 ± 33			
IV	$IP (\mathbf{IV})$	11.91 ± 0.31	1.55 ± 0.12	0.56 ± 0.10	1.28 ± 0.20	0.1531	0.9750.974	9
	$\Delta v (\mathbf{IV})$	274 ± 65	-309 ± 29	-169 ± 44	-76 ± 41			
IVa	$IP (\mathbf{IVa})$	11.64 ± 0.12	1.64 ± 0.05	0.52 ± 0.04	1.08 ± 0.08	0.0534	0.9970.967	8
	$\Delta v (\mathbf{IVa})$	293 ± 78	-313 ± 32	-163 ± 48	-61 ± 51			
V	$IP (\mathbf{V})$	9.86 ± 0.09	1.66 ± 0.14	–	1.04 ± 0.08	0.078	0.9950.995	5
	$\Delta v (\mathbf{V})$	290 ± 10	-298 ± 16	–	-46 ± 9			
VI	$IP (\mathbf{VI})$	10.22 ± 0.23	0.53 ± 0.20	1.70 ± 0.36	0.93 ± 0.08	0.078	0.9490.983	18
	$\Delta v (\mathbf{VI})$	-42 ± 43	-300 ± 43	-677 ± 122	-119 ± 25			
VIa	$IP (\mathbf{VIa})$	10.36 ± 0.25	0.53 ± 0.20	1.83 ± 0.36	1.00 ± 0.09	0.068	0.9380.982	17
	$\Delta v (\mathbf{VIa})$	-48 ± 41	-278 ± 45	-668 ± 118	-129 ± 25			
VII	$IP (\mathbf{VII})$	9.34 ± 0.04	1.26 ± 0.01	0.34 ± 0.01	0.38 ± 0.02	0.012	0.9990.999	5
	$\Delta v (\mathbf{VII})$	309 ± 13	-190 ± 2	-23 ± 6	-17 ± 7			
VIII	$IP (\mathbf{VIII})$	12.11 ± 0.46	1.93 ± 0.54	1.43 ± 0.22	1.49 ± 0.70	0.082	0.9780.998	7
	$\Delta v (\mathbf{VIII})$	15 ± 8	-38 ± 12	-287 ± 11	-26 ± 12			
IX	$IP (\mathbf{IX})$	9.26 ± 0.09	0.84 ± 0.18	0.94 ± 0.06	0.37 ± 0.15	0.125	0.9810.952	13
	$\Delta v (\mathbf{IX})$	50 ± 3	-50 ± 7	-40 ± 6	-8 ± 6			

^aSeries **Ia**, **IIIa**, **IVa**, and **VIa** were formed by excluding from series **II**, **III**, **IV**, and **VI** compounds NCPr-*i*, O=C(OMe)₂, O=PBr₃, and SPh₂ respectively. For H-complexes involving O=CX₂ and SX₂, the Δv values fit to equations of (10) type; therewith the coefficients p for series **III**, **IIIa**, **IV**, and **VIa** are equal respectively to 27 ± 12 , 33 ± 9 , 27 ± 7 , and 28 ± 7 .

Table 4. Inductive *Ind*, resonance *Res*, polarization *Pol*, and sterical $St(C-H) = p\Sigma E_s'$ contributions in the overall changes of *IP* and Δv under the influence of substituents X

Series no.	<i>Ind</i> (CR), %	<i>Res</i> (CR), %	<i>Pol</i> (CR), %	<i>Ind</i> (C-H), %	<i>Res</i> (C-H), %	<i>Pol</i> (C-H), %	<i>St</i> (C-H), %
I	41 ± 5	–	59 ± 5	74 ± 1	–	26 ± 1	–
Ia	42 ± 4	–	58 ± 5	75 ± 1	–	25 ± 1	–
II	24 ± 9	59 ± 10	17 ± 8	42 ± 2	54 ± 3	4 ± 2	–
III	44 ± 7	18 ± 8	38 ± 5	35 ± 3	29 ± 6	18 ± 10	18 ± 8
IIIa	48 ± 5	6 ± 5	46 ± 4	34 ± 2	22 ± 3	22 ± 7	22 ± 6
IV	42 ± 3	25 ± 4	33 ± 5	58 ± 5	28 ± 7	14 ± 7	–
IVa	42 ± 1	30 ± 2	28 ± 2	55 ± 6	34 ± 10	11 ± 9	–
V	46 ± 4	–	54 ± 4	78 ± 4	–	22 ± 4	–
VI	13 ± 5	31 ± 7	56 ± 5	25 ± 4	26 ± 5	23 ± 5	26 ± 7
VIa	14 ± 5	33 ± 6	53 ± 5	24 ± 4	26 ± 5	23 ± 4	27 ± 7
VII	58 ± 1	27 ± 1	15 ± 1	84 ± 1	10 ± 2	6 ± 3	–
VIII	31 ± 9	51 ± 8	18 ± 8	12 ± 4	82 ± 3	6 ± 3	–
IX	17 ± 4	72 ± 5	11 ± 4	41 ± 6	49 ± 7	10 ± 7	–

of substituents X, spoils the statistical indices of the correlation equations: the standard error of approximation S_Y grows, and the correlation factor r decreases. A similar impairment of the statistical characteristics is also observed for equations of (9) type for Δv of series **I**, **II**, **IV**, **V**, **VII–IX**.

In series **III** and **VI** in going from the three-parameter equations (9) to the four-parameter equations (10) the statistical quality improves: S_Y values decrease, and r grows.

$$\Delta v = \Delta v_H + k\Sigma\sigma_I + l\Sigma\sigma_R + m\Sigma\sigma_\alpha + p\Sigma E_S' \quad (10)$$

Therefore among all H-complexes we studied only in the complexes with the hydrogen bond $\text{PhO}-\text{H}\cdots\text{O}=\text{CX}_2$ and $\text{PhO}-\text{H}\cdots\text{O}=\text{SX}_2$ the sterical effect of substituents X statistically significantly affected the Δv values. The values of the sterical contributions $St(\text{C}-\text{H}) = p\Sigma E_S'$ alongside the contribution Ind , Res , and Pol are presented in Table 4.

It follows from Table 4 that in each series **I–IX** the contributions $Pol(\text{CR})$ are larger than $Pol(\text{C}-\text{H})$. These contributions are linearly interdependent (11).

$$Pol(\text{CR}) = 2.22 Pol(\text{C}-\text{H}), \quad (11)$$

$$S_a 0.26, S_Y 6, r 0.956, n 9.$$

The number of experimental points n for drawing the linear plot of (11) type by the least-squares procedure can be increased by two methods.

The first method consists in the change in the sampling size n for substituents X in series **I–IX**. As shown above [see condition (3)], at variation of n are changed the relative contributions Ind , Res , and Pol . In each series **I**, **III**, **IV**, and **VI** we excluded one compound mentioned in Table 3 and thus generated new series **Ia**, **IIIa**, **IVa**, and **VIa** (Tables 3 and 4). This trick permitted increasing the points number from 9 to 13.

The second method is increasing the number of points n from 13 to 14 taking into consideration the origin, point (0, 0). Its position corresponds to the limiting case when $Pol(\text{CR}) = Pol(\text{C}-\text{H}) = 0$.

At the present time we have no DX series where the conditions (1–3) are valid and the contributions $Pol(\text{CR})$ and $Pol(\text{C}-\text{H})$ are lacking. It is clear, that the characteristic feature of such series should be a large value of r in equation (2).

Let us consider some examples of H-complexes and radical cations where the substituents are removed to a considerable distance from the electron-deficient centers $\text{D}^{\delta+}$ and D^+ . For instance, in the H-complexes $\text{PhO}^{\delta-}-\text{H}\cdots\text{O}^{\delta+}=\text{P}(\text{C}_6\text{H}_4\text{X}-p)$ the contribution

$Pol(\text{C}-\text{H}) = 0$ [9]. Another example are the molecules $p\text{-NCC}_6\text{H}_4\text{X}$. In the IR spectra of the H-complexes $\text{PhO}^{\delta-}-\text{H}\cdots\text{N}^{\delta+}=\text{CC}_6\text{H}_4\text{X}-p$ at $X = \text{NMe}_2$, OEt , Me , H , Br , and NO_2 the Δv values equal 219, 188, 179, 172, 163, and 132 cm^{-1} respectively [29]. The ionization potentials corresponding to formation of radical cations $\text{N}^+\equiv\text{CC}_6\text{H}_4\text{X}-p$ at $X = \text{NH}_2$, Me , H , F , Cl , Br , and CN are equal respectively to 12.31, 12.70, 12.61, 12.78, 12.73, 12.77, and 12.98 eV [13]. Our treatment of these data showed that the values Δv and IP depended only on the inductive and resonance effects of the substituents X, whereas the contributions $Pol(\text{C}-\text{H})$ and $Pol(\text{CR})$ were lacking. These examples prove that the point with the coordinates (0, 0) on the plot of $Pol(\text{CR})$ as a function of $Pol(\text{C}-\text{H})$ must correspond not to a hypothetical but to a real series that meets the above shown conditions (1–3).

The calculations demonstrated that the values $Pol(\text{CR})$ and $Pol(\text{C}-\text{H})$ of series **I–IX**, **Ia**, **IIIa**, **IVa**, and **VIa** including the point (0, 0) fit to the linear plot (12), whose statistical qualities are somewhat better than those of the plot (11).

$$Pol(\text{CR}) = 2.22 Pol(\text{C}-\text{H}), \quad (12)$$

$$S_a 0.15, S_Y 5, r 0.973, n 14.$$

In order to elucidate the reason of the existence of the linear relationships (11) and (12) let us consider the energy of the polarization interaction in radical cations and H-complexes.

According to equation (2) in the general case the energy of the polarization interaction E_{es} is a function of three variables, q , α , and r . For radical cations D^+X and H-complexes $\text{PhO}^{\delta-}-\text{H}\cdots\text{D}^{\delta+}\text{X}$ equation (2) can be written as (13) and (14) respectively.

$$E_{es}(\text{CR}) = -q^2(\text{CR})\alpha(\text{CR})/[4r^4(\text{CR})] \quad (13)$$

$$E_{es}(\text{C}-\text{H}) = -q^2(\text{C}-\text{H})\alpha(\text{C}-\text{H})/[8066 \cdot 4r^4(\text{C}-\text{H})] \quad (14)$$

Here $q(\text{CR})$, $\alpha(\text{CR})$, and $r(\text{CR})$ are the charge on the D center, the polarizability of the substituents X, and the distance between the charge and the induced dipole in the radical cations, and $q(\text{C}-\text{H})$, $\alpha(\text{C}-\text{H})$, and $r(\text{C}-\text{H})$ are the same values in the H-complexes.

The factor 8066 was introduced into equation (14) to express the energy $E_{es}(\text{C}-\text{H})$ in eV as the energy $E_{es}(\text{CR})$ ($1 \text{ eV} = 8066 \text{ cm}^{-1}$).

$$\frac{E_{es}(\text{CR})}{E_{es}(\text{C}-\text{H})} = 8066 \frac{q^2(\text{CR})\alpha(\text{CR})r^4(\text{C}-\text{H})}{q^2(\text{C}-\text{H})\alpha(\text{C}-\text{H})r^4(\text{CR})} \quad (15)$$

Due to the validity of conditions (1–3) the expression (15) for each of the narrow series **I–IX** DX ($\text{D} = \text{const}$)

is considerably simplified. The meeting of these conditions means that at $D = \text{const}$ both radical cations and H-complexes contain the same set of substituents X (for instance, in series **II**

X = H, Me, OMe, F, Cl). Therefore in every series the range of changes in the polarizability α of the substituents X in radical cations and H-complexes are equal [expression (16)].

$$\alpha(\text{CR}) = \alpha(\text{C-H}) \quad (16)$$

At $D = \text{const}$ the distance r between the charge and the induced dipole also may be regarded as equal within a good approximation [expression (17)].

$$r(\text{CR}) = r(\text{C-H}) \quad (17)$$

It follows, e.g., from [30] where has been found that the reduction in the interatomic distances C=C and C-X in going from various neutral molecules $\text{H}_2\text{C}=\text{CHX}$ to cations $\text{H}_2\text{C}=\text{C}^+\text{X}$ occurs in the range from 4 to 10%.

$$E_{es}(\text{CR}) = 8066 \frac{q^2(\text{CR})}{q^2(\text{C-H})} E_{es}(\text{C-H}) \quad (18)$$

Taking into consideration (16) and (17) equation (15) transforms into (18).

Compare the expressions (12) and (18). We mentioned before that the polarization effect may be characterized either by its energy E_{es} or by the value of contribution Pol . It is therefore presumable that the values $E_{es}(\text{CR})$ and $E_{es}(\text{C-H})$ like those $Pol(\text{CR})$ and $Pol(\text{C-H})$ are proportional. Consequently the proportionality factor $q^2(\text{CR})/q^2(\text{C-H})$ in equation (18) is the same for all series DX, i.e., it is independent of the type of the donor center D. It follows from the constancy of the charge ratio $q^2(\text{CR})/q^2(\text{C-H})$ in radical cations and H-complexes that for the studied series **I-IX**, **Ia**, **IIIa**, **IVa**, and **VIa** (in other words independent of the D type and sampling size n) the radical cations D^+X and the corresponding H-complexes $\text{PhO}^\delta-\text{H}\cdots\text{DX}^{\delta+}$ apparently hardly differ in the degree of delocalization of the positive charge q .

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