# Physical Chemistry

## Ionization potentials of non-metal monosulfides. Conjugation in radical cations containing Group IV elements

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The first vertical ionization potentials $I(n_S)$ of 69 monosulfides XSY (X, Y = H, Hal, organic, or heteroorganic substituent) are related to the inductive ($\sigma_I$), resonance ($\sigma_R^+$), and polarizability ($\sigma_\alpha$) constants of the substituents by dependences of the $I(n_S) = a + b\Sigma\sigma_I + c\Sigma\sigma_R^+ + d\Sigma\sigma_\alpha$ type. The $I(n_S)$ values are also affected by hyperconjugation which increases on going from XSH to XSY ($Y \neq H$) compounds. The first calculations of the $\sigma_R^+$-parameters characterizing the conjugation of Si-, Ge-, Sn-, and Pb-containing substituents with the $S^{\cdot +}$ radical cation center are reported. The reasons for weakening of resonance donor properties of heteroorganic substituents of the $+M$-type in the systems studied as compared to those of the same substituents in the corresponding aromatic radical cations are considered.

**Key words:** non-metal monosulfides, hydrogen sulfide, diorganylsulfides, organometallic sulfides, derivatives of Group IV elements, ionization potentials, radical cations, conjugation.

According to modern concepts used in physical organometallic chemistry, conjugation in the $R_3MR_\pi$ and $R_3MZ$ (R = Alk; M = Si, Ge, Sn, Pb; $R_\pi$ = Ph, $CH{=}CH_2$, $C{\equiv}CH$, *etc.*; Z = $NR_2$, OR, SR, *etc.*) molecules (see, *e.g.*, Ref. 1) is affected by two oppositely directed effects, namely, by the acceptor and donor effects. The $R_3M$ substituents possess both acceptor and donor properties toward the reaction (indicator) centers of the π- and n-type ($R_\pi$ and Z, respectively). The former are due to d,π- and d,n-conjugation (interactions of the nd-orbitals of the M atom and the antibonding σ*-orbitals of the M—C bonds with the orbitals of $R_\pi$ and Z, respectively), whereas the latter are due to σ,π-conjugation and σ,n-conjugation (interactions of the σ-orbitals of the M—C bonds with the orbitals of $R_\pi$ and Z, respectively). Severe problems arise in attempting to use quantum-chemical methods for quantitative studies of these effects (especially the acceptor effect).[1] For this reason, experimental physicochemical methods are widely used for establishing the peculiarities of conjugation in the $R_3MR_\pi$ molecules. For instance, the $\sigma_R^0$, $\sigma_R$, and $\sigma_R^+$ parameters, which quantitatively characterize the total resonance effect (d,π- and σ,π-conjugation) of $R_3M$ substituents toward the $R_\pi$ indicator center both in the absence and in the presence of a small or large positive charge ($\delta^+$) on the indicator center $R_\pi$, respectively, were calculated using spectroscopic data.[1—4] At fixed M and $R_\pi$, the above-mentioned parameters can differ in magnitude and sign. This is mainly due to the strong dependence of σ,π-conjugation on the charge $\delta^+$ (see Refs. 1—4).

Investigations of this problem for $R_3MZ$ compounds is hampered by the lack of data on the resonance

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σ-parameters of the substituents. At the same time, recently[5,6] we showed that the $\sigma_R^+$ parameters of the $R_3M$ substituents in $R_3MR_\pi$ compounds can be calculated from the ionization potentials (IP) of these molecules.

The aim of this work was to establish dependences between the ionization potentials $I(n_S)$ of XSY (X, Y = H, Hal, organic, or heteroorganic substituent) monosulfides and the parameters characterizing the properties of the X and Y substituents, to calculate the $\sigma_R^+$ parameters of organometallic substituents containing Si, Ge, Sn, or Pb atoms, and to compare them with the standard $\sigma_R^+$ values for the same substituents bonded to the benzene ring.

## Calculation procedure

The first vertical ionization potentials $I(n_S)$ of non-metal monosulfides determined by photoelectron spectroscopy[7–9]

**Table 1.** The first vertical ionization potentials $I(n_S)$ of XSY molecules and the sums of σ-parameters of substituents X and Y

| Compound | X | Y | $I(n_S)$/eV | $\Sigma\sigma_I$ | $\Sigma\sigma_R^+$ | $\Sigma\sigma_p^+$ | $\Sigma\sigma_\alpha$ |
|---|---|---|---|---|---|---|---|
| **1** | H | H | 10.47 | 0 | 0 | 0 | 0 |
| **2** | H | Me | 9.46 | −0.05 | −0.26 | −0.31 | −0.35 |
| **3** | H | Et | 9.29 | −0.05 | −0.25 | −0.30 | −0.49 |
| **4** | H | Pr | 9.19 | −0.05 | −0.25 | −0.30 | −0.54 |
| **5** | H | Pr$^i$ | 9.14 | −0.03 | −0.25 | −0.28 | −0.62 |
| **6** | H | Bu | 9.15 | −0.05 | −0.25 | −0.30 | −0.57 |
| **7** | H | Bu$^i$ | 9.12 | −0.03 | −0.25 | −0.28 | −0.61 |
| **8** | H | Bu$^s$ | 9.10 | −0.03 | −0.25 | −0.28 | −0.68 |
| **9** | H | Bu$^t$ | 9.03 | −0.07 | −0.19 | −0.26 | −0.75 |
| **10** | H | $CH_2CH=CH_2$ | 9.25 | −0.06 | −0.16 | −0.22 | −0.57 |
| **11** | H | $CH_2Ph$ | 9.25 | 0.17 | −0.45 | −0.28 | −0.70 |
| **12** | H | $CF_3$ | 11.35 | 0.38 | 0.23 | 0.61 | −0.25 |
| **13** | Me | Me | 8.67 | −0.10 | −0.52 | −0.62 | −0.70 |
| **14** | Et | Et | 8.44 | −0.10 | −0.50 | −0.60 | −0.98 |
| **15** | Pr | Pr | 8.34 | −0.10 | −0.50 | −0.60 | −1.08 |
| **16** | Pr$^i$ | Pr$^i$ | 8.26 | −0.06 | −0.50 | −0.56 | −1.24 |
| **17** | Bu | Bu | 8.22 | −0.10 | −0.50 | −0.60 | −1.14 |
| **18** | Bu$^t$ | Bu$^t$ | 8.07 | −0.14 | −0.38 | −0.52 | −1.50 |
| **19** | Me | Pr | 8.49 | −0.10 | −0.51 | −0.61 | −0.89 |
| **20** | Me | Bu$^t$ | 8.38 | −0.12 | −0.45 | −0.57 | −1.10 |
| **21** | Me | $C\equiv CH$ | 8.81 | 0.17 | −0.30 | −0.13 | −0.95 |
| **22** | Me | $CH=CH_2$ | 8.45 | 0.08 | −0.55 | −0.47 | −0.85 |
| **23** | Me | Ph | 8.12 | 0.07 | −0.56 | −0.49 | −1.16 |
| **24** | Me | $CH_2Ph$ | 8.42 | 0.12 | −0.71 | −0.59 | −1.05 |
| **25** | Me | Cl | 9.20 | 0.37 | −0.57 | −0.20 | −0.78 |
| **26** | Me | CN | 10.04 | 0.46 | −0.11 | 0.35 | −0.81 |
| **27** | Et | $CH=CH_2$ | 8.50 | 0.08 | −0.54 | −0.46 | −0.99 |
| **28** | Et | Ph | 8.01 | 0.07 | −0.55 | −0.48 | −1.30 |
| **29** | Et | $CH_2CH=CH_2$ | 8.51 | −0.11 | −0.41 | −0.52 | −1.06 |
| **30** | Pr | $CH=CH_2$ | 8.34 | 0.08 | −0.54 | −0.46 | −1.04 |
| **31** | Bu$^t$ | $CH=CH_2$ | 8.33 | 0.06 | −0.48 | −0.42 | −1.25 |
| **32** | Bu$^t$ | Ph | 8.17 | 0.05 | −0.49 | −0.44 | −1.56 |
| **33** | $H_2C=CH$ | $CH=CH_2$ | 8.44 | 0.26 | −0.58 | −0.32 | −1.00 |
| **34** | $H_2C=CHCH_2$ | $CH_2CH=CH_2$ | 8.55 | −0.12 | −0.32 | −0.44 | −1.14 |
| **35** | $H_2C=CH$ | Ph | 8.18 | 0.25 | −0.59 | −0.34 | −1.31 |
| **36** | $H_2C=CHCH_2$ | Ph | 8.13 | 0.06 | −0.46 | −0.40 | −1.38 |
| **37** | F | F | 10.31 | 0.90 | −1.04 | −0.14 | 0.26 |
| **38** | Br | Br | 9.36 | 0.90 | −0.60 | 0.30 | −1.18 |
| **39** | Cl | Cl | 9.70 | 0.84 | −0.62 | 0.22 | −0.86 |
| **40** | NC | CN | 11.32 | 1.02 | 0.30 | 1.32 | −0.92 |
| **41** | F | CN | 10.93 | 0.96 | −0.37 | 0.59 | −0.33 |
| **42** | Cl | CN | 10.52 | 0.93 | −0.16 | 0.77 | −0.89 |
| **43** | Br | CN | 10.32 | 0.96 | −0.15 | 0.81 | −1.05 |
| **44** | $ClCH_2$ | CN | 10.38 | 0.64 | 0.01 | 0.65 | −1.00 |
| **45** | $F_3C$ | $CF_3$ | 11.35 | 0.76 | 0.46 | 1.22 | −0.50 |
| **46** | Cl | $CF_3$ | 10.70 | 0.80 | −0.08 | 0.72 | −0.68 |

*Note.* The $I(n_S)$ values for compounds **1–11**, **13–18**, **22**, **24**, and **26** were taken from Ref. 7 and those for compounds **12**, **19–21**, **23**, **25**, **27–36**, **39**, **40**, and **44–46** were taken from Ref. 8. The $I(n_S)$ values for compounds **37**, **38**, and **41–43** were taken from Ref. 9; the $\sigma_I$, $\sigma_R^+$, $\sigma_p^+ = \sigma_I + \sigma_R^+$, and $\sigma_\alpha$ values were taken from Refs. 5 and 10.

are listed in Table 1. Photoionization of neutral XSY molecules results in the formation of $XS^{\cdot+}Y$ radical cations.

$$XSY \xrightarrow{h\nu} XS^{\cdot+}Y + e^- \qquad (1)$$

The first ionization potential $I(n_S)$ of $H_2S$ molecule (**1**) (10.47 eV) corresponds to the energy of detachment of an electron from the highest occupied molecular orbital (HOMO) on which the n-electrons of the lone electron pair of the S atom are localized. On going from $H_2S$ to HSY and XSY (see Table 1, compounds **2—46**), the $E_{HOMO}$ energies and $I(n_S)$ are changed due to the interaction of the n-electrons with the X and Y substituents. According to the reported data,[7—9,11] the preferred HOMO localization on the S atom is retained.

Studies of conjugation in $(H)XS^{\cdot+}Y$ radical cations using the $I(n_S)$ values can be based on the main results of the analysis of the first ionization potentials ($I_1$) for $XR_\pi$ (X is organic, organometallic, or inorganic substituent; $R_\pi$ = C≡CH, $CH=CH_2$, aromatic, or heteroaromatic substituent) compounds.[5,16] The $I_1$ values correspond to detachment of an electron from the HOMO of the π-type and by definition are equal to the difference between the total energies of the $XR_\pi^{\cdot+}$ radical cation ($E_{tot}^{\cdot+}$) and the corresponding neutral molecule $XR_\pi$ ($E_{tot}$)

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

Calculation of $I_1$ values is a rather complicated problem even for modern quantum chemistry (see, *e.g.*, Ref. 9). In particular, considerable difficulties arise when calculating the relaxation and correlation energies (*R* and *C*, respectively), which characterize changes in the composition of the wave functions of the $XR_\pi$ molecule due to its transformation into the $XR_\pi^{\cdot+}$ radical cation (see Ref. 9).

Taking into account the *R* and *C* contributions, the expression for $I_1$ can be written[12] as

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

As is known,[7,8] the Koopmans approximation

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

ignores the *R* and *C* contributions to $I_1$ and, hence, the rearrangement of the electronic system of the $XR_\pi$ molecule caused by its transformation into the $XR_\pi^{\cdot+}$ radical cation. Previously,[5,6] we showed that the Koopmans approximation (Eq. (4)) is valid for none of the $XR_\pi$ series studied (the acetylene, ethylene, benzene, hexafluorobenzene, naphthalene, anthracene, furan, thiophene, selenophene, and tellurophene derivatives), which means that the experimental $I_1$ value cannot be used as an exact measure of the HOMO energy.

At the same time, the following relationship is valid for all the $XR_\pi$ series studied[5,6]:

$$I_1 = I_H + a\sigma_I + b\sigma_R^+ + c\sigma_\alpha, \qquad (5)$$

where $I_H$ is the $I_1$ value for the unsubstituted $R_\pi H$ molecule; $\sigma_I$, $\sigma_R^+$, and $\sigma_\alpha$ are parameters characterizing the inductive, resonance, and polarizability effects of the substituent X, respectively; and *a*, *b*, and *c* are coefficients dependent on the type of the indicator center $R_\pi$.

Judging from the data of quantum-chemical calculations of neutral $XR_\pi$ ($R_\pi$ = C≡CH, $CH=CH_2$, Ph) molecules, the resonance effects of substituent X on the $E_{HOMO}$ and $I_1$ values are described by the $\sigma_R^0$ constants[13] and $\sigma_R^+$ parameters (Eq. (5)), respectively. The radical cation center $R_\pi^{\cdot+}$ is a typical electron-deficient center, and its conjugation with substituent X is quantitatively characterized by electrophilic $\sigma_R^+$ parameters (see Refs. 1—6, 10).

In addition to the inductive and resonance effects of substituent X, the stabilizing electrostatic attraction between the positive charge of the radical cation (*q*) and the dipole moment induced in the substituent X plays an important role in radical cations $XR_\pi^{\cdot+}$. In classical electrostatics, the energy of such a stabilization is defined by the following formula:

$$E_{st} = -q^2\alpha/(2\varepsilon R^4), \qquad (6)$$

where α is the polarizability of substituent X, ε is the dielectric constant, and *R* is the distance between the charge and the induced dipole.[14] Some problems arise when formula (6) is used for calculating the electrostatic stabilization of organic cations of the $XR_\pi^+$ (X = Alk) type.[14] It is possible to circumvent these difficulties by introducing an additional parameter ($\sigma_\alpha$) characterizing the polarizability effect of substituent X into the Hammett—Taft correlation equations (relation (5)) in addition to the $\sigma_I$ and $\sigma_R^+$ parameters. The $\sigma_\alpha$ constants for a large number of substituents X were calculated by *ab initio* quantum-chemical methods[10,15] and are widely used in studies of ionic reactions in the gas phase.[10,15] Previously,[5,6] we made an indirect assessment of $\sigma_\alpha$ values for several substituents containing atoms of silicon subgroup elements. We assumed that Eq. (5) describing the effect of substituents X on the $I_1$ values of $XR_\pi$ molecules can also be used for studying conjugation in $XS^{\cdot+}Y$ radical cations. The correctness of this assumption was indirectly confirmed by the results of *ab initio* quantum-chemical calculations (in the STO-3G basis set) of π-electron transfer ($q_\pi/e$) between the X substituent and $R_\pi$ for X = $NH_2$, OH, F, $CH=CH_2$, Me, $CF_3$, CN, CHO, and $NO_2$ in three groups of cations, namely, $XCH=CHCH_2^+$ (I), $4\text{-}XC_6H_4CH_2^+$ (II), and $XCH_2^+$ (III).[16]

Let us denote the $q_\pi$ values for groups I, II, and III as $q_\pi$(I), $q_\pi$(II), and $q_\pi$(III), respectively. Statistical processing of the known $q_\pi$ values revealed linear dependences (7)—(9). The first dependence

$$q_\pi(\mathrm{I}) = 1.45q_\pi(\mathrm{II}) - 0.030, \qquad (7)$$
$$S_a = 0.06,\ S_b = 0.008,\ S_Y = 0.017,\ r = 0.994,\ n = 9,$$

has a very high correlation coefficient and confirms similarity of resonance effects in typical conjugated systems I and II.[2,3] The dependences

$$q_\pi(\mathrm{III}) = 1.29q_\pi(\mathrm{I}) - 0.056, \qquad (8)$$
$$S_a = 0.11,\ S_b = 0.024,\ S_Y = 0.045,\ r = 0.976,\ n = 9;$$

$$q_\pi(\mathrm{III}) = 1.84q_\pi(\mathrm{II}) - 0.098, \qquad (9)$$
$$S_a = 0.22,\ S_b = 0.029,\ S_Y = 0.062,\ r = 0.955,\ n = 9,$$

are much less satisfactory. One of the reasons is, in particular, the "leveling" of the resonance properties of typical donor substituents X ($NH_2$, OH, F) in the $XCH_2^+$ cations (see Ref. 16). Nevertheless, the fact that the linear dependences (8) and (9) are valid makes it possible to draw an analogy between the conjugation in typical conjugated systems and in the $XCH_2^+$ cations and, hence, in the $XS^{\cdot+}Y$ radical cations as well. The latter have both the unpaired electron and vacant 3d-orbitals of the S atom,[17] which provides an additional way for resonance interaction to occur.

Correlation equations were obtained using the STATGRAPHICS 3.0 program package on an IBM AT 286 personal computer. The data were processed by the least squares method at a 95% confidence level.

## Results and Discussion

The following correlation equations are valid for the ionization potentials (IP) of molecules **1—46** (see Table 1):

$$I(n_S) = 9.40 + 1.75\Sigma\sigma_p^+, \qquad (10)$$
$$S_a = 0.06,\ S_b = 0.12,\ S_Y = 0.42,\ r = 0.908,\ n = 46;$$

$$I(n_S) = 9.50 + 1.64\Sigma\sigma_I + 1.93\Sigma\sigma_R^+, \qquad (11)$$
$$S_a = 0.12,\ S_b = 0.17,\ S_c = 0.24,\ S_Y = 0.42,\ r = 0.906,\ n = 46.$$

The low correlation coefficients $r$ of Eqs. (10) and (11) indicate that not only the inductive and resonance effects of substituents X and Y affect the $I(n_S)$ values.

Introduction of the $\sigma_\alpha$ parameter characterizing stabilization of the charge $q$ of the radical cation due to the polarizability effects of substituents X and Y leads to the following equations:

$$I(n_S) = 10.31 + 1.51\Sigma\sigma_p^+ + 1.09\Sigma\sigma_\alpha, \qquad (12)$$
$$S_a = 0.06,\ S_b = 0.04,\ S_c = 0.06,\ S_Y = 0.15,\ r = 0.989,\ n = 46;$$

$$I(n_S) = 10.34 + 1.46\Sigma\sigma_I + 1.60\Sigma\sigma_R^+ + 1.08\Sigma\sigma_\alpha, \qquad (13)$$
$$S_a = 0.06,\ S_b = 0.06,\ S_c = 0.09,\ S_d = 0.06,$$
$$S_Y = 0.15,\ r = 0.989,\ n = 46,$$

for which the correlation coefficients are much higher, whereas the standard errors are much lower than those for relations (10) and (11).

The influence of the inductive and resonance effects of substituents X and Y on the $I(n_S)$ values is easily seen even in the Koopmans approximation (4). The increase in the electron donor effect of substituents X and Y (increase in the negative $\sigma_I$, $\sigma_R^+$, and $\sigma_p^+$ values) decreases the $I(n_S)$ values, thus destabilizing the HOMO *via* increasing its energy. The acceptor effect of substituents X and Y on the $I(n_S)$ value is oppositely directed. An increase in the polarizability of substituents X and Y (increase in the negative $\sigma_\alpha$ values) stabilizes the charge $q$ (see Eq. (6)), thus decreasing the total energy of the radical cation ($E_{tot}{}^{\cdot +}$ in Eq. (2)) and the $I_1$ and $I(n_S)$ ionization potentials.

Using Eq. (13), we can calculate the contributions of the inductive effect ($In = 1.46\Sigma\sigma_I$), conjugation ($Res = 1.60\Sigma\sigma_R^+$), and polarizability ($P = 1.08\Sigma\sigma_\alpha$) to the $I(n_S)$ values of substituents X and Y. The *In*, *Res*, and *P* contributions for the series of compounds **1—46** are 1.7, 2.4, and 2.0 eV (28, 40, and 32%), respectively (see Table 1). For each compound the ratio of these contributions depends on the nature of substituents X and Y. For instance, on going from $H_2S$ to $Me_2S$ the *In*, *Res*, and *P* contributions to the change in the IP are 0.15, 0.83, and 0.76 eV (8, 48, and 44%, respectively), whereas on going from $H_2S$ to $Bu^t{}_2S$ they are equal to 0.20, 0.61, and 1.62 eV (8, 25, and 67%, respectively). Hence, the Koopmans approximation (4), which ignores the *P* contribution to the IP value, is invalid for both $XR_\pi$[5,6] and XSY molecules.

The absolute terms of Eqs. (12) and (13) (10.31 and 10.34 eV, respectively) are somewhat smaller than the IP of $H_2S$ (10.47 eV). This requires a separate analysis of the IP values of HSY and XSY compounds, which can be considered as mono- and disubstituted derivatives of hydrogen sulfide.

The following equations are valid for disubstituted XSY derivatives (compounds **13—46**, series *A*):

$$I(n_S) = 10.25 + 1.49\Sigma\sigma_p^+ + 1.03\Sigma\sigma_\alpha, \qquad (14)$$
$$S_a = 0.08,\ S_b = 0.05,\ S_c = 0.08,\ S_Y = 0.15,\ r = 0.990,\ n = 34;$$

$$I(n_S) = 10.33 + 1.43\Sigma\sigma_I + 1.56\Sigma\sigma_R^+ + 1.07\Sigma\sigma_\alpha, \qquad (15)$$
$$S_a = 0.13,\ S_b = 0.08,\ S_c = 0.10,\ S_d = 0.09,\ S_Y = 0.15,$$
$$r = 0.990,\ n = 34.$$

The corresponding equations for monosubstituted HSY derivatives (compounds **2—12**, series *B*) are

$$I(n_S) = 10.42 + 1.98\Sigma\sigma_p^+ + 1.12\Sigma\sigma_\alpha, \qquad (16)$$
$$S_a = 0.11,\ S_b = 0.12,\ S_c = 0.22,\ S_Y = 0.08,\ r = 0.993,\ n = 11;$$

$$I(n_S) = 10.38 + 2.46\Sigma\sigma_I + 1.50\Sigma\sigma_R^+ + 1.25\Sigma\sigma_\alpha, \qquad (17)$$
$$S_a = 0.05,\ S_b = 0.10,\ S_c = 0.10,\ S_d = 0.10,$$
$$S_Y = 0.03,\ r = 0.999,\ n = 11.$$

Joint consideration of $H_2S$ and its monosubstituted derivatives (compounds **1—12**, series *C*) leads to Eqs. (18) and (19) instead of Eqs. (16) and (17)

$$I(n_S) = 10.45 + 1.96\Sigma\sigma_p^+ + 1.19\Sigma\sigma_\alpha, \qquad (18)$$
$$S_a = 0.06,\ S_b = 0.10,\ S_c = 0.13,\ S_Y = 0.07,\ r = 0.994,\ n = 12;$$

$$I(n_S) = 10.44 + 2.42\Sigma\sigma_I + 1.48\Sigma\sigma_R^+ + 1.36\Sigma\sigma_\alpha, \qquad (19)$$
$$S_a = 0.03,\ S_b = 0.10,\ S_c = 0.10,\ S_d = 0.07,$$
$$S_Y = 0.04,\ r = 0.999,\ n = 12.$$

The absolute terms of Eqs. (14)—(19) increase on going from series *A* to series *B* and further to series *C* and virtually coincide with the IP of $H_2S$ in the last-named case. It is believed that this is due to hyperconjugation, *i.e.*, the additional resonance donor effect of certain substituents toward the radical cation center $S^{\cdot +}$. All things being the same, the increase in this effect must decrease the $I(n_S)$ value and, hence, the absolute terms in Eqs. (14)—(19). According to conventional concepts (see, *e.g.*, Ref. 3), the alkyl groups R at the reaction (indicator) center play the dominating role in hyperconjugation. The number of compounds containing R—S fragments is maximum for series *A* and minimum for series *C*. Therefore, the contribution of hyperconjugation to the decrease in the absolute term

**Table 2.** The $\sigma_p^+$ and $\sigma_R^+$ parameters of organometallic substituents calculated from the $I(n_S)$ values of XSY molecules using Eqs. (12), (14), and (16)

| Compound | X | Y | $I(n_S)$ /eV | $\Sigma\sigma_\alpha(X + Y)$ | $\Sigma\sigma_p^+(X + Y)$ | $\sigma_p^+(X)$ | $\sigma_p^+(Y)$ | $\sigma_I(Y)$ | $\sigma_R^+(Y)$ ($\sigma_R^+(S)$) | $\sigma_R^+(B)$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **47** | H | $SiH_3$ | 9.97 | −0.59 | 0.11 | 0 | 0.11 | −0.04 | 0.15 | 0.03 |
| | | | | | 0.20 | 0 | 0.20 | | 0.24 | |
| **48** | Me | $SiH_3$ | 9.10 | −0.94 | −0.12 | −0.31 | 0.19 | −0.04 | 0.23 | |
| | | | | | −0.12 | −0.31 | 0.19 | | 0.23 | |
| **49** | $H_3Si$ | $SiH_3$ | 9.70 | −1.18 | 0.44 | 0.22 | 0.22 | −0.04 | 0.26 | |
| | | | | | 0.45 | 0.22 | 0.22 | | 0.26 | |
| | | | | | | | | | (0.24) | |
| **50** | Me | $SiMe_3$ | 8.69 | −1.07 | −0.31 | −0.31 | 0.00 | −0.15 | 0.15 | 0.02 |
| | | | | | −0.30 | −0.31 | 0.01 | | 0.16 | |
| **51** | $Me_3Si$ | $SiMe_3$ | 8.74 | −1.44 | −0.02 | −0.01 | −0.01 | −0.15 | 0.14 | |
| | | | | | 0 | 0 | 0 | | 0.15 | |
| | | | | | | | | | (0.15) | |
| **52** | Me | $GeMe_3$ | 8.50 | −0.95 | −0.52 | −0.31 | −0.21 | −0.11 | −0.10 | −0.11 |
| | | | | | −0.51 | −0.31 | −0.20 | | −0.09 | |
| **53** | $Me_3Ge$ | $GeMe_3$ | 8.40 | −1.20 | −0.42 | −0.21 | −0.21 | −0.11 | −0.10 | |
| | | | | | −0.40 | −0.20 | −0.20 | | −0.09 | |
| | | | | | | | | | (−0.10) | |
| **54** | Me | $SnMe_3$ | 8.37 | −0.95 | −0.60 | −0.31 | −0.29 | −0.13 | −0.16 | −0.21 |
| | | | | | −0.60 | −0.31 | −0.29 | | −0.16 | |
| **55** | $Me_3Sn$ | $SnMe_3$ | 8.22 | −1.20 | −0.54 | −0.27 | −0.27 | −0.13 | −0.14 | |
| | | | | | −0.52 | −0.26 | −0.26 | | −0.13 | |
| | | | | | | | | | (−0.15) | |
| **56** | Me | $PbMe_3$ | 8.13 | −0.95 | −0.76 | −0.31 | −0.45 | −0.12 | −0.33 | −0.26 |
| | | | | | −0.76 | −0.31 | −0.45 | | −0.33 | |
| **57** | $Me_3Pb$ | $PbMe_3$ | 7.78 | −1.20 | −0.83 | −0.41 | −0.41 | −0.12 | −0.29 | |
| | | | | | −0.80 | −0.40 | −0.40 | | −0.28 | |
| | | | | | | | | | (−0.31) | |
| **58** | H | $CH_2SiMe_3$ | 8.96 | −0.66 | −0.36 | 0 | −0.36 | −0.05 | −0.31 | −0.49 |
| | | | | | −0.42 | 0 | −0.42 | | −0.37 | |
| **59** | Me | $CH_2SiMe_3$ | 8.35 | −1.01 | −0.58 | −0.31 | −0.27 | −0.05 | −0.22 | |
| | | | | | −0.57 | −0.31 | −0.26 | | −0.21 | |
| **60** | $Me_3SiCH_2$ | $CH_2SiMe_3$ | 8.03 | −1.32 | −0.58 | −0.29 | −0.29 | −0.05 | −0.24 | |
| | | | | | −0.55 | −0.28 | −0.28 | | −0.23 | |
| | | | | | | | | | (−0.37) | |
| **61** | Me | $CH_2Si(OMe)_3$ | 8.50 | −0.97 | −0.50 | −0.31 | −0.19 | −0.10 | −0.09 | −0.14 |
| | | | | | −0.50 | −0.31 | −0.19 | | −0.09 | |
| **62** | Et | $CH_2Si(OMe)_3$ | 8.35 | −1.11 | −0.50 | −0.30 | −0.20 | −0.10 | −0.10 | |
| | | | | | −0.51 | −0.30 | −0.21 | | −0.11 | |
| **63** | Pr | $CH_2Si(OMe)_3$ | 8.29 | −1.16 | −0.50 | −0.30 | −0.20 | −0.10 | −0.10 | |
| | | | | | −0.52 | −0.30 | −0.22 | | −0.12 | |
| **64** | $Bu^n$ | $CH_2Si(OMe)_3$ | 8.27 | −1.19 | −0.49 | −0.30 | −0.19 | −0.10 | −0.09 | |
| | | | | | −0.50 | −0.30 | −0.20 | | −0.10 | |
| **65** | $Bu^i$ | $CH_2Si(OMe)_3$ | 8.21 | −1.23 | −0.50 | −0.28 | −0.22 | −0.10 | −0.12 | |
| | | | | | −0.52 | −0.28 | −0.24 | | −0.14 | |
| **66** | $Bu^t$ | $CH_2Si(OMe)_3$ | 8.11 | −1.37 | −0.47 | −0.26 | −0.21 | −0.10 | −0.11 | |
| | | | | | −0.49 | −0.26 | −0.23 | | −0.13 | |
| | | | | | | | | | (−0.11) | |
| **67** | H | $CH(SiMe_3)_2$ | 8.55 | −0.97 | −0.39 | 0 | −0.39 | −0.05 | −0.34 | −0.55 |
| | | | | | −0.46 | 0 | −0.46 | | −0.41 | |
| | | | | | | | | | (−0.41) | |
| **68** | H | $C(SiMe_3)_3$ | 8.18 | −1.28 | −0.41 | 0 | −0.41 | −0.05 | −0.36 | −0.63 |
| | | | | | −0.48 | 0 | −0.48 | | −0.43 | |
| **69** | Me | $C(SiMe_3)_3$ | 7.66 | −1.63 | −0.62 | −0.31 | −0.31 | −0.05 | −0.26 | |
| | | | | | −0.57 | −0.31 | −0.26 | | −0.21 | |
| | | | | | | | | | (−0.43) | |

*Note.* The $I(n_S)$ values for compounds **47—51**, **58—60**, and **67—69** were taken from Refs. 18, 19 and those for compounds **52—57** were taken from Ref. 20. The $I(n_S)$ values for compounds **61—66** were taken from Ref. 21. The $\sigma_I$ and $\sigma_\alpha$ values were taken from Refs. 2, 5, and 6; the $\sigma_\alpha$ parameter for $CH_2Si(OMe)_3$ was calculated from the $\sigma_\alpha$ value of $Si(OEt)_3$ (−0.63)[6] using the known procedure.[22] The $\sigma_R^+(B)$ values were taken from Ref. 2.

values of the equations considered is maximum for series *A* and minimum for series *C*.

As the IP of molecules **1—46** (see Table 1), the vertical ionization potentials $I(n_S)$ of Si-, Ge-, Sn-, and Pb-containing XSY compounds **47—69** (Table 2) correspond to detachment of an electron from the HOMO localized mainly on the S atom.[18—21] We calculated the $\sigma_p^+(Y)$ parameters of organometallic substituents Y (see Table 2) from the $I(n_S)$ and $\sigma_\alpha$ values using Eqs. (12), (14), and (16). Two $\sigma_p^+(Y)$ values are given in Table 2 for each Y. The first values were calculated using the general equation (12), which is valid for $H_2S$ and any its derivatives. The second $\sigma_p^+(Y)$ values were calculated from the IP of the molecules of the XSY type using Eq. (14) for compounds **48—57**, **59—66**, and **69** or from the IP of the molecules of the HSY type using Eq. (16) for compounds **47**, **58**, **67**, and **68**.

The first and second $\sigma_p^+(Y)$ values for substituents Y in the XSY molecules differ only slightly. Based on the aforesaid hyperconjugation considerations, we believe that the second $\sigma_p^+(Y)$ values for substituents Y in the HSY molecules are more accurate so only they are used below.

The resonance $\sigma_R^+(Y)$ parameters of organometallic substituents Y and their most reliable values of $\sigma_R^+(S)$ listed in parentheses in Table 2 were calculated from the relationship $\sigma_R^+(Y) = \sigma_p^+(Y) - \sigma_I(Y)$. The $\sigma_R^+(S)$ parameters for the resonance acceptors of the $-M$-type and not too strong donors of the $+M$-type ($Me_3M$ substituents with M = Si, Ge, Sn, Pb) were calculated as the arithmetic means of four close $\sigma_R^+(Y)$ values (five values for $SiH_3$ and twelve values for $CH_2Si(OMe)_3$). The $\sigma_R^+(Y)$ parameters for strong resonance $+M$-donors (the $CH_2SiMe_3$, $CH(SiMe_3)_2$, and $C(SiMe_3)_3$ substituents) change over a wider range. Negative $\sigma_R^+(Y)$ values decrease on going from HSY to MeSY or YSY compounds (**58—60** and **68**, **69**, respectively; Y = $CH_2SiMe_3$, $C(SiMe_3)_3$). This is likely due to the negative direct polar (counter-) conjugation between the Me and Y substituents, as well as between the two Y substituents. This effect was reported for several organometallic systems.[4,23—25] It weakens the $+M$-donor properties of substituents Y (their $\sigma_R^+(Y)$ parameters increase). Therefore the $\sigma_R^+(Y)$ values for the $HSC(SiMe_3)_nH_{3-n}$ ($n$ = 1—3) molecules with no counterconjugation are the most reliable values of the $\sigma_R^+(S)$ parameters (see Table 2) for the $C(SiMe_3)_nH_{3-n}$ substituents.

~~Let us compare the values of the $\sigma_R^+(S)$ parameters~~ with the standard $\sigma_R^+(B)$ values (see Table 2) used for quantitative characterization of conjugation between the substituents (including organometallic ones) and the benzene ring, which either carries a large excess positive charge[2] or is a radical cation center.[5,6]

The substituents can be divided into three groups:

1. Resonance acceptors of the $-M$-type, namely, $SiH_3$ and $SiMe_3$ ($\sigma_R^+(S) > \sigma_R^+(B)$), for which d,n-conjugation is stronger than both σ,n-conjugation in $S^{\cdot+}$—$SiR_3$ radical cations and d,π-conjugation in $^{+\cdot}PhSiR_3$ (R = H, Me).

2. Not too strong resonance donors of the $+M$-type, namely, $GeMe_3$, $SnMe_3$, $PbMe_3$, and $CH_2Si(OMe)_3$ ($\sigma_R^+(S) \approx \sigma_R^+(B)$), for which the effects of σ,n- and σ,π-conjugation in $S^{\cdot+}$—$MMe_3$ and $^{+\cdot}PhMMe_3$ (M = Ge, Sn, Pb) radical cations are commensurable in magnitude and dominate over d,n- and d,π-conjugation.

3. Typical resonance donors of the $+M$-type, namely, $CH_2SiMe_3$, $CH(SiMe_3)_2$, and $C(SiMe_3)_3$ ($\sigma_R^+(S) < \sigma_R^+(B)$), for which the effect of σ,n-conjugation in $S^{\cdot+}$—$C(SiMe_3)_nH_{3-n}$ radical cations is weaker than σ,π-conjugation in $^{+\cdot}PhC(SiMe_3)_nH_{3-n}$ ($n$ = 1—3).

By definition, no d,n- and d,π-conjugation can occur with participation of $CH_2Si(OMe)_3$ and $C(SiMe_3)_nH_{3-n}$ substituents.[1—3]

As is known,[5,6] the $\sigma_R^+(B)$ values are related by linear dependences to the $\sigma_R^+(E)$, $\sigma_R^+(A)$, $\sigma_R^+(N)$, $\sigma_R^+(F)$, and $\sigma_R^+(T)$ parameters characterizing resonance interactions in organometallic derivatives of ethylene (E), acetylene (A), naphthalene (N), furan (F),

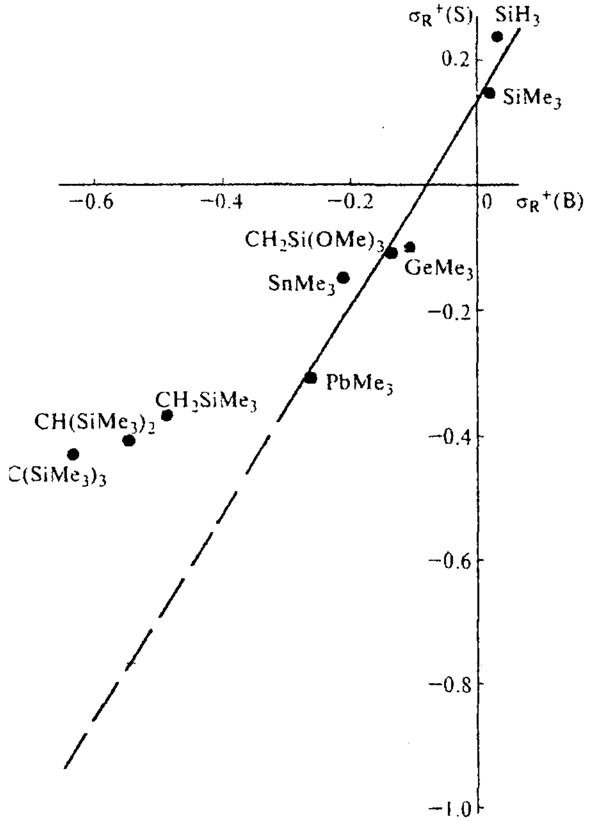

**Fig. 1.** Dependence of $\sigma_R^+(S)$ and $\sigma_R^+(B)$ parameters characterizing the conjugation of substituents with an $S^{\cdot+}$ radical cation center and a benzene ring, respectively.

and thiophene (T). Unlike these dependences, the linear equation relating the $\sigma_R{}^+(S)$ parameters to the $\sigma_R{}^+(B)$ ones

$$\sigma_R{}^+(S) = 0.92\sigma_R{}^+(B) + 0.07, \tag{20}$$

$S_a = 0.13$, $S_b = 0.05$, $S_Y = 0.09$, $r = 0.934$, $n = 9$,

has the low correlation coefficient *r*.

The more satisfactory correlation

$$\sigma_R{}^+(S) = 1.68\sigma_R{}^+(B) + 0.14, \tag{21}$$

$S_a = 0.19$, $S_b = 0.03$, $S_Y = 0.05$, $r = 0.975$, $n = 6$,

is observed between the $\sigma_R{}^+(S)$ and $\sigma_R{}^+(B)$ parameters for the $SiH_3$, $SiMe_3$, $GeMe_3$, $SnMe_3$, $PbMe_3$, and $CH_2Si(OMe)_3$ substituents. The deviation of the $\sigma_R{}^+(S)$ values for the $CH_2SiMe_3$, $CH(SiMe_3)_2$, and $C(SiMe_3)_3$ substituents from the linear dependence (21) toward larger values is 0.31, 0.37, and 0.48, respectively (see Fig. 1). Judging from the values of the $\sigma_R{}^+(B)$ parameters, the $C(SiMe_3)_nH_{3-n}$ ($n$ = 1—3) substituents are much stronger resonance donors than $MMe_3$ (M = Ge, Sn, Pb) and $CH_2Si(OMe)_3$ (see Table 2 and Ref. 2). At the same time, unlike $MMe_3$ and $CH_2Si(OMe)_3$, the $C(SiMe_3)_nH_{3-n}$ substituents are much weaker donors toward the $S^{\cdot+}$ radical cation center .

Thus, typical $+M$-substituents in the $S^{\cdot+}$—$C(SiMe_3)_nH_{3-n}$ radical cations and in $^+CH_2X$ (X = $NH_2$, OH, F) cations[16] behave analogously. Their resonance donor properties toward the $S^{\cdot+}$ and $^+CH_2$ indicator centers appear to be weaker than those expected from correlation dependences for the series of compounds in which the above-mentioned substituents are the constituents of the classical conjugated systems.

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