Effect of substituents on the first ionization potentials of aromatic and heteroaromatic compounds. The $\sigma_R{}^+$ resonance parameters of Si-, Ge-, Sn-, and Pb-containing fragments

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The first vertical ionization potentials (*IP*) of monosubstituted benzenes, hexafluorobenzenes, naphthalenes, anthracenes, furans, thiophenes, and selenophenes and the second *IP* of monosubstituted tellurophenes are related to the inductive, resonance, and polarization parameters of substituents by dependences of the type $IP = a + b\sigma_I + c\sigma_R{}^+ + d\sigma_\alpha$. The contribution of polarizability effect, $d\sigma_\alpha$, to the *IP* value is determined by the degree of delocalization of the positive charge in radical cations formed upon photoionization of the compounds studied. The $\sigma_R{}^+$ resonance parameters of nineteen Si-, Ge-, Sn-, and Pb-containing substituents in naphthalene, furan, and thiophene series were calculated.

Key words: aromatic and heteroaromatic compounds, ionization potentials; polarizability of substituents; conjugation; substituents containing Group 14 elements.

In physical organometallic chemistry, the conjugation between an indicator center R_π (Ph, HC≡C, *etc.*) and substituents ER_3, CH_2ER_3 (E = Si, Ge, Sn, Pb; R are organic groups) in molecules $R_\pi ER_3$ and $R_\pi CH_2ER_3$ is quantitatively characterized by non-universal (*i.e.*, depending on both the type of R_π and charges on its atoms) resonance parameters σ_R (see, *e.g.*, Refs. 1—3). For model systems (R_π = Ph), the $\sigma_R{}^+$ parameters characterizing resonance properties of substituents ER_3 and CH_2ER_3 towards the R_π fragment on which a large positive charge (~0.1 e)[1] is induced under experimental conditions are known.[2—4] Recently, we calculated their values for R_π = $H_2C{=}CH$ and HC≡C when analyzing the ionization potentials (*IP*) of ethylene[2] and acetylene[3] derivatives. It was shown[2,3] that *IP* values depend on three effects of substituents, *viz.*, the inductive effect, conjugation, and polarizability, whose relative contribution is determined by the type of R_π, and that even an *a priori* qualitative estimate can hardly be made. The polarizability effect has long remained poorly studied, despite the fact that it is impossible to perform correct calculations of $\sigma_R{}^+$ values without taking into account the inductive and polarizability effects.[2,3]

The aim of this work was to establish correlations between the vertical *IP* of a number of aromatic and heteroaromatic compounds and the effects of substituents; to calculate the $\sigma_R{}^+$ parameters of Si-, Ge-, Sn-, and Pb-containing substituents in naphthalene, furan, and thiophene derivatives; and to compare them with the values of $\sigma_R{}^+$ parameters for the standard benzene series.

Calculation procedure

In this work, we performed a comparative analysis of *IP* corresponding to the π-MOs of benzene, hexafluorobenzene, naphthalene (1- and 2-substituted), anthracene (9-substituted), furan, thiophene, selenophene, and tellurophene (2-substituted) derivatives (Table 1). To study the electronic effects of substituents on the *IP*, we chose such π-MOs whose energies depend on both inductive and resonance effects due to symmetry factors. Below are listed the notations of *IP*, the MO symmetry, and the number of the band in the photoelectron spectrum (the last two items are given in parentheses) according to the data presented in Table 1: IP^{FB} (b_1; the HOMO for compounds **2**, **7—10**, **14—16**, **18**, and **20**; the second band for compound **1**; and e_{1g} for compound **13**), IP^N (π_6, HOMO), IP^{AN} (π_8 (b_1), HOMO), IP^F (π_3 ($1a_2$), HOMO), IP^T (π_3 ($1a_2$), HOMO), IP^S (π_3 ($1a_2$), HOMO), IP^{TPh} (π_3 ($1a_2$), the second band).

Previously, taking monosubstituted benzenes,[3] ethylenes,[2] and acetylenes[3] $R_\pi X$ as examples, we have established that *IP* are related to the effects of substituents by relationships of the type

$$IP = IP_0 + a\sigma_I + b\sigma_R{}^+ + c\sigma_\alpha, \qquad (1)$$

where IP_0 is the *IP* value for an unsubstituted $R_\pi H$ molecule, and σ_I, $\sigma_R{}^+$, and σ_α are the parameters characterizing respectively the inductive, resonance, and polarization effects of substituents X. The values of coefficients *a*, *b*, and *c* depend on the type of indicator center R_π (Ph, $H_2C{=}CH$, HC≡C).

Having written Eq. (1) as

$$IP = IP_0 + In + Res + P, \qquad (2)$$

we can evaluate (in eV) the inductive ($In = a\sigma_I$), resonance ($Res = b\sigma_R{}^+$), and polarization ($P = c\sigma_\alpha$) contributions of

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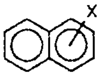
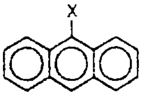
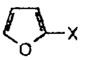
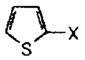
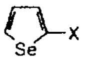
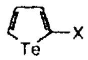
Table 1. Ionization potentials (IP/eV) and σ-constants of organic substituents X

Compound	X	IP^{FB},	$IP^{N(1)}$, $IP^{N(2)}$,	IP^{AN},	IP^{F},	IP^{T},	IP^{S},	IP^{TPh},	σ_I	σ_R^+	σ_α
		C_6F_5X									
1	H	10.10	8.15	7.43	8.89	8.87	8.96	8.88	0	0	0
2	Me	9.81	7.85, 7.93	7.24	8.37	8.43	8.50	8.43	−0.05	−0.26	−0.35
3	Et	—	—, 7.85	—	—	—	—	—	−0.05	−0.25	−0.49
4	Bu^t	—	—	7.13	8.19	8.32	—	—	−0.07	−0.19	−0.75
5	CH_2COOH	—	7.99, 8.05	—	—	—	—	—	+0.10	−0.11	−0.50
6	CH_2Cl	—	—	—	—	8.89	—	—	+0.13	−0.14	−0.54
7	NH_2	8.90	7.48, 7.55	—	—	—	—	—	+0.08	−1.38	−0.16
8	NHMe	8.65	—	—	—	—	—	—	−0.03	−1.78	−0.30
9	NMe_2	8.48	—	—	—	—	—	—	+0.15	−1.85	−0.44
10	OH	9.37	—	—	—	—	—	—	+0.33	−1.25	−0.03
11	OMe	—	7.70, 7.82	7.21	—	8.18	—	—	+0.29	−1.07	−0.17
12	SMe	—	—	—	—	7.95	—	—	+0.23	−0.83	−0.68
13	F	10.20	8.15, 8.23	7.46	—	—	—	—	+0.45	−0.52	+0.13
14	Cl	9.90	8.13, 8.11	7.45	—	8.89	8.80	8.89	+0.42	−0.31	−0.43
15	Br	9.80	8.09, —	7.48	—	8.82	8.66	8.84	+0.45	−0.30	−0.59
16	CN	10.45	8.59, 8.56	7.80	9.47	—	9.40	—	+0.51	+0.15	−0.46
17	CHO	—	8.33, —	—	—	9.37	9.25	—	+0.33	+0.40	−0.46
18	COOH	10.20	8.29, 8.26	—	9.16	9.14	9.19	9.15	+0.34	+0.08	−0.34
19	COOMe	—	—	—	9.00	8.98	9.05	9.00	+0.34	+0.14	−0.49
20	NO_2	10.66	8.59, 8.63	7.88	9.75	9.73	9.57	—	+0.65	+0.14	−0.26

Note. The IP^{FB} values were taken from Ref. 5 (for the IP^{FB} value for compound **2**, see Ref. 6). The IP^{N} values were taken from Ref. 7, the first and second figures correspond to 1-substituted ($IP^{N(1)}$) and 2-substituted ($IP^{N(2)}$) naphthalenes, respectively. The IP^{AN} values were taken from Ref. 8. The IP^{F} values were taken from Ref. 9, except for the IP^{F} value for compound **4** taken from Ref. 10. The IP^{T} were taken from Ref. 9, except for those for compounds **4** and **11** taken from Refs. 11, 12. The IP^{T} value for compound **12** was calculated from the charge transfer frequency (16500 cm^{-1}) in the UV spectra of complexes with tetracyanoethylene following the previously described procedure.[13] The values for compounds **15**—**17** were taken from Ref. 12, and those for compounds **18** and **19** were taken from Ref. 9. For compounds **1**, **2**, **14**, and **20** averaged IP^{S} values taken from Refs. 9, 12 are given. The IP^{TF} values were taken from Ref. 9. The σ_I, σ_R^+, and σ_α were taken from Refs. 2, 14.

substituents to the change in IP at R_π = const. These contributions can be comparable.[3]

From relationships (1) and (2) it follows that the Koopmans theorem[8] $IP_I = -E_{HOMO}$ is a rather rough approximation for molecules $R_\pi X$.[2,3] In fact, first, the P contribution to the E_{HOMO} energy is ignored. Second, according to the results of recent quantum-chemical calculations,[15] the resonance interactions between R_π (Ph, $H_2C=CH$, and $HC\equiv C$) and X in neutral isolated molecules $R_\pi X$ are characterized by the $\sigma_R{}^0$ constants rather than by the $\sigma_R{}^+$ constants.

Let us consider the second and third terms in Eq. (1) in detail.

Detachment of an electron from the π-MOs mentioned above upon photoionization of neutral molecules $R_\pi X$ (see Table 1) in the gas phase

$$R_\pi X \xrightarrow{h\nu} R_\pi X^{+\cdot} + e^- \qquad (3)$$

results in the formation of radical cations $R_\pi X^{+\cdot}$ carrying a positive charge on R_π (aromatic or heteroaromatic ring). Therefore an adequate description of resonance interactions in radical cations $R_\pi X^{+\cdot}$ (R_π = Ph, $H_2C=CH$, $HC\equiv C$)[2,3] can be achieved only by using $\sigma_R{}^+$ parameters rather than $\sigma_R{}^0$ parameters in Eq. (1).[2,3,16] Below we will show that this is also valid for compounds listed in Table 1.

The polarization term $P = c\sigma_\alpha$ in Eq. (1) describes the effect of electrostatic attraction between the positive charge (q) of radical cation $R_\pi X^{+\cdot}$ and the dipole moment induced by this charge in the polarizable substituent X [14,17] on the IP of molecules $R_\pi X$. In the Hammett—Taft correlation equations, stabilization of the charge q due to polarizability of substituents X is quantitatively characterized by constants σ_α.[14,17] The σ_α values were calculated for most organic substituents X by *ab initio* quantum-chemical methods[17] and are widely used in the studies of ionic gas-phase reactions.[17] The use of σ_α in the analysis of the effect of substituents on IP has only just begun.[2,3]

The following relationship[17] is useful[3] for estimating the dependence of the polarization contribution on the degree of delocalization of charge q in radical cations $R_\pi X^{+\cdot}$ at a qualitative level:

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

where E_{st} is the energy of electrostatic stabilization of charge q, α is the polarizability of substituent X, ε is the dielectric constant, and r is the distance between the charge and the polarizability center of substituent X.

The correlation equations discussed below were calculated using the standard STATGRAPHICS 3.0 program package on a PC/AT 286 computer. The data were processed by the least squares method at a confidence level of 95%.

Results and Discussion

The following relationships are valid for monosubstituted benzenes[3] (their ionization potentials are denoted as IP^{B}) and eight series of compounds studied in this work:

$$IP^{B} = 9.25 + 1.00\sigma_{I} + 0.89\sigma_{R}^{+} + 0.42\sigma_{\alpha}, \quad (5)$$
$S_a = 0.08$, $S_b = 0.13$, $S_c = 0.04$, $S_d = 0.13$, $S_Y = 0.12$, $r = 0.980$, $n = 26$,

$$IP^{FB} = 10.17 + 0.72\sigma_{I} + 0.81\sigma_{R}^{+} + 0.63\sigma_{\alpha}, \quad (6)$$
$S_a = 0.07$, $S_b = 0.14$, $S_c = 0.04$, $S_d = 0.14$, $S_Y = 0.09$, $r = 0.991$, $n = 12$,

$$IP^{N(1)} = 8.11 + 0.71\sigma_{I} + 0.50\sigma_{R}^{+} + 0.25\sigma_{\alpha}, \quad (7)$$
$S_a = 0.06$, $S_b = 0.11$, $S_c = 0.05$, $S_d = 0.11$, $S_Y = 0.07$, $r = 0.974$, $n = 12$,

$$IP^{N(2)} = 8.14 + 0.71\sigma_{I} + 0.46\sigma_{R}^{+} + 0.24\sigma_{\alpha}, \quad (8)$$
$S_a = 0.05$, $S_b = 0.08$, $S_c = 0.04$, $S_d = 0.10$, $S_Y = 0.06$, $r = 0.982$, $n = 11$,

$$IP^{AN} = 7.42 + 0.67\sigma_{I} + 0.41\sigma_{R}^{+} + 0.17\sigma_{\alpha}, \quad (9)$$
$S_a = 0.05$, $S_b = 0.08$, $S_c = 0.06$, $S_d = 0.08$, $S_Y = 0.06$, $r = 0.973$, $n = 9$,

$$IP^{F} = 8.85 + 1.58\sigma_{I} + 0.38\sigma_{R}^{+} + 0.70\sigma_{\alpha}, \quad (10)$$
$S_a = 0.08$, $S_b = 0.26$, $S_c = 0.45$, $S_d = 0.17$, $S_Y = 0.09$, $r = 0.987$, $n = 7$,

$$IP^{T} = 8.93 + 1.01\sigma_{I} + 0.93\sigma_{R}^{+} + 0.55\sigma_{\alpha}, \quad (11)$$
$S_a = 0.10$, $S_b = 0.18$, $S_c = 0.09$, $S_d = 0.18$, $S_Y = 0.13$, $r = 0.967$, $n = 12$,

$$IP^{S} = 9.00 + 1.03\sigma_{I} + 0.86\sigma_{R}^{+} + 0.82\sigma_{\alpha}, \quad (12)$$
$S_a = 0.07$, $S_b = 0.15$, $S_c = 0.12$, $S_d = 0.19$, $S_Y = 0.08$, $r = 0.974$, $n = 9$,

$$IP^{TPh} = 8.89 + 1.23\sigma_{I} + 0.58\sigma_{R}^{+} + 0.75\sigma_{\alpha}, \quad (13)$$
$S_a = 0.04$, $S_b = 0.14$, $S_c = 0.10$, $S_d = 0.16$, $S_Y = 0.04$, $r = 0.983$, $n = 6$.

Taking into account that $\sigma^{+}_{p} = \sigma_{I} + \sigma_{R}^{+}$, one can expect that the IP will depend on only two variables (σ_{p}^{+} and σ_{α}). Actually, these dependences for, *e.g.*, naphthalene, furan, and thiophene series, have the form

$$IP^{N(1)} = 8.17 + 0.55\sigma_{p}^{+} + 0.27\sigma_{\alpha}, \quad (14)$$
$S_a = 0.04$, $S_b = 0.04$, $S_c = 0.12$, $S_Y = 0.08$, $r = 0.969$, $n = 12$,

$$IP^{F} = 8.91 + 1.15\sigma_{p}^{+} + 0.62\sigma_{\alpha}, \quad (15)$$
$S_a = 0.09$, $S_b = 0.10$, $S_c = 0.20$, $S_Y = 0.11$, $r = 0.980$, $n = 7$,

$$IP^{T} = 8.95 + 0.95\sigma_{p}^{+} + 0.55\sigma_{\alpha}, \quad (16)$$
$S_a = 0.08$, $S_b = 0.07$, $S_c = 0.17$, $S_Y = 0.12$, $r = 0.970$, $n = 12$,

Equations (5)—(13) were used to calculate the contributions *In*, *Res*, and *P* (relationship (2)) to IP for nine series of $R_{\pi}X$, including R_{π} = Ph. In Table 2, three types of contributions *In*, *Res*, and *P* are listed for each R_{π}: (1) the *In*(X), *Res*(X), and *P*(X) values are the contributions to the IP calculated upon varying the σ_{I}, σ_{R}^{+}, and σ_{α} parameters of substituents X from minimum to maximum values (as follows from Table 1, the sets of substituents X in the nine series of compounds $R_{\pi}X$ are different; therefore it is impossible to obtain reliable data on the dependence of these contributions on R_{π} by comparing the magnitudes of their contributions *In*(X), *Res*(X), and *P*(X)) in the series, (2) the *In*(Me), *Res*(Me), and *P*(Me) values are the contributions to IP arising on going from unsubstituted compounds $R_{\pi}H$ to corresponding methyl derivatives $R_{\pi}Me$ (*i.e.*, due to the introduction of Me substituents), and (3) this type of contribution is similar to the second type; however, it was calculated for *tert*-butyl derivatives.

Let us analyze briefly the second and third types of contributions (see Table 2).

At R_{π} = const, the *P* contribution increases on going from X = Me to X = Bu^{t}, since in this case the value of the parameter σ_{α} increases (see Table 1). For all $R_{\pi}Bu^{t}$ molecules, the *P* contribution to the change in IP is larger than the *In* and *Res* contributions. For $R_{\pi}Me$ and $R_{\pi}Bu^{t}$ molecules, the ratio of contributions *Res* and *P* depends on the type of R_{π}. At X = const (Me or Bu^{t}), this ratio for aromatic compounds (I^{B}, $I^{N(1)}$, $I^{N(2)}$, I^{AN}) changes only slightly, whereas for heteroaromatic compounds (I^{F}, I^{T}, I^{S}, I^{TPh}) it depends strongly on the type of R_{π}. The *P*(Me) and *P*(Bu^{t}) values increase substan-

Table 2. Values of *In*, *Res*, and *P* contributions (%) to total changes in the ionization potentials IP of molecules $R_{\pi}X$ caused by effects of organic substituents X

IP type	*In*(X)	*Res*(X)	*P*(X)	*In*(Me)	*Res*(Me)	*P*(Me)	*In*(Bu^{t})	*Res*(Bu^{t})	*P*(Bu^{t})
IP^{B}	23	65	12	12	53	35	13	30	57
IP^{FB}	20	62	18	8	45	47	8	22	70
$IP^{N(1)}$	32	57	11	15	50	35	15	29	56
$IP^{N(2)}$	37	52	11	17	50	33	16	28	56
IP^{AN}	43	44	13	15	55	30	19	31	50
IP^{F}	62	9	29	19	24	57	15	10	75
IP^{T}	29	55	16	10	50	40	11	27	62
IP^{S}	40	34	26	9	39	52	8	19	73
IP^{TPh}	46	21	33	13	32	55	12	14	74

tially on going from aromatic derivatives to heteroaromatic derivatives.

Such a type of dependence of the *P* contributions on the type of R_π is determined to a great extent by conditions of delocalization of the positive charge in radical cations $R_\pi Me^{+\cdot}$ and $R_\pi(Bu^t)^{+\cdot}$. There is a cyclic conjugation of π-electrons in neutral aromatic molecules (benzene, naphthalene, and anthracene derivatives) that weakens on going to heteroaromatic systems (furan, thiophene, selenophene, and tellurophene derivatives) and is,[18] judging by different criteria for aromaticity, strongly dependent on the type of R_π.

Let us assume that, as has been reported previously,[19] the degree of delocalization of the unpaired electron and the positive charge *q* over the skeleton of a radical cation is determined by the electronic structure of initial neutral molecules. Then aromatic radical cations must differ from heteroaromatic radical cations in a higher degree of delocalization of the charge *q* and, hence, from the formal point of view, in larger distance *r* between the charge *q* and the substituent X in $R_\pi X^{+\cdot}$. The latter, taking into account relationship (4), must result in a decrease in E_{st} and in the *P* contribution in relationship (2). This is confirmed by the data in Table 2.

Extending the analogy between the properties of neutral compounds and radical cations, we compared the *P*(Me) and *P*(Bu^t) values with the structural aromaticity indices (i)[18] of heteroaromatic compounds (the *i* values for benzene, furan, thiophene, selenophene, and tellurophene are 100, 43, 66, 59, and 48%, respectively) and obtained the following relationships:

$$P(\mathrm{Me}) = 73 - 0.40i, \quad (17)$$
$$S_a = 6,\ S_b = 0.1,\ S_Y = 4,\ r = 0.921,\ n = 5,$$

$$P(\mathrm{Bu^t}) = 83 - 0.33i, \quad (18)$$
$$S_a = 5,\ S_b = 0.08,\ S_Y = 4,\ r = 0.920,\ n = 5.$$

Hence, the degree of aromaticity of neutral unsubstituted heteroaromatic molecules $R_\pi H$ strongly affects the degree of delocalization of the positive charge over the skeleton of corresponding radical cations $R_\pi Me^{+\cdot}$ and $R_\pi(Bu^t)^{+\cdot}$.

In this connection, the "anomalously" high *P*(Me) and *P*(Bu^t) values in hexafluorobenzene derivatives (see Table 2) become unclear. Due to the effects of counterconjugation,[5] the conjugation of substituents X with the π-system in compounds C_6F_5X (their molecules contain five other substituents of the +M type in addition to substituent X) is appreciably weaker than that in compounds PhX. (For the effect of counterconjugation on the *IP* of ethylene derivatives, see Ref. 2.) For this reason, the *Res*(Me) and *Res*(Bu^t) values in hexafluorobenzene derivatives decrease, whereas the *P*(Me) and *P*(Bu^t) contributions to *IP* increase.

All of the said above serves as grounds for the correct evaluation of the σ_R^+ parameters of substituents Y (ER_3, CH_2ER_3) in $R_\pi Y$ molecules. Information on *IP* of compounds $R_\pi Y$ is scarce (Table 3). The σ_R^+ parameters of substituents Y bonded to naphthalene, furan, and thiophene rings were calculated using Eqs. (14)–(16). From the data in Table 3 it follows that the parameters $\sigma_R^+(N)$, $\sigma_R^+(F)$, and $\sigma_R^+(T)$ appreciably differ from standard $\sigma_R^+(B)$ values in the series of benzene derivatives; at the same time, the former parameters are related to the latter ones by the following linear dependences:

$$\sigma_R^+(N) = 1.33\sigma_R^+(B) + 0.05, \quad (19)$$
$$S_a = 0.11,\ S_b = 0.04,\ S_Y = 0.08,\ r = 0.984,\ n = 7,$$

$$\sigma_R^+(F) = 0.87\sigma_R^+(B) + 0.16, \quad (20)$$
$$S_a = 0.07,\ S_b = 0.02,\ S_Y = 0.04,\ r = 0.983,\ n = 7,$$

$$\sigma_R^+(T) = 0.94\sigma_R^+(B) + 0.18, \quad (21)$$
$$S_a = 0.14,\ S_b = 0.04,\ S_Y = 0.05,\ r = 0.968,\ n = 5,$$

$$\sigma_R^+(T) = 1.17\sigma_R^+(F) + 0.02, \quad (22)$$
$$S_a = 0.18,\ S_b = 0.03,\ S_Y = 0.06,\ r = 0.976,\ n = 4,$$

The analysis of σ_R^+ values (see Table 3) and relationships (19)—(22) between them must be based on the fundamental distinction between the mechanisms of conjugation of organic (X) and organoelement substituents with the π-system of indicator center R_π.

In molecules $R_\pi X$, the organic substituents X are resonance acceptors of the −M type (X = CHO, NO_2, *etc.*) or resonance donors of the +M type (X = F, OH, *etc.*).

In molecules $R_\pi ER_3$, the substituents ER_3 are simultaneously resonance acceptors and resonance donors.[1] According to modern concepts,[1] the acceptor −M-effect (d,π-conjugation, *i.e.*, the joint participation of *n*d orbitals of atoms E and antibonding σ^*-orbitals of the bonds formed by E atoms with R, in the conjugation with the π-system of the R_π fragment) weakens in the order Si > Ge > Sn > Pb. The donor +M-effect (hyperconjugation of the s,π- and s,π^*-types, *i.e.*, mixing of σ(E—R)-orbitals of the substituent with π^*-orbitals of the R_π fragment) increases[1] in the order C < Si < Ge < Sn < Pb. Only hyperconjugation is observed in compounds $R_\pi CH_2ER_3$.

The positive and negative values of the parameters σ_R^+ listed in Table 3 indicate the dominating role of d,π-conjugation and hyperconjugation, respectively, in the overall resonance effect of substituents ER_3 toward the R_π fragment.

From analysis of relationship (19) and comparison of magnitudes and signs of parameters $\sigma_R^+(B)$ and $\sigma_R^+(N)$, one can conclude that both d,π-conjugation (the acceptor effect) and hyperconjugation (the donor effect) in naphthalene derivatives are stronger than those in benzene derivatives. d,π-Conjugation and hyperconjugation in ethylene[2] and acetylene[3] organoelement derivatives are also stronger than in benzene derivatives.

There is a distinctive feature of conjugation in furan and thiophene derivatives. From relationships (20)—(22) and analysis of σ_R^+ values (see Table 3) it follows that the positive σ_R^+ values increase appreciably, whereas the negative σ_R^+ values decrease on going from R_π =

Table 3. Resonance parameters of organoelement substituents Y bonded to naphthalene ($\sigma_R{}^+$(N)), furan ($\sigma_R{}^+$(F)), and thiophene ($\sigma_R{}^+$(T)) rings

Y	$IP^{N(1)}$ [a]	IP^F	IP^T	σ_I	σ_α	$\sigma_R{}^+$(B)	$\sigma_R{}^+$(N)	$\sigma_R{}^+$(F)	$\sigma_R{}^+$(T)
		eV							
SiH_3	8.02	8.75[b]	—	−0.04	−0.59	0.03	0.06	0.22	—
$SiHMe_2$	—	8.62[c]	—	−0.12	−0.68	0.02	—	0.23	—
$SiMe_3$	7.92	8.48[d]	8.64[e]	−0.15	−0.72	0.02	0.04	0.17	0.25
$Si(OEt)_3$	—	8.66[c]	—	−0.10	−0.63	0.11	—	0.22	—
$GeMe_3$	7.88	8.47[f]	8.52[g]	−0.11	−0.60	−0.10	−0.13	0.05	0.01
$SnMe_3$	7.87	8.33[h]	8.49[h]	−0.13	−0.60	−0.21	−0.12	−0.05	−0.01
$PbMe_3$	—	—	8.46[i]	−0.12	−0.60	−0.26	—	—	−0.05
CH_2SiMe_3	7.67	8.15[h]	8.26[h]	−0.05	−0.66	−0.49	−0.53	−0.25	−0.27
CH_2GeMe_3	7.61	—	—	−0.04	−0.61	−0.59	−0.69	—	—
CH_2SnMe_3	7.40	—	—	−0.05	−0.61	−0.76	−1.06	—	—

[a] The *IP* values were calculated from charge transfer frequencies (ν_{CT}) in the UV spectra complexes with (CTC)[20] following the previously described procedure.[13]

[b] Averaged over the *IP* value taken from Ref. 21 and that calculated from ν_{CT} (20800 cm^{-1}) in the UV spectra of CTC following the previously described procedure.[22]

[c] Data taken from Ref. 21.

[d] Averaged over data taken from Refs. 10, 21.

[e] Averaged over data taken from Refs. 11, 23.

[f] Calculated from ν_{CT} (20000 cm^{-1}) in the UV spectra of CTC following the previously described procedure.[22]

[g] Calculated from ν_{CT} (20300 cm^{-1})[24] in the UV spectra of CTC following the previously described procedure.[13]

[h] Data taken from Ref. 23.

[i] Calculated from ν_{CT} (19900 cm^{-1})[24] in the UV spectra of CTC following the previously described procedure.[13]

phenyl to R_π = 2-furyl and 2-thienyl. Hence, d,π-conjugation in furan and thiophene derivatives is stronger while hyperconjugation is weaker than those in benzene derivatives.

Specific features of conjugation of the furan and thiophene heteroaromatic systems with substituents ER_3 and CH_2ER_3 is likely predetermined[25] by the properties of the ground electron state of neutral molecules containing organic substituents X. Thus, *ab initio* quantum-chemical calculations of compounds $R_\pi X$ (R_π = phenyl, 2-furyl, 2-thienyl) made it possible to divide indicator centers R_π by their conjugation with X. If X is a −M resonance acceptor (CHO, NO_2), then donor properties of the R_π fragment toward X change in the order 2-thienyl > 2-furyl > phenyl.[25] From the analysis of the $\sigma_R{}^+$ values (see Table 3) one can conclude that donor properties of the R_π fragment toward ER_3 substituents of the −M type change in the same order due to the fact that d,π-conjugation dominates in certain $R_\pi ER_3$ molecules over hyperconjugation.

If X is a +M resonance donor (F, OH), then acceptor properties of the R_π fragment toward X change in the order phenyl > 2-thienyl > 2-furyl.[25] According to these regularities and to the values of the $\sigma_R{}^+$ parameters (see Table 3), the substituents ER_3 and CH_2SiMe_3 are the strongest resonance +M donors toward R_π = phenyl; these properties weaken on going from 2-thienyl- and 2-furyl derivatives.

References

1. A. N. Egorochkin, *Usp. Khim.*, 1992, **61**, 1092 [*Russ. Chem. Rev.*, 1992, **61**, 600 (Engl. Transl.)].
2. A. N. Egorochkin, S. E. Skobeleva, and T. G. Mushtina, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1626 [*Russ. Chem. Bull.*, 1997, **46**, 1549 (Engl. Transl.)].
3. A. N. Egorochkin, S. E. Skobeleva, and T. G. Mushtina, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1481 [*Russ. Chem. Bull.*, 1998, **47**, 1436 (Engl. Transl.)].
4. A. N. Egorochkin and G. A. Razuvaev, *Usp. Khim.*, 1987, **56**, 1480 [*Russ. Chem. Rev.*, 1987, **56**, 846 (Engl. Transl.)].
5. G. G. Furin, A. V. Zibarev, L. N. Mazalov, and V. D. Yumatov, *Elektronnaya struktura ftororganicheskikh soedinenii* [*Electronic Structure of Fluoroorganic Compounds*], Nauka, Novosibirsk, 1988 (in Russian).
6. B. C. Trudell and S. J. W. Price, *Canad. J. Chem.*, 1979, **57**, 2256.
7. L. Klasinc, B. Kovac, and H. Gusten, *Pure Appl. Chem.*, 1983, **55**, 289.
8. V. I. Vovna, *Elektronnaya struktura organicheskikh soedinenii* [*Electronic Structure of Organic Compounds*], Nauka, Moscow, 1991 (in Russian).
9. F. Fringuelli, G. Marino, A. Taticchi, G. Distefano, F. P. Colonna, and S. Pignataro, *J. Chem. Soc., Perkin Trans. 2*, 1976, 276.
10. T. Veszpremi, L. Nyulaszi, and J. Nagy, *J. Organomet. Chem.*, 1987, **331**, 175.
11. T. Veszpremi, Y. Harada, K. Ohno, and H. Mutoh, *J. Organomet. Chem.*, 1983, **252**, 121.

12. V. I. Nefedov and V. I. Vovna, *Elektronnaya struktura organicheskikh i elementoorganicheskikh soedinenii* [*Electronic Structure of Organic and Organoelement Compounds*], Nauka, Moscow, 1989 (in Russian).
13. A. N. Egorochkin, M. A. Lopatin, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1988, **299**, 909 [*Dokl. Chem.*, 1988 (Engl. Transl.)].
14. C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
15. S. Marriott and R. D. Topsom, *J. Mol. Struct.*, 1984, **106**, 277.
16. A. N. Egorochkin, S. E. Skobeleva, and T. G. Mushtina, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 70 [*Russ. Chem. Bull.*, 1997, **46**, 65 (Engl. Transl.)].
17. R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.*, 1987, **16**, 1.
18. C. W. Bird, *Tetrahedron*, 1985, **41**, 1409.
19. V. D. Pokhodenko, L. S. Degtyarev, V. G. Koshechko, and V. S. Kuts, *Problemy khimii svobodnykh radikalov* [*Problems of Free Radical Chemistry*], Naukova dumka, Kiev, 1984 (in Russian).
20. C. G. Pitt, *J. Organomet. Chem.*, 1973, **61**, 49.
21. B. C. Zykov, N. P. Erchak, V. I. Khvostenko, E. Lukevitzs, V. F. Matorykina, and N. L. Asfandiarov, *J. Organomet. Chem.*, 1983, **253**, 301.
22. A. N. Egorochkin, M. A. Lopatin, G. A. Razuvaev, N. P. Erchak, L. M. Ignatovich, and E. Ya. Lukevits, *Dokl. Akad. Nauk SSSR*, 1988, **298**, 895 [*Dokl. Chem.*, 1988 (Engl. Transl.)].
23. A. Modelli, G. Distefano, D. Jones, and G. Seconi, *J. Electron Spectrosc. and Related Phenom.*, 1983, **31**, 63.
24. M. A. Lopatin, V. A. Kuznetsov, A. N. Egorochkin, O. A. Pudova, N. P. Erchak, and E. Ya. Lukevits, *Dokl. Akad. Nauk SSSR*, 1979, **246**, 379 [*Dokl. Chem.*, 1979 (Engl. Transl.)].
25. J. Kao and L. Radom, *J. Am. Chem. Soc.*, 1979, **101**, 311.

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