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Conjugation in radical cations of benzene, ethylene, and acetylene derivatives. Nonuniversality of the resonance parameters of group 14 organoelement substituents

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The first vertical ionization potentials I_1 of molecules $R_\pi X$ (X = Ph, $H_2C=CH$, and $HC\equiv C$) depend on the joint influence of the inductive, resonance, and polarizability effects of substituents X, which are characterized by parameters σ_I, σ_R^+, and σ_α, respectively. The mechanism of conjugation in radical cations formed upon ionization of $R_\pi X$ is changed as compared to neutral $R_\pi X$ molecules, while the substituent X becomes polarized. The conjugation and polarizability effects are strenthened in the sequence Ph < $H_2C=CH$ < $HC\equiv C$ as R_π changes from Ph to $H_2C=CH$ and $HC\equiv C$. The σ_R^+ parameters of Si-, Ge-, and Sn-containing substituents X are dependent on the type of R_π but are connected by linear dependences in the series of benzene, ethylene, and acetylene derivatives.

Key words: ionization potential, radical cations, conjugation, polarizability, group 14 substituents, non-universality of resonance parameters.

The mechanism of conjugation of organoelement substituents MR_3 (M = Si, Ge, Sn, and Pb; R are organic radicals) with indicator centers R_π (Ph, $H_2C=CH$, $HC\equiv C$, furyl, thienyl, *etc.*) in compounds $R_\pi MR_3$ is more complex than that in organic derivatives $R_\pi R$.[1] The substituent MR_3 exhibits simultaneously acceptor (d,π-conjugation, *i.e.*, the interaction of *n*d orbitals of M and σ*-orbitals of the M—C bond with R_π) and donor (σ,π-conjugation, *i.e.*, the interaction of σ-orbitals of the M—C bond with R_π) properties toward the R_π fragment. Only σ,π-conjugation occurs in compounds $R_\pi CH_2MR_3$.[1] The quantitative characteristics of conjugation, *i.e.*, parameters σ_R of substituents MR_3 and CH_2MR_3,[1,2] are not universal and depend on both the type of fragment R_π and charges on its atoms. In the case of a small charge on R_π (0.01e; H-complexes of $R_\pi MR_3$ and $R_\pi CH_2MR_3$ with phenol) and a large charge (>0.9e; the excited state of $R_\pi MR_3$ complexes with iodine and tetracyanoethylene), the degree of conjugation in isolated neutral molecules is characterized by parameters σ_R^0, σ_R, and σ_R^+, respectively, which can differ in both magnitude and sign. The main reason for these distinctions is the dependence of σ,π-conjugation on the charge on R_π.[1-6] These problems were studied in detail for benzene derivatives (R_π = Rh)[1-7] and only fragmentarily for compounds with other type of R_π[1,3-5,8] because of scarce information on the experimental values of σ_R^0, σ_R, and σ_R^+. Recently,[8] we have shown that information on the σ_R^+ parameters of substituents can be obtained from the first vertical ionization potentials I_1 of organoelement compounds.

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The aim of this work is to study inductive, resonance, and electrostatic interactions in radical cations formed upon separation of an electron from the highest occupied molecular orbitals (HOMOs) of molecules $R_{\pi}X$ (R_{π} = Ph, $H_2C{=}CH$, and $HC{\equiv}C$; and X are substituents), to calculate the values of σ_R^+ parameters of the substituents X (X = MR_3 and CH_2MR_3), and to establish the dependence of σ_R^+ on the type of R_{π} using the I_1 ionization potentials.

Procedure for Calculations

The energy of conjugation between R_{π} and X was estimated using the PMO method.[7,8]

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

Results and Discussion

The first vertical ionization potentials I_1 of molecules $R_{\pi}X$ (R_{π} = Ph and $HC{\equiv}C$; X are substituents) measured by the photoelectron spectroscopy (PES) method with an accuracy of 0.01 eV are listed in Table 1. The use of I_1 values for studying the intramolecular interactions is based on the following grounds.

In the case of the PES method, irradiation of a neutral molecule M by a photon with the energy $h\nu$ results in the formation of an $M^{+\cdot}$ radical cation.[18]

$$M + h\nu \longrightarrow M^{+\cdot} + e^- . \qquad (1)$$

By definition, the I_1 value is the difference between the total energies of the radical cation, in which an electron is separated from the HOMO, and the neutral molecule.

$$I_1 = E^{+\cdot}_{tot} - E_{tot}. \qquad (2)$$

The relaxation (*R*) and correlation (*C*) energies, which characterize changes in the composition of the wave functions in $M^{+\cdot}$ as compared to M, should be taken into account in quantum-chemical calculations of $E^{+\cdot}_{tot}$.[18,19]

The expression for I_1 can be written[19] as

$$I_1 = I_1^0 - R + C. \qquad (3)$$

The Koopmans approximation[18,19]

$$I_1^0 = -E_{HOMO} \qquad (4)$$

ignores the contributions of *R* and *C*, *i.e.*, in the general case the experimental I_1 values cannot be used as a measure of the HOMO energy (E_{HOMO}).

The resonance effect of substituents X and E_{HOMO} of neutral molecules $R_{\pi}X$ (R_{π} = Ph, $H_2C{=}CH$, $HC{\equiv}C$) is described by the σ_R^0 constants.[20] Unlike M, radical cations $M^{+\cdot}$ have electron-deficient centers. It has been shown in the studies of heterolytic and several homolytic processes[21] as well as charge-transfer complexes[5] that the conjugation of the substituents with such centers is characterized by electrophilic σ_R^+ constants. An adequate description of the resonance effect of substituents on the I_1 value of benzene and ethylene derivatives (see Refs. 7 and 8, respectively) can be achieved only by using σ_R^+ constants rather than σ_R^0 constants. Hence, the Koopmans approximation (4) is too rough for these compounds. However, it is likely that the conjugation in $M^{+\cdot}$ is satisfactorily described by σ_R^+ constants taking into account the resonance component of *R* and *C* contributions in formula (3). Therefore, σ_I and σ_R^+ constants were used[8,16] in estimating the inductive and resonance effects of organic substituents X on the I_1 values in compounds PhX and $HC{\equiv}CX$ as compared to compounds $H_2C{=}CHX$.[8]

The HOMOs of compounds under consideration (except for acetylene derivatives **25** and **26** [9]) are the π-HOMO of ethylene (E = −11.40 eV) and the e_{1g} orbital of benzene (E = −9.24 eV) perturbed by the interactions with substituents X. For acetylene derivatives **25** and **26**, the symbol I_1^{II} in Table 1 is retained by convention, since the second ionization potentials (11.57 and 11.40 eV) correspond to the $\pi(C{\equiv}C)$-orbitals in these molecules.[9]

Among the studied compounds PhX, the strongest p,π-conjugation between the substituent and the π-system occurs in aniline and its *N*-methyl derivatives (compounds **16**—**18** in Table 1). Data on the structure of the HOMOs of molecules **16**—**18** are contradictory. The HOMOs of these molecules are formed[9,12,22,23] by mixing the orbital of the lone electron pair of the nitrogen atom and the π_s orbital of the benzene ring with symmetry b_1. The contribution of the $2p_{\pi}$ orbital of the N atom to the aniline HOMO is equal to 40%,[22] whereas the I_1^I ionization potentials of molecules **16**—**18** correspond to the π-type HOMOs. On the contrary, it had been assumed in early studies[14,24] that predominant contributions to the HOMOs of molecules **16**—**18** come from the nitrogen atoms and, therefore, the I_1^I values can be considered as corresponding to the lone electron pair of nitrogen. We believe that the opinion of the authors of the later studies[9,12,22,23] is more correct.

The following relationships are valid for ionization potentials of benzene (I_1^I, compounds **1**, **2**, **4**—**8**, and **11**—**29**), ethylene (I_1^{III}, according to the literature data[8]), and acetylene (I_1^{II}, compounds **1**—**4**, **6**—**10**, **12**, **14**, **15**, **21**—**26**, and **28**) derivatives containing no substituents MR_3 (M = Si, Ge, Sn):

$$I_1^{I} = 9.10 + 0.89\sigma_p^+ \qquad (5)$$
$$(S_a = 0.03,\ S_b = 0.05,\ S_Y = 0.16,\ r = 0.969,\ n = 26),$$

$$I_1^{III} = 10.14 + 1.34\sigma_p^+ \qquad (6)$$
$$(S_a = 0.04,\ S_b = 0.09,\ S_Y = 0.21,\ r = 0.950,\ n = 27),$$

$$I_1^{II} = 10.63 + 1.72\sigma_p^+ \qquad (7)$$
$$(S_a = 0.08,\ S_b = 0.24,\ S_Y = 0.36,\ r = 0.871,\ n = 19),$$

$$I_1{}^{I} = 9.03 + 1.17\sigma_I + 0.83\sigma_R{}^{+} \quad (8)$$
$(S_a = 0.04,\ S_b = 0.14,\ S_c = 0.05,\ S_Y = 0.14,\ r = 0.972,\ n = 26)$,

$$I_1{}^{III} = 10.09 + 1.57\sigma_I + 1.29\sigma_R{}^{+} \quad (9)$$
$(S_a = 0.06,\ S_b = 0.20,\ S_c = 0.10,\ S_Y = 0.21,\ r = 0.949,\ n = 27)$,

$$I_1{}^{II} = 10.63 + 1.72\sigma_I + 1.72\sigma_R{}^{+} \quad (10)$$
$(S_a = 0.13,\ S_b = 0.42,\ S_c = 0.41,\ S_Y = 0.37,\ r = 0.853,\ n = 19)$.

The low correlation coefficients r in Eqs. (5)—(10) point to the fact that not only the inductive and resonance effects of organic substituents X characterized by

Table 1. The first vertical ionization potentials of molecules PhX ($I_1{}^{I}$) and HC≡CX ($I_1{}^{II}$), energies of perturbation δE^{I} and δE^{II}, and σ-parameters of substituents X

Compound	X	$I_1{}^{I}$ [a]	$I_1{}^{II}$ [b]	δE^{I}	δE^{II}	σ_I [c]	$\sigma_R{}^{+}$ [c]	$\sigma_p{}^{+}$ [c]	σ_α [d]
		eV							
1	H	9.24	11.40	0	0	0	0	0	0
2	Me	8.72	10.36	0.32	0.45	−0.05	−0.26	−0.31	−0.35
3	Et	—	10.18	—	0.42	−0.05	−0.25	−0.30	−0.49
4	Pr	8.73	10.09	0.24	0.43	−0.05	−0.25	−0.30	−0.54
5	Pr^i	8.73	—	0.22	—	−0.03	−0.25	−0.28	−0.62
6	Pr^{sec}	8.61	9.58	0.33	0.83	−0.04	−0.37	−0.41	−0.62
7	Bu	8.69	10.05	0.25	0.43	−0.05	−0.25	−0.30	−0.57
8	Bu^t	8.74	9.92	0.11	0.26	−0.07	−0.19	−0.26	−0.75
9	C_6H_{13}	—	10.00	—	0.46	−0.05	−0.25	−0.30	−0.58
10	*cyclo*-C_6H_{11}	—	9.92	—	0.30	−0.02	−0.27	−0.29	−0.62
11	$CH_2CH=CH_2$	8.65	—	0.29	—	−0.06	−0.16	−0.22	−0.57
12	CH_2OH	8.90	10.50	0.22	0.29	0.03	−0.07	−0.04	−0.36
13	CH_2OMe	9.12	—	−0.03	—	0.03	−0.07	−0.04	−0.42
14	CH_2Cl	9.27	10.76	−0.13	−0.06	0.13	−0.14	−0.01	−0.54
15	CH_2Br	9.23	10.65	−0.11	−0.04	0.14	−0.12	0.02	−0.61
16	NH_2	8.05	—	1.20	—	0.08	−1.38	−1.30	−0.16
17	NHMe	7.65	—	1.43	—	−0.03	−1.78	−1.81	−0.30
18	NMe_2	7.45	—	1.76	—	0.15	−1.85	−1.70	−0.44
19	OH	8.56	—	1.00	—	0.33	−1.25	−0.92	−0.03
20	OMe	8.42	—	1.04	—	0.29	−1.07	−0.78	−0.17
21	F	9.20	11.26	0.54	0.79	0.45	−0.52	−0.07	0.13
22	Cl	9.07	10.58	0.41	0.58	0.42	−0.31	0.11	−0.43
23	Br	9.04	10.31	0.40	0.64	0.45	−0.30	0.15	−0.59
24	CN	9.71	11.60	−0.15	−0.39	0.51	0.15	0.66	−0.46
25	CHO	9.59	11.57	−0.21	−0.54	0.33	0.40	0.73	−0.46
26	COOH	9.60	11.40	−0.16	−0.18	0.34	0.08	0.42	−0.34
27	COOMe	9.50	—	−0.13	—	0.34	0.14	0.48	−0.49
28	CF_3	9.86	12.10	−0.34	−0.70	0.38	0.23	0.61	−0.25
29	NO_2	9.99	—	−0.21	—	0.65	0.14	0.79	−0.26
30	SiH_3	9.18	10.73	−0.23	−0.27	−0.04	0.03[e] (0.13)[f]	−0.01[e] (0.09)[f]	−0.59
31	$SiMe_3$	8.94	10.18	−0.15	−0.03	−0.15	0.02[e] (0)[f]	−0.13[e] (−0.15)[f]	−0.72
32	$GeMe_3$	8.95	10.00	−0.07	0.37	−0.11	−0.11[e] (−0.22)[f]	−0.21[e] (−0.33)[f]	−0.60
33	$SnMe_3$	8.75	—	0.11	—	−0.13	−0.21[e]	−0.34	−0.60
34	$SnEt_3$	—	9.00	—	0.63	−0.15	(−0.36)[f]	(−0.51)[f]	−1.06
35	$PbMe_3$	8.54	—	0.33	—	−0.12	−0.26[e]	−0.38[e]	−0.60
36	CH_2SiMe_3	8.42	9.04	0.49	1.30	−0.05	−0.49[e] (−0.74)[f]	−0.54[e] (−0.79)[f]	−0.66
37	$C(SiMe_3)_3$	8.10	—	0.55	—	−0.05	−0.63[e]	−0.68[e]	−1.28
38	CH_2GeMe_3	8.40	—	0.54	—	−0.04	−0.59[e]	−0.63[e]	−0.61
39	CH_2SnMe_3	8.21	—	0.72	—	−0.05	−0.76[e]	−0.81[e]	−0.61

[a] The values of $I_1{}^{I}$ for compounds **1—29** were taken from Ref. 9; those for compounds **30**, **36**, and **37** were taken from Ref. 10. The values of $I_1{}^{I}$ for compounds **31—33** and **35** were taken from Ref. 11; those for compounds **38** and **39** were taken from Ref. 12.

[b] The values of $I_1{}^{II}$ for compounds **1—3**, **8**, **12**, **14**, **15**, **21—26**, and **28** were taken from Refs. 9 and 12; those for compounds **4**, **7**, and **9** were taken from Ref. 13. The values of $I_1{}^{II}$ for compounds **6** and **10** were taken from Ref. 14. The values of $I_1{}^{II}$ for compounds **30**, **31**, **32**, and **34** were taken from Ref. 12; that for compound **36** was taken from Ref. 15.

[c] For σ_I, $\sigma_R{}^{+}$, and $\sigma_p{}^{+} = \sigma_I + \sigma_R{}^{+}$ values for substituents X in compounds **1—29**, see Refs. 8 and 16.

[d] The σ_α parameters for substituents X in compounds **1—29**, **31**, and **37** [16] and **30**, **32—36**, **38**, and **39** [8] were taken from the literature or calculated using the previously described procedure.[17]

[e] The value for PhX.[2,7,8]

[f] The value for HC≡CX calculated in this work.

σ_I, σ_R^+, and σ_p^+ ($\sigma_p^+ = \sigma_I + \sigma_R^+$) constants affect the I_1 value in $R_\pi X$. The quality of correlation equations (5)—(10) decreases on going from R_π = Ph to R_π = $H_2C{=}CH$ and $HC{\equiv}C$ (the correlation coefficient r decreases and the standard error S_Y increases), *i.e.*, the contribution of an additional factor to the I_1 value increases as R_π changes in this series. As follows from the results of previously reported studies,[16,22] this factor is the effect of polarizability of substituents X. The positive charge q of radical cations formed upon photoionization of molecules $R_\pi X$ in the gas phase induces a dipole moment of the substituent X. In the classical electrostatics, the energy of charge stabilization (the electrostatic attraction between the charge and the induced dipole moment) is defined as

$$E_{st} = -\frac{q^2\alpha}{2\varepsilon R^4}, \tag{11}$$

where α is the polarizability of X, ε is the dielectric constant, and R is the distance between the charge and the induced dipole. Considerable difficulties in the use of approximation (11) for calculating E_{st} for a number of R_πAlk systems arise when the charge and induced dipole are parts of the same ion.[22]

In another approach,[16,23] the polarizability effect of substituents is characterized by σ_α constants obtained from *ab initio* quantum-chemical calculations of electrostatic polarization potentials. The relationship between I_1 and σ_α (as a quantitative measure of stabilization of the charge q of the radical cation due to polarizability of substituent X) follows from Eq. (2). The degree of stabilization of the charge q increases and, hence, the total energy $E_{tot}^{+\cdot}$ of the radical cation and the I_1 value decrease as the negative σ_α values increase (see Table 1).

Taking account of this parameter leads to Eqs. (12)—(17). The statistical characteristics of these equations are much better as compared to those of Eqs. (5)—(10):

$$I_1^{I} = 9.29 + 0.91\sigma_p^+ + 0.47\sigma_\alpha \tag{12}$$
($S_a = 0.05$, $S_b = 0.04$, $S_c = 0.11$, $S_Y = 0.12$, $r = 0.981$, $n = 26$),

$$I_1^{III} = 10.43 + 1.40\sigma_p^+ + 0.63\sigma_\alpha \tag{13}$$
($S_a = 0.07$, $S_b = 0.07$, $S_c = 0.14$, $S_Y = 0.16$, $r = 0.970$, $n = 27$),

$$I_1^{II} = 11.28 + 1.47\sigma_p^+ + 1.42\sigma_\alpha \tag{14}$$
($S_a = 0.10$, $S_b = 0.12$, $S_c = 0.20$, $S_Y = 0.18$, $r = 0.968$, $n = 19$),

$$I_1^{I} = 9.25 + 1.00\sigma_I + 0.89\sigma_R^+ + 0.42\sigma_\alpha \tag{15}$$
($S_a = 0.08$, $S_b = 0.13$, $S_c = 0.04$, $S_d = 0.13$, $S_Y = 0.12$, $r = 0.980$, $n = 26$),

$$I_1^{III} = 10.49 + 1.27\sigma_I + 1.43\sigma_R^+ + 0.70\sigma_\alpha \tag{16}$$
($S_a = 0.11$, $S_b = 0.17$, $S_c = 0.08$, $S_d = 0.17$, $S_Y = 0.16$, $r = 0.970$, $n = 27$),

$$I_1^{II} = 11.43 + 1.09\sigma_I + 1.79\sigma_R^+ + 1.53\sigma_\alpha \tag{17}$$
($S_a = 0.11$, $S_b = 0.19$, $S_c = 0.17$, $S_d = 0.18$, $S_Y = 0.16$, $r = 0.975$, $n = 19$).

It is possible to calculate the contributions of the inductive (*In*), conjugation (*Res*), and polarizability effects (*P*) of the substituent to I_1 from Eqs. (15)—(17). If these dependences are written in general form $I_1 = a + b\sigma_I + c\sigma_R^+ + d\sigma_\alpha$, then $In = b\sigma_I$, $Res = c\sigma_R^+$, and $P = d\sigma_\alpha$ (Table 2). For each series of compounds (PhX, $H_2C{=}CHX$, and $HC{\equiv}CX$), the overall ranges of changes in contributions under consideration and ratios upon varying the σ_I, σ_R^+, and σ_α parameters in the series from minimum to maximum values and the values of changes in the I_1 ionization potentials of benzene (ethylene, acetylene) due to the introduction of Me and CMe_3 substituents, which have close values of σ_I and σ_R^+ parameters but differ strongly in σ_α values, are listed in Table 2. It can be seen in Table 2 that the contributions of *In*, *Res*, and *P* and the ratios *P*/*Res* and *P*/(*In* + *Res*) in the series and between the series vary over a wide range. However, for any X the contribution *P* as well as the *P*/*Res* and *P*/(*In* + *Res*) ratios increase in the sequence Ph < $H_2C{=}CH$ < $HC{\equiv}C$ as R_π changes from Ph to $H_2C{=}CH$ and $HC{\equiv}C$.

Qualitatively, the increase in the contribution *P* in this series can be explained using formula (11). In the

Table 2. The inductive (*In*), resonance (*Res*), and polarization (*P*) components of changes (*In* + *Res* + *P*) in the I_1 ionization potentials of benzene, ethylene, and acetylene caused by introduction of organic substituents X

Compound	X	*In*		*Res*		*P*		*In* + *Res* + *P*		$\frac{P}{Res}$	$\frac{P}{In + Res}$
		eV	ΔI_1 (%)	eV	ΔI_1 (%)	eV	ΔI_1 (%)	eV	ΔI_1 (%)		
PhX	Me	0.05	12	0.23	53	0.15	35	0.43	100	0.65	0.53
	Bu^t	0.07	13	0.17	30	0.32	57	0.56	100	1.88	1.33
	The overall range for the series	0.72	23	2.01	65	0.38	12	3.11	100	0.19	0.14
$H_2C{=}CHX$	Me	0.06	9	0.37	55	0.24	36	0.67	100	0.65	0.56
	Bu^t	0.09	10	0.27	31	0.52	59	0.88	100	1.93	1.44
	The overall range for the series	0.76	19	2.54	65	0.61	16	3.91	100	0.24	0.18
$HC{\equiv}CX$	Me	0.05	5	0.46	44	0.54	51	1.05	100	1.17	1.06
	Bu^t	0.08	5	0.34	22	1.15	73	1.57	100	3.38	2.74
	The overall range for the series	0.64	18	1.65	45	1.35	37	3.64	100	0.82	0.59

case of R_π = Ph the charge of the radical cation $R_\pi Me_3^{+\cdot}$ is delocalized over the aromatic ring (the degree of delocalization is equal to 70% for the phenyl cation).[27] For R_π = $H_2C{=}CH$ and $HC{\equiv}C$, the efficiency of charge delocalization decreases. The energy of charge stabilization is strongly dependent on the distance R (Eq. (11)). This makes it possible to consider, in the first approximation, the interaction of substituent Me only with the charge of the neighboring carbon atom. Then the numerator of the fraction in formula (11) is minimum for R_π = Ph. The C_{ar}—Me, =C—Me, and ≡C—Me distances in neutral compounds $R_\pi Me$ are equal to 1.51, 1.51, and 1.47 Å, respectively; those in radical cations are shortened by ~0.05 Å.[25,28] Therefore, the denominator of the fraction in formula (11) is minimum for R_π = C≡CH. Hence, stabilization of the positive charge in radical cations due to polarizability of the substituent, the value of contribution P, and the coefficients at σ_α in Eqs. (12)—(14) and (15)—(17) increase as R_π changes in the series Ph < $H_2C{=}CH$ < $HC{\equiv}C$.

Let us consider now the conjugation in radical cations formed upon separation of an electron from the HOMOs of molecules $R_\pi X$ (X are organic substituents). In a conventional version of the PMO method[7,8] the quantitative measure of conjugation is the perturbation energy δE, which can be calculated from the relationship

$$\delta E = E_{\text{HOMO}} - E(\pi), \qquad (18)$$

where $E(\pi)$ is the energy of the initial unperturbed orbital, which is dependent on only the inductive effect of substituents X. Relationship (18) is based on the Koopmans approximation (4), which is too rough in our case. Let us make a more accurate estimation of δE taking R_π = Ph as an example. Using Eq. (15), the HOMO energy of radical cations can be defined as

$$E^{\text{I}}_{\text{HOMO}} = -(I_1{}^{\text{I}} - 0.42\sigma_\alpha). \qquad (19)$$

In this case

$$E(\pi) = -9.24 + \sigma_{\text{I}}. \qquad (20)$$

Then

$$\delta E^{\text{I}} = -(I_1{}^{\text{I}} - 0.42\sigma_\alpha) - (-9.24 + \sigma_{\text{I}}). \qquad (21)$$

The δE^{III} and δE^{II} values (see Table 1) for the $H_2C{=}CHX$ and $HC{\equiv}CX$ series were calculated in a similar way.[8]

The δE values are related to $\sigma_R{}^+$ constants of substituents X by linear dependences

$$\delta E^{\text{I}} = -0.89\sigma_R{}^+ - 0.04 \qquad (22)$$
$$(S_a = 0.04,\ S_b = 0.03,\ S_Y = 0.12,\ r = 0.977,\ n = 26),$$

$$\delta E^{\text{III}} = -1.43\sigma_R{}^+ - 0.02 \qquad (23)$$
$$(S_a = 0.08,\ S_b = 0.04,\ S_Y = 0.16,\ r = 0.966,\ n = 27),$$

$$\delta E^{\text{II}} = -1.81\sigma_R{}^+ - 0.04 \qquad (24)$$
$$(S_a = 0.16,\ S_b = 0.04,\ S_Y = 0.15,\ r = 0.942,\ n = 19).$$

The absolute terms in Eqs. (22)—(24), comparable to standard deviations, can be neglected. Comparison of the slopes of the straight lines (22)—(24) shows that conjugation of substituents X with electron-deficient radical cationic centers increases as R_π changes in the sequence Ph < $H_2C{=}CH$ < $HC{\equiv}C$.

Using Eq. (17) and σ_α values determined previously,[8] we calculated the $\sigma_R{}^+(\text{II})$ parameters of organoelement substituents bonded to the triple bond (see Table 1, compounds **30—32**, **34**, **36**). The $\sigma_R{}^+(\text{II})$ parameters differ from the $\sigma_R{}^+(\text{I})$ and $\sigma_R{}^+(\text{III})$ parameters for the same substituents bonded to the benzene ring or to the double bond. Thus, the $\sigma_R{}^+(\text{I})$, $\sigma_R{}^+(\text{III})$, and $\sigma_R{}^+(\text{II})$ values for the CH_2SiMe_3 substituent are equal to −0.49, −0.65,[8] and −0.74, respectively. Despite the fact that the $\sigma_R{}^+$ parameters of organoelement substituents are not universal, the following linear dependences are valid for them

$$\sigma_R{}^+(\text{III}) = 1.38\sigma_R{}^+(\text{I}) \qquad (25)$$
$$(S_a = 0.10,\ S_Y = 0.11,\ r = 0.975,\ n = 12)^8,$$

$$\sigma_R{}^+(\text{II}) = 1.56\sigma_R{}^+(\text{I}) \qquad (26)$$
$$(S_a = 0.16,\ S_Y = 0.07,\ r = 0.985,\ n = 5)$$

(see Table 1, the $\sigma_R{}^+(\text{II})$ and $\sigma_R{}^+(\text{I})$ values for the substituents in compounds **30—32**, **34**, and **36**).

Corrections of the coefficients in relationships (25) and (26) are inevitable as new information $I_1{}^{\text{III}}$ and $I_1{}^{\text{II}}$ for compounds with organoelement substituents becomes available. At the same time, they can be used to estimate the $\sigma_R{}^+(\text{III})$ and $\sigma_R{}^+(\text{II})$ values that have only been reported in Ref. 8 and in this work.

In conclusion, we present relationships that are valid for the compounds PhX, $H_2C{=}CHX$, and $HC{\equiv}CX$ studied in this work and earlier[8] and any substituents X:

$$I_1{}^{\text{I}} = 9.27 + 0.94\sigma_{\text{I}} + 0.91\sigma_R{}^+ + 0.43\sigma_\alpha \qquad (27)$$
$$(S_a = 0.06,\ S_b = 0.11,\ S_c = 0.04,\ S_d = 0.09,\ S_Y = 0.12,\ r = 0.980,\ n = 35),$$

$$I_1{}^{\text{III}} = 10.50 + 1.23\sigma_{\text{I}} + 1.43\sigma_R{}^+ + 0.69\sigma_\alpha \qquad (28)$$
$$(S_a = 0.08,\ S_b = 0.14,\ S_c = 0.05,\ S_d = 0.13,\ S_Y = 0.13,\ r = 0.981,\ n = 37),$$

$$I_1{}^{\text{II}} = 11.43 + 1.08\sigma_{\text{I}} + 1.79\sigma_R{}^+ + 1.53\sigma_\alpha \qquad (29)$$
$$(S_a = 0.08,\ S_b = 0.16,\ S_c = 0.12,\ S_d = 0.14,\ S_Y = 0.14,\ r = 0.985,\ n = 24).$$

In these relationships the resonance effects of organic substituents are characterized by conventional $\sigma_R{}^+$ constants[8,16] while those of organoelement substituents are characterized by $\sigma_R{}^+(\text{I})$ (tabulated values[2,7,8]), $\sigma_R{}^+(\text{III})$ (the literature data[8]) and $\sigma_R{}^+(\text{II})$ (this work) parameters.

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