

First ionization potentials and conjugation in molecules of ethylene derivatives containing organoelemental substituents of Group IV elements

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Unlike the E_{HOMO} energies, the first vertical ionization potentials (I_1) of monosubstituted ethylenes depend not only on both the inductive and resonance effects but also on the polarizability of the substituents, which can be characterized by the σ_α parameters. The σ_R^+ , σ_p^+ , and σ_α parameters for 12 silicon-, germanium-, and tin-containing groups were determined using the equations relating the I_1 values and the σ_1 , σ_R^+ , σ_p^+ , and σ_α parameters of the substituents in the molecules of organic compounds. The conjugation of organoelemental substituents with the double bond is stronger than that with benzene ring; the σ_R^+ parameters in the ethylene and benzene series are related by a linear dependence.

Key words: ionization potential; silylethylenes, germylethylenes, stannylethylenes; σ -constants of substituents, correlation equations.

The modern model of conjugation (see, for instance, Ref. 1) in the organoelemental compounds of the R_3ER_π type ($E = Si, Ge, Sn$, and Pb ; R is an organic radical; R_π is an unsaturated group: Ph , $CH=CH_2$, $C\equiv CR$, furyl, thienyl, etc.) is based on the concept of dual (simultaneously acceptor and donor) resonance properties of organoelemental substituents R_3E (E is a Group IV element) toward the reaction (or indicator) centers R_π . The resonance acceptor effect (d, π -conjugation) is the interaction between the vacant nd -orbitals of E atoms and the antibonding σ^* -orbitals of the $E-R$ bonds of the R_3E substituent containing an R_π group. The resonance donor effect (σ, π -conjugation) is due to the interaction between σ -orbitals of the $E-R$ bond in R_3E with fragment R_π . The overall effect (simultaneous effect of the d, π - and σ, π -conjugation) cannot be characterized by universal parameters, since the conjugation between R_3E and R_π depends on the nature of the organic radical, unsaturated group, and the Group IV element; in the case of fixed R , E , and R_π it depends on the magnitude of the negative effective charge on R_π .¹

Of two components (the acceptor and donor one) of the overall resonance effect, only the σ, π -conjugation is dependent on the charge on R_π .¹⁻⁴ Hence, varying the negative effective charge on R_π in a wide range makes it possible to observe not only changes in the relative contributions of the two indicated components of the overall resonance effect, but (in the limiting case) also inversion of the sign of the overall effect.¹⁻⁷ The problem of inversion of the donor-acceptor properties of the R_3E substituents remains inadequately studied despite its importance for both creation of a general theory of conjugation in organic compounds of Group IV elements and for studying the ionic reactions with participation of such type derivatives.

Investigation of the ionization potentials of the R_3ER_π type compounds can make an appreciable contribution to the solution of this problem and accumulation of data on the resonance parameters of the R_3E substituents. Thus, an analysis of the first ionization potentials of benzene derivatives ($R_\pi = Ph$) made it possible to obtain new information on the conjugation between R_3E substituents and an indicator center R_π , which has an appreciably decreased negative effective charge.⁴ However, no similar studies were performed for other indicator R_π centers.

The main goal of this work is to reveal characteristic features of conjugation in the silicon-, germanium-, and tin-containing derivatives of ethylene by establishing correlations between the ionization potentials of such type of organoelemental compounds and the donor-acceptor properties of the substituents and by comparing the degrees of conjugation in substituted ethylenes and benzenes considered as model systems for studying the effects of the substituents.

Procedure of Calculations

The most reliable values of the first vertical ionization potentials (I_1) of organic and organoelemental derivatives of ethylene were obtained by the photoelectron spectroscopy method with an accuracy of ± 0.01 eV.⁸⁻¹⁸ As is known, irradiation of molecule M by a photon with the energy $h\nu$ results in the electron abstraction and formation of an $M^\cdot+$ radical cation



In the Koopmans approximation,^{4,11}

$$E_{HOMO} = -I_1. \quad (2)$$

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Table 1. Energy characteristics of molecular orbitals and σ -parameters of substituents X for compounds $XCH=CH_2$ (1–38)

Compound	X	$I_1 = -E_{HOMO}^a$ eV	$-E(\pi)$	$\delta E = E_{HOMO} - E(\pi)^b$	σ_1^c	σ_R^d	σ_p^d	σ_α^d
1	Me	9.69	10.46	0.77 (0.53)	-0.05	-0.26	-0.31	-0.35
2	Et	9.72	10.46	0.74 (0.40)	-0.05	-0.25	-0.30	-0.49
3	Pr	9.52	10.46	0.94 (0.56)	-0.05	-0.25	-0.30	-0.54
4	Pr ⁱ	9.7	10.48	0.78 (0.35)	-0.03	-0.25	-0.28	-0.62
5	Bu	9.48	10.46	0.98 (0.58)	-0.05	-0.25	-0.30	-0.57
6	Bu ^t	9.7	10.44	0.74 (0.22)	-0.07	-0.19	-0.26	-0.75
7	CH_2CMe_3	9.6	10.42	0.82 (0.35)	-0.09	-0.22	-0.31	-0.67
8	$CH_2CH=CH_2$	9.62	10.45	0.83 (0.43)	-0.06	-0.16	-0.22	-0.57
9	CH_2Ph	9.71	10.68	0.97 (0.48)	0.17	-0.45	-0.28	-0.70
10	CH_2CN	10.18	10.68	0.50 (0.12)	0.17	-0.01	0.16	-0.55
11	CH_2OH	10.16	10.54	0.38 (0.13)	0.03	-0.07	-0.04	-0.36
12	CH_2Cl	10.34	10.64	0.30 (-0.08)	0.13	-0.14	-0.01	-0.54
13	CH_2Br	10.18	10.65	0.47 (0.04)	0.14	-0.12	0.02	-0.61
14	NH_2	8.64	10.59	1.95 (1.84)	0.08	-1.38	-1.30	-0.16
15	OMe	9.05	10.80	1.75 (1.63)	0.29	-1.07	-0.78	-0.17
16	OEt	9.15	10.77	1.62 (1.46)	0.26	-1.07	-0.81	-0.23
17	OBu	9.07	10.77	1.70 (1.52)	0.26	-1.09	-0.83	-0.26
18	OCOMe	9.85	10.93	1.08 (-)	0.42	-0.61	-0.19	-
19	F	10.5	10.96	0.46 (0.55)	0.45	-0.52	-0.07	0.13
20	Cl	10.2	10.93	0.73 (0.43)	0.42	-0.31	0.11	-0.43
21	Br	9.9	10.96	1.06 (0.65)	0.45	-0.30	0.15	-0.59
22	I	10.08	10.93	0.85 (-)	0.42	-0.28	0.14	-
23	COOH	10.91	10.85	-0.06 (-0.30)	0.34	0.08	0.42	-0.34
24	COOMe	11.12	10.85	-0.27 (-0.61)	0.34	0.14	0.48	-0.49
25	CHO	10.95	10.84	-0.11 (-0.43)	0.33	0.40	0.73	-0.46
26	CN	11.1	11.02	-0.08 (-0.40)	0.51	0.15	0.66	-0.46
27	$SiMe_3$	9.86	10.36	0.50 (0.00)	-0.15	-0.03 [0.02]	-0.18 [-0.13]	-0.72
28	CH_2SiMe_3	9.1	10.46	1.36 (0.90)	-0.05	-0.65 [-0.49]	-0.70 [-0.54]	-0.66
29	SiH_3	10.37	10.47	0.10 (-)	-0.04	0.22 [0.03]	0.18 [-0.01]	-0.59
30	$Si(CH=CH_2)_3$	9.8	10.32	0.52 (-)	-0.19	-0.03 [0.01]	-0.22 [-0.18]	-0.69
31	$Si(OEt)_3$	10.16	10.41	0.25 (-)	-0.10	0.13 [0.11]	0.03 [0.01]	-0.63
32	CH_2SiH_3	9.49	10.46	0.97 (-)	-0.05	-0.38 [-0.22]	-0.43 [-0.27]	-0.61
33	$CH_2Si(OEt)_3$	9.47	10.41	0.94 (-)	-0.10	-0.35 [-0.09]	-0.45 [-0.19]	-0.63
34	CH_2SiCl_3	10.03	10.65	0.62 (-)	0.14	-0.20 [-0.22]	-0.06 [-0.08]	-0.47
35	CH_2GeMe_3	8.85	10.47	1.62 (-)	-0.04	-0.83 [-0.59]	-0.87 [-0.63]	-0.61
36	CH_2GeEt_3	8.8	10.46	1.66 (-)	-0.05	-0.86 [-0.62]	-0.91 [-0.67]	-0.61
37	CH_2SnMe_3	8.6	10.46	1.86 (-)	-0.05	-1.00 [-0.76]	-1.05 [-0.81]	-0.61
38	CH_2SnBu_3	8.4	10.46	2.06 (-)	-0.05	-1.14 [-0.75]	-1.19 [-0.80]	-0.61

^a The values of I_1 for compounds 1, 3, 5, 9, 11, 12, 23, 25, 27, 28, 31, 32, and 35 were taken from Ref. 8; those for compounds 2, 4, 6–8, 10, 16, 24, 26 were taken from Ref. 9. The values of I_1 for compounds 13, 17, 18 were taken from Ref. 10; those for compounds 14, 20–22 were taken from Ref. 11. The I_1 values for compounds 15 and 19 were taken from Refs. 12 and 13, respectively; those for compounds 29 and 30 were taken from Ref. 14. The values of I_1 for compounds 33 and 34 were calculated from the charge transfer frequencies in the UV spectra of complexes with tetracyanoethylene⁸ (see Ref. 15); those for compounds 36–38 were taken from Refs. 16–18, respectively.

^b The δE values calculated using Eq. (16) are given in parentheses.

^c The σ_1 values were taken from Refs. 7 and 20.

^d The σ_R^+ and σ_p^+ values of substituents in molecules 1–26, and the σ_α values in molecules 1–28 were taken from Ref. 20. The σ_R^+ values of substituents in compounds 27–38 and the σ_α values of substituents in compounds 29–38 were calculated using Eqs. (8), (16), and (17); the σ_R^+ and σ_p^+ values for organoelemental substituents in benzene derivatives⁷ are given in square brackets. It is assumed that $\sigma_p^+ = \sigma_1 + \sigma_R^+$.

In the case of rigorous fulfillment of relation (2), a quantum-chemical calculation of radical cation $M^{\cdot+}$ can be performed using wave functions of the neutral molecule M. However, as was established by the example of benzene derivatives,⁴ intramolecular resonance interactions in M and $M^{\cdot+}$ appreciably differ. This means that the conjugation between the R_3E and Ph groups in neutral $PhER_3$ compounds is characterized by the σ_R^0 resonance parameters, whereas that in radical

cations, when the negative effective charge on the Ph group is substantially decreased, is characterized by the σ_R^+ parameters.⁴

In the studies of ethylene derivatives $R_3ECH=CH_2$ we met conventional conditions for studying the conjugation in R_3ER_π molecules by analyzing the I_1 values: a common indicator center R_2 (Ph⁴ or $CH=CH_2$ in this work); a common type of the HOMO in the indicator series (for $R_\pi = Ph^4$ and $CH=CH_2$,

the HOMOs belongs to the π type); and retention of the predominant localization of the HOMO on the R_{π} group when mixing the orbitals of substituents and R_{π} .

According to the PMO theory,^{19,20} the HOMOs of ethylene derivatives $XCH=CH_2$ are the π -HOMO of ethylene (with an energy of -10.51 eV) perturbed by the inductive and resonance interactions with substituents X. The energy of perturbation (δE) is the most important characteristic of mixing of the initial unperturbed π -MO (with energy $E(\pi)$) with σ , π -, or n -orbitals of substituents X and can be calculated using the formula

$$\delta E = E_{\text{HOMO}} - E(\pi). \quad (3)$$

The energy of the initial unperturbed orbital, $E(\pi)$, differs from the E_{HOMO} energy of ethylene by a value numerically equal to the inductive constant of substituent X.²⁰ For this reason, the following equality is valid

$$E(\pi) = -10.51 + \sigma_1(X). \quad (4)$$

It should be noted that the δE values in Eq. (3) characterize the effect of conjugation between X and $CH=CH_2$ only on the E_{HOMO} of $XCH=CH_2$ compounds and do not take into account plausible participation of other orbitals in conjugation.

Experimental $I_1 = -E_{\text{HOMO}}$ values as well as calculated $E(\pi)$ and δE values for the compounds studied are given in Table 1. The values of the σ_1 , σ_R^+ , and σ_a parameters for organic²⁰ and organoelemental⁷ substituents were taken from the literature. The calculations were carried out on an IBM AT personal computer using the STATGRAPHICS (Version 3.0) program package.

Results and Discussion

The following dependences are valid for compounds 1–26 (see Table 1) containing organic groups as substituents:

$$I_1 = 10.12 + 1.31\sigma_p^+, \quad (5)$$

$$S_a = 0.04, S_b = 0.09, S_y = 0.20, r = 0.950, n = 26;$$

$$I_1 = 10.06 + 1.55\sigma_1 + 1.26\sigma_R^+, \quad (6)$$

$$S_a = 0.06, S_b = 0.20, S_c = 0.10, S_y = 0.20, r = 0.950, n = 26.$$

This fact indicates that the inductive and resonance effects of substituents (characterized by the σ_1 and σ_R^+ parameters, respectively) have a comparable influence on the I_1 and hence the E_{HOMO} values.

The energy of perturbation, δE , considered as a measure of the effect of conjugation on the E_{HOMO} in molecules 1–26 is defined by the expression

$$\delta E = -1.25\sigma_R^+ + 0.36, \quad (7)$$

$$S_a = 0.11, S_b = 0.06, S_y = 0.23, r = 0.920, n = 26.$$

We used relation (5) written as

$$\sigma_p^+ = 0.69I_1 - 6.98. \quad (8)$$

$$S_a = 0.05, S_b = 0.46, S_y = 0.15, r = 0.950, n = 26$$

to calculate previously unknown σ_p^+ and σ_R^+ ($\sigma_R^+ = \sigma_p^+ - \sigma_1$) parameters of organoelemental substituents in the molecules of compounds 27–38 (see Table 1).

The values of the σ_R^+ parameters for the substituents in the ethylene derivatives 27–32 and 35–38 and the corresponding parameters for the same substituents in benzene derivatives ($\sigma_R^+(Ph)$)⁷ are related by a linear dependence:

$$\sigma_R^+ = 1.41\sigma_R^+(Ph) + 0.03, \quad (9)$$

$$S_a = 0.08, S_b = 0.04, S_y = 0.08, r = 0.988, n = 10.$$

The I_1 values for compounds 33 and 34 were calculated from the frequencies of the UV spectra of complexes with tetracyanoethylene⁸ using a method¹⁵ whose accuracy is less than that of photoelectron spectroscopy. Therefore the σ_p^+ and σ_R^+ values for the $CH_2Si(OEt)_3$ and CH_2SiCl_3 groups are less precise than those for other substituents, and the equation

$$\sigma_R^+ = 1.38\sigma_R^+(Ph) - 0.02, \quad (10)$$

$$S_a = 0.10, S_b = 0.04, S_y = 0.11, r = 0.975, n = 12$$

for all 12 organoelemental substituents (compounds 27–38, Fig. 1) has a lower correlation coefficient as compared to Eq. (9). The absolute terms in Eqs. (9) and (10) can be neglected since their values do not exceed their standard deviations.

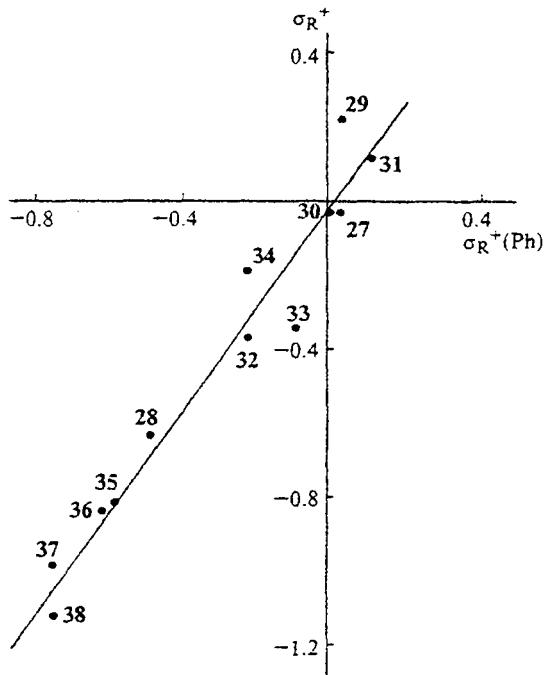


Fig. 1. Correlation between the σ_R^+ parameters of organoelemental substituents in ethylene derivatives with the $\sigma_R^+(Ph)$ parameters of the same substituents in benzene derivatives (see Eq. (10)). Numbering of points corresponds to that of compounds in Table 1.

Equations (9) and (10) can be used to estimate the σ_R^+ values of various organometallic substituents at the double bond using the known $\sigma_R^+(Ph)$ values.^{7,21}

It follows from Eqs. (9) and (10) that a decrease in the negative effective charge on the carbon atoms of the indicator center R_π results in increasing the resonance interaction of the organoelemental substituents with the double bond as compared to that with the benzene ring. The σ_R^+ values of substituents have both positive (in molecules 29 and 31) and negative (in molecules 27, 28, 30, and 32–38) values. The positive sign of σ_R^+ indicates that d,π-conjugation dominates over σ,π-conjugation in the $XCH=CH_2$ derivatives for $X = SiH_3$ and $Si(OEt)_3$. On the contrary, if $X = SiMe_3$ and $Si(CH=CH_2)_3$ (negative σ_R^+) the contribution of σ,π-conjugation to the overall resonance effect is larger than that of d,π-conjugation. There is only the resonance donor effect (σ,π-conjugation) in molecules of compounds 28 and 32–38.

The increase in σ,π-conjugation with decreasing negative effective charge on R_π is characterized by $\sigma_R - \sigma_R^+$ differences. This effect is also more pronounced for $R_\pi = CH=CH_2$. Thus, the $\sigma_R - \sigma_R^+$ and σ_R (in parentheses, data taken from Ref. 22) values for the substituents $X = SiMe_3$, CH_2SiMe_3 , CH_2GeMe_3 , and CH_2GeEt_3 are equal to 0.08 (0.05), 0.41 (−0.24), 0.54 (−0.29), and 0.55 (−0.31) for $R_\pi = CH=CH_2$. In the case of $R_\pi = Ph$ analogous data are equal to 0.03 (0.05), 0.27 (−0.22), 0.33 (−0.26), and 0.36 (−0.26), respectively.

The experimental value of the ionization potential of the unsubstituted ethylene ($I_1 = 10.51$ eV) substantially differs from the corresponding values calculated using Eqs. (5) and (6). Additionally, Eq. (7) contains a non-zero absolute term.

This is due to the fact that the ionization potential I_1 is dependent on one more parameter (σ_a), which can be calculated by *ab initio* quantum-chemical methods.²³ The σ_a value characterizes the degree of stabilization of the positive charge on the reaction (indicator) center at the expense of polarizability of the substituents. Fluorine atom ($\sigma_a = 0.13$, compound 19) is the only substituent²¹ causing destabilization of the positive charge. Taking into account this parameter, σ_a , as well as the inductive and resonance σ constants of the substituents is of particular importance when studying the gas-phase reactions,^{21,23} to which the process of photoionization belongs.

Since the ionization potential I_1 is equal to the difference between the energies of the $M^\cdot+$ radical cation and the neutral molecule M (see Eq. (1)), one should expect an increase in $M^\cdot+$ stabilization as compared to M (a decrease in I_1) with increasing polarizability of the substituents.

The effect of polarizability of the substituents on the I_1 values was established for 27 compounds (1–17, 19–21, and 23–28), for which the tabulated data on the σ_a values are available^{21,23} or they can be calculated

using the known method.²⁴ For these compounds, Eqs. (5) and (6) take the form

$$I_1 = 10.14 + 1.34\sigma_p^+, \quad (11)$$

$$S_a = 0.04, S_b = 0.09, S_c = 0.21, r = 0.950, n = 27;$$

$$I_1 = 10.09 + 1.57\sigma_1 + 1.29\sigma_R^+, \quad (12)$$

$$S_a = 0.06, S_b = 0.20, S_c = 0.10, S_y = 0.21, r = 0.949, n = 27.$$

Taking into account the σ_a parameter brings these equations to the form

$$I_1 = 10.43 + 1.40\sigma_p^+ + 0.63\sigma_a, \quad (13)$$

$$S_a = 0.07, S_b = 0.07, S_c = 0.14, S_y = 0.16, r = 0.970, n = 27;$$

$$I_1 = 10.49 + 1.27\sigma_1^+ + 1.43\sigma_R^+ + 0.70\sigma_a, \quad (14)$$

$$S_a = 0.11, S_b = 0.17, S_c = 0.08, S_d = 0.17, S_y = 0.16, r = 0.970, n = 27,$$

Dependences (13) and (14) have higher correlation coefficients r and lower values of the standard error S_y as compared to the corresponding Eqs. (11) and (12). It is also essential that the values of the absolute terms in Eqs. (13) and (14) differ only slightly from the I_1 value for ethylene (−10.51 eV).

Expression (14) makes it possible to estimate the energy of perturbation δE in the $XCH=CH_2$ molecules. Since the δE value depends only on the inductive and resonance effects of the substituents on the HOMO^{19,20} (see Eqs. (3) and (4)), taking into account Eq. (14) we get for the HOMO energy

$$E_{HOMO} = -(I_1 - 0.70\sigma_a). \quad (15)$$

Then Eq. (3) is transformed into the following expression:

$$\delta E = -(I_1 - 0.70\sigma_a) - (-10.51 + \sigma_1). \quad (16)$$

The following dependence is valid for 26 compounds (1–17, 19–21, and 23–28) and ethylene ($\delta E = 0$, $\sigma_R^+ = 0$):

$$\delta E = 1.43\sigma_R^+ - 0.02, \quad (17)$$

$$S_a = 0.08, S_b = 0.04, S_y = 0.16, r = 0.966, n = 27.$$

The absolute term in Eq. (17), which is less than the standard deviation, can be neglected. In contrast to relation (7), the straight line corresponding to dependence (17) passes through the origin, which has a strict physical meaning.

Simultaneous solution of Eqs. (16) and (17) makes it possible to obtain previously unknown values of the σ_a parameters for the organoelemental substituents in the molecules of compounds 29–38.

All ethylene derivatives studied (see Table 1), except for compounds 18 and 22 whose σ_a values are not available, are described by equations analogous to Eqs. (13) and (14), which take the following form:

$$I_1 = 10.42 + 1.39\sigma_p^+ + 0.59\sigma_a, \quad (18)$$

$$S_a = 0.06, S_b = 0.05, S_c = 0.11, S_y = 0.14, r = 0.981, n = 37;$$

$$I_1 = 10.50 + 1.23\sigma_p^+ + 1.43\sigma_R^+ + 0.69\sigma_a, \quad (19)$$

$$S_a = 0.08, S_b = 0.14, S_c = 0.05, S_d = 0.13, S_y = 0.13, r = 0.981, n = 37.$$

The results obtained (in particular, rather high correlation coefficients in Eqs. (18) and (19)) make it possible to draw additional conclusions of a general character.

Unlike the σ_1 constants, which are universal characteristics of the inductive effect of organic and organoelemental substituents, the σ_R^+ parameters are universal only for the organic groups. The σ_R^+ values of organoelemental substituents can vary in their magnitudes and signs as the reaction (indicator) center changes, though they are related by a linear dependence in the benzene and ethylene series.

The vertical ionization potentials I_1 as a quantitative measure of the HOMO energy should be used carefully. First, the I_1 values (unlike the E_{HOMO}) depend not only on the inductive and resonance effects, but also on the polarizability effect, which is characterized by the σ_a parameters of substituents. Second, the conjugation effect on the E_{HOMO} (as follows, for instance, from quantum-chemical calculations²⁵) and I_1 is described by the σ_R^0 and σ_R^+ parameters, respectively. As a rule, these parameters differ markedly from each other for both organic and organoelement substituents. Hence, the Koopmans relationship is not rigorously fulfilled for ethylene derivatives as well as for substituted benzenes.⁴ In this case the energy of perturbation δE determined using Eq. (16) characterizes the mixing of the orbitals in the radical cation rather than that of the orbitals of neutral molecules (as should be in the case of rigorous fulfillment of the Koopmans relationship).

The study of the ionization potentials I_1 of di-, tri-, and tetrasubstituted ethylenes is difficult since none of these series contains such a full set of substituents (see, for instance, Ref. 26) as the series of monosubstituted ethylene derivatives does (see Table 1). Additionally, in the case of polysubstituted ethylenes the effects of direct polar conjugation (for substituents of different kinds) and counterconjugation (for substituents of the same kind) should also be taken into account.²⁷ Therefore, the effect of substituents on the I_1 value can be nonadditive. We tested this assumption using 10 *trans*-XHC=CHX derivatives. For these compounds, the I_1^{calc} and $\Delta I_1 = I_1^{\text{calc}} - I_1^{\text{exp}}$ values were calculated using Eq. (19) under the assumption of the additivity of the effect of the two substituents. The experimental I_1^{exp}

values for compounds 1–8 and 9–10 were taken from Refs. 28 and 26, respectively. The I_1^{exp} , ΔI_1 , and σ_p^+ values for each X are given below.

X	$I_1^{\text{exp}}/\text{eV}$	$\Delta I_1/\text{eV}$	σ_p^+
C(SiMe ₃) ₃	7.78	-1.66	-0.92
CH ₂ SiMe ₃	8.30	-0.69	-0.70
Me	9.37	-0.21	-0.31
Bu ^t	8.99	-0.24	-0.26
SiMe ₃	9.19	-0.13	-0.18
F	10.38	-0.08	-0.07
H	10.51	0	0
Cl	9.72	0.33	0.11
Br	9.55	0.39	0.15
CN	11.15	0.40	0.66

The ΔI_1 differences considered as an indicator of nonadditivity of the effect of two X substituents on the I_1 values of *trans*-XHC=CHX molecules can be either negative (if $\sigma_p^+(X) < 0$, i.e., if the substituent exhibits an overall donor electron effect) or positive (if $\sigma_p^+ > 0$).

An approximate linear dependence is observed between the ΔI_1 differences and the σ_p^+ parameters of substituent X:

$$\Delta I_1 = 1.26\sigma_p^+, \quad (20)$$

$$S_a = 0.20, S_y = 0.27, r = 0.908, n = 10.$$

Hence the nonadditivity of the effect of two X substituents on the I_1 values of the *trans*-XHC=CHX molecules is due to the σ - and π -components, analogously to *p*-disubstituted benzenes.²⁷

In the case of tetrasubstituted X₂C=CX₂ derivatives, the values and signs of ΔI_1 differences and those of σ_p^+ parameters of substituent X are also correlated. Thus, for X = CH₂SiMe₃ ($I_1^{\text{exp}} = 7.15$ eV,²⁸ $\sigma_p^+ = -0.70$) $\Delta I_1 = -2.44$ eV, whereas for X = CN ($I_1^{\text{exp}} = 11.79$ eV,²⁶ $\sigma_p^+ = +0.66$) $\Delta I_1 = +0.81$ eV.

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