The first ionization potentials and conjugation in benzene derivatives containing organosilicon, organogermanium, organotin, and organolead substituents

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The inductive and resonance effects of silicon-, germanium-, tin-, and lead-containing and some organic substituents on the HOMO energies (E_{HOMO}) for 43 monosubstituted and p-disubstituted benzene derivatives were analyzed in the Koopmans approximation. A linear dependence between the perturbation energy δE and the resonance σ_R^+ parameters of the substituents was established. The Koopmans approximation is a rough approximation for the compounds studied, since to provide for its rigorous fulfilment, the δE values must depend on the σ_R^0 parameters of the substituents. The principal regularities of increasing the σ,π-conjugation between the organoelement substituents and the π-system caused by a positive charge on the benzene ring were established.

Key words: silylbenzenes, germylbenzenes, stannylbenzenes, ionization potentials; photoelectron spectra; σ,π-conjugation, d,π-conjugation.

Based on the data from various methods used in physical organometallic chemistry,[1—12] it is impossible to characterize the degree of conjugation in compounds $R_3E—R_\pi$ (E = Si, Ge, Sn, and Pb; R is an organic radical; R_π is an unsaturated fragment: Ph, $H_2C=CH$, $RC{\equiv}C$, *etc.*) using universal parameters analogous to the σ_R constants, since the resonance interactions between fragments R_3E and R_π depend on the position of E in the periodic table, the nature of R and R_π, and the effective charge on R_π as well. To investigate the charge dependence of conjugation, IR and UV spectroscopy are conventionally used.[9—12] An analysis of the data on the first vertical ionization potentials (I_1) seems to be promising. For instance, in the Koopmans approximation[4,5]

$$E_{HOMO} = -I_1, \qquad (1)$$

i.e., the energy of the highest occupied molecular orbital (HOMO) is equal to the first ionization potential but is opposite in sign. The detachment of an electron from the HOMO of $R_3E—R_\pi$ must result in a change in the charge on R_π and, therefore, in the degree of conjugation between R_3E and R_π.

The purpose of this work is to study the conjugation of Si-, Ge-, Sn-, and Pb-containing substituents with the aromatic ring in photoionization of the corresponding benzene derivatives.

On going from C_6H_6 to monosubstituted (C_6H_5Y) or p-disubstituted (p-XC_6H_4Y) derivatives, the degenerate π-HOMO of benzene (of symmetry e_{1g}) is split into two π-orbitals (π_2 and π_3) of symmetry a_2 and b_1, respectively, due to a decrease in the molecular symmetry. It is known[3—5] that the energy of the π_3-orbital depends on both the inductive and the resonance effects of substituents X and Y. In Table 1, the published data[1—8,11] on the ionization potentials I_1 (corresponding to the detachment of an electron from the π_3-orbital) as well as on the σ_I, σ_R^0, and σ_R^+ parameters of substituents X and Y for organoelement derivatives of benzene (and some of their organic analogs) are collected. For all compounds considered, except for 15, the π_3-orbital is the highest occupied molecular orbital.

Method of Calculations

In the Koopmans approximation (see Eq. (1)) $I_1 = -E_{HOMO}$, *i.e.*, the HOMO in the benzene derivatives studied is benzene orbital e_{1g} with an energy of −9.24 eV, perturbed by electronic interactions (inductive effect and conjugation) with the substituents. According to PMO theory,[16,17] the HOMO in the C_6H_5Y molecule is formed due to mixing of an initial unperturbed π-MO (with energy $E(\pi)$) and the σ- or n-orbitals of the substituents Y (with energy $E(Y)$). The perturbation energy (δE) can be calculated in two ways:[18] using Eq. (2)

$$\delta E = P^2/\Delta E, \qquad (2)$$

where $P = -|(E(\pi) - E_{HOMO})(E(Y) - E_{HOMO})|^{1/2}$ is a matrix element characterizing the perturbation and $\Delta E = E(\pi) - E(Y)$ is the difference between the energies of the initial unperturbed orbitals, and using Eq. (3)

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

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Table 1. Energetic characteristics of the molecular orbitals and σ-parameters of the substituents in compounds C_6H_5Y and *p*-XC_6H_4Y

Compound	X	Y	$I_1 = -E_{HOMO}$	$-E(\pi)$	$\delta E = E_{HOMO} - E(\pi)$	$\Sigma\sigma_I$	$\Sigma\sigma_R^0$	$\Sigma\sigma_R^+$	$\Delta\sigma = \Sigma\sigma_R^+ - \Sigma\sigma_R^0$
			eV						
1	H	H	9.24	9.24	0	0	0	0	0
2	H	Me	8.84	9.19	+0.35	−0.05	−0.08	−0.26	−0.18
3	H	SiH_3	9.18	9.20	+0.02	−0.04	+0.14	+0.03	−0.11
4	H	CMe_3	8.83	9.17	+0.34	−0.07	−0.06	−0.19	−0.13
5	H	$SiMe_3$	9.05	9.09	+0.04	−0.15	+0.05	+0.02	−0.03
6	H	$GeMe_3$	9.00	9.13	+0.13	−0.11	+0.01	−0.10	−0.11
7	H	$SnMe_3$	8.94	9.11	+0.17	−0.13	+0.01	−0.21	−0.22
8	H	$SiMe_2Ph$	8.98	9.10	+0.12	−0.14	+0.05	+0.04	−0.01
9	H	$SiPh_3$	8.96	9.10	+0.14	−0.14	+0.06	−0.01	−0.07
10	H	$GePh_3$	8.95	9.40	+0.45	+0.16	-0	−0.23	−0.23
11	H	$SnPh_3$	9.04	9.42	+0.38	+0.18	-0	−0.28	−0.28
12	H	$PbPh_3$	8.95	9.46	+0.51	+0.22	-0	−0.29	−0.29
13	H	CF_3	9.90	9.62	−0.28	+0.38	+0.15	+0.23	+0.08
14	H	$SiMeF_2$	9.55	9.48	−0.07	+0.24	+0.18	+0.13	−0.05
15	H	SiF_3	10.23	9.67	−0.56	+0.43	+0.23	+0.27	+0.04
16	H	CCl_3	9.32	9.62	+0.30	+0.38	+0.08	−0.02	−0.28
17	H	$SiMe_2Cl$	9.30	9.35	+0.05	+0.11	+0.10	−0.06	−0.16
18	H	$SiMeCl_2$	9.52	9.48	−0.04	+0.24	+0.15	−0.11	−0.26
19	H	$SiCl_3$	9.46	9.63	+0.17	+0.39	+0.17	−0.23	−0.40
20	H	$SnPh_2Cl$	9.29	9.64	+0.35	+0.40	0	−0.36	−0.36
21	H	$SiMeBr_2$	9.10	9.49	+0.39	+0.25	+0.05	−0.33	−0.38
22	H	$SiBr_3$	9.06	9.63	+0.57	+0.39	+0.20	−0.50	−0.70
23	H	$GePh_2Br$	9.17	9.59	+0.42	+0.35	0	−0.40	−0.40
24	H	CH_2CMe_3	8.77	9.19	+0.42	−0.05	−0.08	−0.25	−0.17
25	H	CH_2SiMe_3	8.42	9.19	+0.77	−0.05	−0.20	−0.49	−0.29
26	H	CH_2GeMe_3	8.40	9.20	+0.80	−0.04	−0.23	−0.59	−0.36
27	H	CH_2SnMe_3	8.21	9.19	+0.98	−0.05	−0.26	−0.76	−0.50
28	H	$C(SiMe_3)_3$	8.10	9.19	+1.09	−0.05	−0.22	−0.63	−0.41
29	H	$SiMe_2SiMe_3$	8.35	9.09	+0.74	−0.15	+0.04	−0.40	−0.44
30	CMe_3	CMe_3	8.40	9.10	+0.70	−0.14	−0.12	−0.38	−0.26
31	$SiMe_3$	$SiMe_3$	8.98	8.94	−0.04	−0.30	+0.10	+0.04	−0.06
32	$GeMe_3$	$GeMe_3$	8.60	9.02	+0.42	−0.22	+0.02	−0.20	−0.22
33	$SnMe_3$	$SnMe_3$	8.50	8.98	+0.48	−0.26	+0.02	−0.42	−0.44
34	$PbMe_3$	$PbMe_3$	8.25	9.00	+0.75	−0.24	−0.04	−0.52	−0.48
35	CH_2SiMe_3	CH_2SiMe_3	7.75	9.14	+1.39	−0.10	−0.40	−0.98	−0.58
36	CH_2SiEt_3	CH_2SiEt_3	7.75	9.14	+1.39	−0.10	−0.40	−1.04	−0.64
37	$C(SiMe_3)_3$	$C(SiMe_3)_3$	7.45	9.14	+1.69	−0.10	−0.44	−1.26	−0.82
38	F	$SiMe_3$	9.00	9.54	+0.54	+0.30	−0.25	−0.50	−0.25
39	Cl	CMe_3	8.82	9.59	+0.77	+0.35	−0.26	−0.50	−0.24
40	Cl	$SiMe_3$	9.03	9.51	+0.48	+0.27	−0.16	−0.29	−0.13
41	Cl	$GeMe_3$	8.84	9.55	+0.71	+0.31	−0.20	−0.41	−0.21
42	Cl	$SnMe_3$	8.95	9.53	+0.58	+0.29	−0.20	−0.52	−0.32
43	NO_2	$SiMe_3$	9.80	9.74	−0.06	+0.50	+0.24	+0.16	−0.08

Note. The values of I_1 for compounds **1—5**, **14**, **17—19**, **24**, **25**, **28—30**, and **35—37** were taken from Ref. 5; those for compounds **6—8**, **13**, **16**, **20**, **23**, **26**, **27**, and **32—34** were taken from Ref. 3. The values of I_1 for compounds **9—12** were taken from Ref. 8; those for compounds **21** and **22** were calculated from the charge transfer frequencies in the UV spectra of complexes with tetracyanoethylene[11] following the previously described procedure.[13,14] The values of I_1 for compounds **31** and **38—43** were taken from Refs. 6, 7. The values of σ_I, σ_R^+, and σ_R^0 for the organic substituents were taken from Refs. 1, 15, those for the organoelement substituents were taken from Refs. 2, 11. In some instances the σ_R^+ parameters of the organoelement substituents were determined as the difference $\sigma_R^+ - \sigma_I$. It is assumed that the σ_I parameters of the substituents in molecules **28** and **25**, and also those in **29** and **5** as well are equal.

The values of $E(\pi)$ and $E(Y)$ are calculated under the assumption that the energies of the unperturbed orbitals only depend on the inductive effect of the substituents. There are no general methods of calculation of energy $E(Y)$ in the literature; however, as shown previously,[18,19] one can calculate energies $E(\pi)$ for compounds C_6H_5Y and those for compounds *p*-XC_6H_4Y with reasonably high accuracy. Therefore, to calculate δE, Eq. (3) was used.

The $E(\pi)$ values were calculated as follows. Because of the inductive effect of substituents Y, the energy $E(\pi)$ in compounds C_6H_5Y differs from the energy of the benzene orbital e_{1g} (−9.24 eV) by the value Δ. An analysis of the photoelectron spectroscopy data[18,19] showed that Δ in C_6H_5Y molecules is numerically equal to the inductive constant σ_I of substituent Y. Therefore, the equations for calculating $E(\pi)$ in the molecules of monosubstituted (C_6H_5Y) and *p*-disubstituted (*p*-XC_6H_4Y) derivatives of benzenes (taking into account the additivity of the inductive effect of substituents X and Y on $E(\pi)$) are

$$E(\pi) = -9.24 + \sigma_I(Y), \qquad (4)$$

$$E(\pi) = -9.24 + \sigma_I(X) + \sigma_I(Y). \qquad (5)$$

The calculations were carried out on an IBM AT personal computer using the standard STATGRAPHICS (Version 3.0) program package. The values of the σ_I, σ_R^0, and σ_R^+ parameters of organic[1,15] and organoelement[2,11] substituents were taken from the literature.

Results and Discussion

The σ_R^0 parameters characterize the ability of organic and organoelement substituents to conjugate with the π-system in isolated molecules in their ground electronic state. The reorganization of the π-system caused by complexation (hydrogen bond, charge-transfer complexes) and all the more by transition of the molecule to the electron-excited state leads to the impossibility of an adequate description of the resonance properties of substituents X and Y in molecules C_6H_5Y and *p*-XC_6H_4Y using σ_R^0 parameters (see Refs. 20, 21). A similar situation also occurs in the search for a correlation between the δE and $\Sigma\sigma_R^0$ values for the compounds listed in Table 1. The dependence obtained

$$\delta E = -2.26\Sigma\sigma_R^0 + 0.35, \qquad (6)$$

$$S_a = 0.20,\ S_b = 0.03,\ S_y = 0.22,\ r = 0.87,\ n = 43,$$

with a low correlation coefficient (0.87) cannot be considered as even approximate.[22] In addition, the large value of the constant term in Eq. (6) has no physical meaning, since for benzene $\delta E = 0$ and $\sigma_H^0 = 0$.

The σ_R^+ parameters characterize the ability of the substituents to enter into conjugation with the π-system of the benzene ring, on which an appreciable positive charge is induced in experimental conditions. The values of the difference $\Delta\sigma = \sigma_R^+ - \sigma_R^0$ (see the last column in Table 1) are, as a rule, negative. Hence, it follows that an increase in the resonance donor effect (the σ,π-conjugation) of organoelement substituents with respect to the π-system of the benzene ring occurs due to the effect of the positive charge on the benzene ring. The higher the polarizability of the chemical bonds of the fragments $C(Ar)ER_3$ and $C(Ar)CH_n(ER_3)_{3-n}$ in compounds $PhER_3$ and $PhCH_n(ER_3)_{3-n}$ is, the greater this increase is.[11] Therefore, the quantitative characteristics of the increase in the σ,π-conjugation (the differences $\Delta\sigma = \sigma_R^+ - \sigma_R^0$) and polarizabilities (the sums of bond refractions ΣR_D) are related by linear dependences of the $\Delta\sigma = a\Sigma R_D + b$ type. The values of coefficients *a* and *b* vary on going from compounds $PhER_3$ to $PhCH_n(ER_3)_{3-n}$, since in the first case the conjugation of the substituents with the π-system of the ring involves not only the donor but also the acceptor component.[11]

For deeper insight into the distinctions between the σ_R^+ and σ_R^0 parameters let us consider the general principles listed above as applied to the compounds studied, which can be divided into five series.

The first series is formed by compounds **2**—**12**. The only resonance effect in alkylbenzenes (compounds **2** and **4**) is σ,π-conjugation. This effect is increased if the ring has a positive charge, therefore the values of $\Delta\sigma = \sigma_R^+ - \sigma_R^0$ are negative. The organoelement substituents ER_3 exhibit resonance effects of both types with respect to the benzene ring, donor (σ,π-conjugation) and acceptor (d,π-conjugation). According to the published data,[12] the latter consists in simultaneous participation of the vacant *n*d-orbitals of E atoms and antibonding σ^*-orbitals of bonds (formed by E atoms) in the conjugation. The effect of d,π-conjugation becomes weaker in the order Si > Ge > Sn > Pb and is independent of the charge on the π-system, whereas σ,π-conjugation becomes stronger in the order C < Si < Ge < Sn < Pb and even if the π-system has a positive charge as well.[9—12] If the benzene ring has no charge, d,π-conjugation dominates over σ,π-conjugation, which is reflected in the positive values of the σ_R^0 parameter, reaching its maximum for E = Si. If the benzene ring has a positive charge, then the higher the atomic number of E in $PhER_3$ is, the larger the increase in the σ,π-conjugation (increasing negative $\Delta\sigma$ values) observed. In this case, the σ_R^+ parameter for the organosilicon substituents SiH_3, $SiMe_3$, and $SiMe_2Ph$ still retains its positive value. Larger negative $\Delta\sigma$ values are characteristic of $PhEPh_3$ as compared to the corresponding methyl derivatives $PhEMe_3$. This is due to the stronger polarizability of the E—C(Ar) bonds as compared to the E—C(Alk) bonds. Thus, for instance, the refractions R_D of the Sn—C(Alk) and Sn—C(Ar) bonds in the Vogel system are 4.17 and 4.55 cm^3, respectively.[23] As a consequence, judging from the σ_R^+ values, substituents EMe_3 and EPh_3 (E = Ge, Sn, and Pb) become resonance donors due to the influence of the positive charge on the ring.

The second series is formed by compounds **13**—**23**. For these derivatives, the inversion of the resonance properties, controlled by the polarizability of the bonds, is more pronounced than in the first series. As follows from the positive values of σ_R^0, most substituents in the compounds of the second series in the absence of a positive charge on the benzene ring are typical resonance acceptors (predominance of d,π-conjugation over σ,π-conjugation). The positive charge on the benzene ring has little effect on the donor-acceptor properties of the fluorosilyl substituents; the acceptor chlorosilyl fragments are transformed into resonance donors (negative values of σ_R^+ and differences $\Delta\sigma$), while the bromosilyl substituents become resonance donors (a further increase in the negative values of σ_R^+ and $\Delta\sigma$ as compared to the chlorosilyl fragments). These facts are explained by the substantial difference in the polarizability of the Si—Hal bonds. The values of R_D for Hal = F, Cl, and Br are 1.7, 7.11, and 10.24 cm^3, respectively;[23] the refraction of the Si—F bond (1.7 cm^3) is lower than the R_D of the Si—C(Alk) bond (2.47 cm^3). Therefore, the increase in σ,π-conjugation with an increase in the atomic number of the halogen in $PhEMe_nHal_{3-n}$ is very sharply expressed.

The third series is formed by compounds **24—29**. There is no resonance acceptor effect of d,π-conjugation in benzyl derivatives **24—27**. The resonance donor effect of σ,π-conjugation is enhanced as the atomic number of E increases and if a positive charge appears on the benzene ring (negative values of $\Delta\sigma$, which increase in the sequence C < Si < Ge < Sn). The σ_R^0 parameters for compounds **25** and **28** differ insignificantly; a more important difference is observed between the σ_R^+ values. An increase in n in the $CH_{3-n}(SiMe_3)_n$ fragment is accompanied by an increase in ΣR_D, since the refractions of the C—H and C—Si bonds are 1.68 and 2.47 cm^3, respectively. Therefore, the values of σ_R^+ and $\Delta\sigma$ for compound **28** are more negative than for compound **25**. The $SiMe_2SiMe_3$ substituent participates in both d,π-conjugation and σ,π-conjugation with the π-system. If the benzene ring has no charge, the first type of conjugation is predominant (positive σ_R^0 values), whereas the second type of conjugation becomes dominant (negative values of σ_R^+ and $\Delta\sigma$) if the benzene ring has a positive charge.

The fourth series is formed by compounds **30—37**, containing two substituents of the same type at the *para*-position with respect to each other. We assumed that the values of $\Sigma\sigma_R^0$, $\Sigma\sigma_R^+$, and $\Delta\sigma$ are doubled compared with those for the corresponding monosubstituted benzenes. At the same time, it cannot be ruled out (in particular, for silyl derivatives **35—37** containing strong resonance donors) that the donor properties of the two *para*-substituents can become mutually weaker due to negative direct polar (counter-) conjugation.[16,24]

The fifth series is formed by compounds **38—43**, containing two substituents of different types at the *para*-position with respect to each other. As for the compounds of the fourth series, we assumed that the electronic effects of the substituents in these benzene derivatives are additive. This assumption is reasonably justified for compounds **38—42**, since in this case the substituents are either moderate resonance donors or the difference between their donor-acceptor properties is rather small. Therefore, the contribution of counter-conjugation and direct polar conjugation cannot be essential.

Thus, the effect of σ,π-conjugation of the substituents with the π-system is increased if a positive charge appears on the benzene ring. The quantitative characteristics of this effect (σ_R^+) essentially differ in value and often in sign from the σ_R^0 parameters, which characterize σ,π-conjugation in neutral molecules. Therefore, the correlation between perturbation energy δE and the σ_R^+ parameters of the substituents (see Eq. (6)), but not that between perturbation energy δE and the σ_R^0 values, must be more reasonable, since energies δE were obtained from ionization potentials I_1 determined by photoelectron spectroscopy. The abstraction of an electron in photoionization of molecule M

$$M \xrightarrow{h\nu} M^{\cdot +} + e^- \qquad (7)$$

results in the formation of a radical cation $M^{\cdot +}$. The Koopmans approximation (1) is only valid if it is possible to carry out an independent rigorous quantum-chemical calculation of the total energy of the radical cation $M^{\cdot +}$ using the wave functions for the neutral molecule M.

If the molecular orbitals of M and $M^{\cdot +}$ differ significantly (*i.e.*, the Koopmans relation is not valid), then Eq. (1) turns into

$$E_{HOMO} + \Delta E_d = -I_1, \qquad (8)$$

where ΔE_d is the so-called Koopmans deficiency. The reason for the appearance of energetic contribution ΔE_d lies in the photoionization (when reorganization of the electronic levels occurs) and change in the basis set of the wave functions and interelectronic interactions due to a decrease in the number of electrons as well.[4]

Three circumstances are of importance for our purposes. First, the ΔE_d values make the greatest contribution to ionization of the inner orbitals, while their contribution to ionization of delocalized HOMOs is small.[4] Secondly, it follows from Eq. (8) that the allowance for the ΔE_d contribution was made for the values of ionization potentials I_1; therefore, the use of I_1 to calculate perturbation energy δE following Eqs. (2) and (3) allows us to ignore a detailed analysis of the role of the Koopmans deficiency in the photoionization. Third, since a positive charge appears on the benzene ring (see Eq. (7)) in photoionization, we must characterize the resonance interactions between the substituents and the π-system by the σ_R^+ parameters. In accordance with this, we obtained an adequate dependence for compounds **1—43** (see Table 1)

$$I_1 = 9.19 + 1.18\Sigma\sigma_I + 1.31\Sigma\sigma_R^+, \qquad (9)$$

$$S_a = 0.02,\ S_b = 0.07,\ S_r = 0.05,\ S_y = 0.11,\ r = 0.98,\ n = 43,$$

where σ_I and σ_R^+ are the inductive and the resonance parameters of the substituents, respectively. Hence, for the compounds studied, Koopmans relation (1) is valid to a first approximation when both the first ionization potential I_1 and the energy E_{HOMO} nearly entirely depend on the donor-acceptor properties of the substituents bound to the benzene ring.

At the same time, the Koopmans relation is only partially valid. This follows from a comparison of our results and the data from nonempirical quantum-chemical calculations for monosubstituted benzenes, ethylenes, and acetylenes. In those molecules, the organic substituents are both resonance donors (NH_2, OH, F, *etc.*) and acceptors (CHO, CN, NO_2, *etc.*).[15] A linear dependence between the $\sigma_R{}^0$ constants and the Δq_π values, which quantitatively characterize the effect of conjugation, was established in those calculations. A good correlation between Δq_π and $\sigma_R{}^0$ in the benzene, ethylene, and acetylene series lead the authors of Ref. 15 to propose these equations as a reliable method for determination of the unknown values of the $\sigma_R{}^0$ constants. Thus, it follows from the published data[15] that if Koopmans relation (1) is valid, the first ionization potential I_1 and the HOMO energy, determined as $E_{HOMO} = -I_1$, must depend on both the inductive σ_I and the resonance $\sigma_R{}^0$ parameters of the substituents. Thus, it does follow from Eq. (9) that the value of I_1 depends on parameters σ_I and $\sigma_R{}^+$.

Data processing for the first ionization potentials using the σ_I and $\sigma_R{}^0$ parameters only leads to an approximate dependence

$$I_1 = 8.88 + 1.09\Sigma\sigma_I + 2.23\Sigma\sigma_R{}^0, \qquad (10)$$

$S_a = 0.04$, $S_b = 0.16$, $S_c = 0.21$, $S_y = 0.23$, $r = 0.91$, $n = 43$

with a smaller correlation coefficient than for Eq. (9). It is impossible to explain the small value of the constant term (8.88) in Eq. (10), since the constant term for the unsubstituted benzene ($\sigma_I = 0$ and $\sigma_R{}^0 = 0$) should not sharply differ from 9.24, as is the case, for instance, in Eq. (9).

It follows from the above discussion that perturbation energy δE, determined from Eq. (2) or Eq. (3), must characterize mixing of the orbitals modified by the positive charge on the benzene ring, but not that of the orbitals of the neutral compounds (as could be expected in the case when the Koopmans relation is fulfilled).

This is confirmed by the existence of a satisfactory dependence for compounds **1—43**

$$\delta E = -1.33\Sigma\sigma_R{}^+ + 0.02, \qquad (11)$$

$S_a = 0.08$, $S_b = 0.02$, $S_y = 0.11$, $r = 0.97$, $n = 43$,

The constant term of this dependence can be neglected since it is comparable to the standard deviation (0.02).

Equation (11) in the form

$$\Sigma\sigma_R{}^+ = -0.70\delta E, \qquad (12)$$

$S_a = 0.03$, $S_y = 0.08$, $r = 0.97$

can be used to make rough estimates of unknown $\sigma_R{}^+$.

With respect to the limited use of the Koopmans relation, the fulfillment of Eqs. (9) and (10) for the compounds studied allows us to consider the change in the energy of the HOMO formed from the e_{1g} orbitals of the unsubstituted benzene as a result of both the inductive and the resonance effects of the substituents. The opposite assumption that the electronic effects in question only affect the HOMOs of the compounds studied obviously needs proving. One preliminary indirect confirmation was obtained from a comparison of Eq. (11) and the similar dependence for certain monosubstituted benzene derivatives C_6H_5Z that we studied additionally (see below).

Z	I_1/eV	δE/eV	$\sigma_R{}^+$
NMe_2	7.45	1.94	−1.85
NHMe	7.65	1.56	−1.78
NH_2	8.02	1.30	−1.38
OMe	8.45	1.08	−1.07
F	9.20	0.49	−0.52
Cl	9.10	0.56	−0.31
H	9.24	0	0
NO_2	10.32	−0.43	0.14

(the values of I_1 were taken from Refs. 3, 4, and 25; those of σ_I and $\sigma_R{}^+$ for substituents Z were taken from Ref. 1; the δE values were calculated from Eq. (3)). At least for the first four compounds (in which substituents Z are the strongest resonance donors), we can assume that in addition to the HOMO, the lower orbitals also participate in conjugation of Z with the π-system.

The following dependence is valid for compounds C_6H_5Z

$$\delta E = -1.000\sigma_R{}^+ - 0.03, \qquad (13)$$

$S_a = 0.09$, $S_b = 0.10$, $S_y = 0.18$, $r = 0.98$, $n = 8$.

It can be seen from the comparison of dependences (11) and (13) plotted in Fig. 1 that the line corresponding to Eq. (13) has a gentler slope. For a fixed value of the $\sigma_R{}^+$ parameter, perturbation energy δE for compounds **1—43**

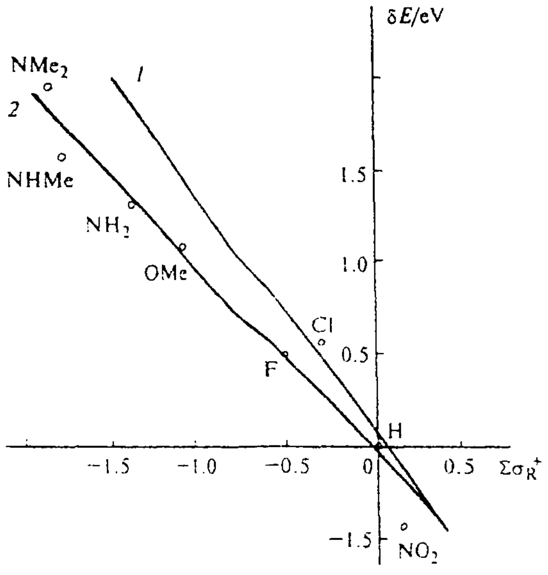

Fig. 1. Correlation between the values of δE and $\Sigma\sigma_R{}^+$ for compounds **1—43** (*1*) (see Table 1 and Eq. (11)) and C_5H_5Z (*2*) (see Eq. (13)). Points belonging to line *2* are shown.

(see Table 1) is higher than for monosubstituted benzenes C_6H_5Z. A particularly large discrepancy between the δE values in Eq. (11) and Eq. (13) is observed for large negative σ_R^+ values, *i.e.*, when substituents X, Y, and Z are the strongest resonance electron donors. It is in such instances that one could expect that the values of δE and σ_R^+ in Eq. (13) are not identical characteristics of conjugation in molecules C_6H_5Z.

By definition, the quantity δE characterizes the effect of conjugation between substituent Z and the π-system only on the E_{HOMO} of compounds C_6H_5Z. The σ_R^+ parameter as a characteristic of conjugation of substituents Z with the π-system contains no restrictions on the type of the orbitals whose interactions provide the overall conjugation effect in the molecules. If conjugation in monosubstituted benzenes C_6H_5Z (Z are strong resonance donors) occurs with the participation of the HOMO and lower orbitals, while only the HOMO participates in conjugation in compounds **1**—**43** (see Table 1), then perturbation energy δE must be higher for compounds of the second type at the same σ_R^+ value. This is just observed experimentally (*cf.* Eqs. (11) and (13), see Fig. 1). Notice also that as a result of counterconjugation between two identical substituents belonging to strong resonance donors, energies δE in *p*-disubstituted benzenes **35**—**37** become lower than the doubled δE values in the corresponding monosubstituted derivatives (compounds **25** and **28**). Any correction of the δE values for compounds **35**—**37** undertaken to make allowance for the effect of counterconjugation on δE must only lead to an increase in the difference in the slopes of the lines corresponding to Eqs. (11) and (13).

References

1. C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
2. A. N. Egorochkin and G. A. Razuvaev, *Usp. Khim.*, 1987, **56**, 1480 [*Russ. Chem. Rev.*, 1987, **56**, 846 (Engl. Transl.)].
3. V. I. Nefedov and V. I. Vovna, *Elektronnaya struktura organicheskikh i elementoorganicheskikh soedinenii* [*The Electronic Structure of Organic and Organoelement Compounds*], Nauka, Moscow, 1989 (in Russian).
4. V. F. Traven', *Elektronnaya struktura i svoistva organicheskikh molekul* [*The Electronic Structure and Properties of Organic Molecules*], Khimiya, Moscow, 1989 (in Russian).
5. H. Bock and B. Solouki, in *The Chemistry of Organic Silicon Compounds*, Eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1989, Part 1, 555.
6. Y. Limouzin and J. C. Maire, *J. Organomet. Chem.*, 1975, **92**, 159.
7. Y. Limouzin and J. C. Maire, *J. Organomet. Chem.*, 1976, **105**, 179.
8. I. Novak and A. W. Potts, *J. Organomet. Chem.*, 1984, **262**, 17.
9. A. N. Egorochkin, S. E. Skobeleva, E. T. Bogoradovsky, and T. P. Zubova, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1041 [*Russ. Chem. Bull.*, 1994, **43**, 976 (Engl. Transl.)].
10. A. N. Egorochkin, S. E. Skobeleva, and T. G. Mushtina, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 289 [*Russ. Chem. Bull.*, 1995, **44**, 280 (Engl. Transl.)].
11. A. N. Egorochkin, G. A. Razuvaev, and M. A. Lopatin, *J. Organomet. Chem.*, 1988, **344**, 49.
12. A. N. Egorochkin, *Usp. Khim.*, 1992, **61**, 1092 [*Russ. Chem. Rev.*, 1992, **61** (Engl. Transl.)]
13. A. N. Egorochkin, M. A. Lopatin, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, 1988, **299**, 909 [*Dokl. Chem.*, 1988, **299** (Engl. Transl.)].
14. E. M. Voigt and C. Reid, *J. Am. Chem. Soc*, 1964, **86**, 3930.
15. S. Marriott and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1045.
16. M. J. S. Dewar and R. G. Dougherty, *The PMO Theory of Organic Chemistry*, Plenum Press, New York, 1975.
17. C. G. Pitt, *J. Organomet. Chem.*, **1973**, **61**, 49.
18. V. N. Baidin, I. I. Kritskaya, M. M. Timoshenko, Yu. A. Ustynyuk, and Yu. V. Chizhov, in *Uspekhi fotoniki* [*Advances in Photonics*], Izd. Leningr. Univ., Leningrad, 1983, Issue 8, 8 (in Russian).
19. A. N. Nesmeyanov, V. N. Baidin, Yu. V. Chizhov, M. M. Timoshenko, Yu. S. Nekrasov, and I. I. Kritskaya, *Dokl. Akad. Nauk SSSR*, 1981, 256, 121 [*Dokl. Chem.*, 1981, **256** (Engl. Transl.)].
20. A. N. Egorochkin, S. E. Skobeleva, and V. L. Tsvetkova, *Metalloorg. Khim.*, 1993, **6**, 191 [*Organomet. Chem. USSR*, 1993, **6** (Engl. Transl.)].
21. A. N. Egorochkin, V. A. Kuznetsov, and M. A. Lopatin, *Dokl. Akad. Nauk SSSR*, 1978, **243**, 368 [*Dokl. Chem.*, 1978, **243** (Engl. Transl.)].
22. Yu. A. Zhdanov and V. I. Minkin, *Korrelyatsionnyi analiz v organicheskoi khimii* [*Correlation Analysis in Organic Chemistry*], Izd. Rostov Univ., Rostov-on-Don, 1966 (in Russian).
23. S. S. Batsanov, *Strukturnaya refraktometriya* [*Structural Refractometry*], Vysshaya Shkola, Moscow, 1976 (in Russian).
24. A. Pross, L. Radom, and R. W. Taft, *J. Org. Chem.*, 1980, **45**, 818.
25. J. E. Frey, *Appl. Spectrosc. Rev.*, 1987, **23**, 247.

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