

Nongeneral Character of the Resonance Parameters Σ_R^+ of Silicon-, Germanium-, and Tin-Containing Substituents in Radical Cations

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Abstract—The resonance parameters σ_R^+ of substituents Y in radical cations $YD^{+\cdot}$ [where D is a π - or n -type center, and Y = MMe_3 , CH_2MMe_3 (M = Si, Ge, Sn), $C(SiMe_3)_3$] depend on the nature of both Y and D. Using radical cations $YD^{+\cdot}$ (Y = CH_2SiMe_3 , $SnMe_3$) as examples, it was found that the two conjugation parameters, constants σ_R^+ of substituents Y and perturbation energy calculated by the modified molecular orbital perturbation method, are linearly related to each other. The energies of donor and acceptor components of the overall resonance effect of CH_2SiMe_3 and $SnMe_3$ with respect to radical cation centers $D^{+\cdot}$ were estimated for the first time. The donor energy constituent in $YD^{+\cdot}$ is considerably greater than in neutral DY molecules.

In keeping with the modern views [1, 2], conjugation in $DMMe_3$ and DCH_2MMe_3 molecules is determined by properties of both MMe_3 or CH_2MMe_3 substituent (M = Si, Ge, Sn) and reaction center D; the latter may be an α,β -unsaturated or aromatic hydrocarbon radical (R_π), as well as an atom (X) possessing unshared electron pairs. Therefore, the ability of substituents like MMe_3 and CH_2MMe_3 to be involved in conjugation with D cannot be described by universal resonance parameters like σ_R which are invariant from D. The absence of universality is closely related to the mechanism of conjugation in molecules like $DMMe_3$ and DCH_2MMe_3 , which is more complex than in analogous carbon derivatives (M = C).

The mechanism of conjugation is based on the concept involving dual (acceptor and donor simultaneously) resonance properties of MMe_3 substituents (M = Si, Ge, Sn) with respect to D in $DMMe_3$ molecules [1, 2]. Acceptor resonance effect (d,π or d,n conjugation) implies interaction between vacant nd orbitals of atoms M and antibonding σ^* orbitals of the M–C bonds in MMe_3 , on the one hand, and R_π group (or X atom), on the other. This effect becomes weaker as the atomic number of M rises in the series $Si > Ge > Sn$; when M = C, acceptor resonance effect is absent. Donor resonance effect (σ,π or σ,n conjugation) is interaction between σ orbitals of the M–C bond in MMe_3 and R_π group (or X atom), and it becomes

stronger as the atomic number of M rises ($C < Si < Ge < Sn$); i.e., the effect is minimal for M = C.

The CH_2MMe_3 substituents in DCH_2MMe_3 molecules act as weak acceptors and strong donors with respect to D [1]. Clearly predominating donor resonance effect of σ,π and σ,n conjugation originates from interaction between σ orbitals of the C–M bonds in CH_2MMe_3 and R_π group (or X) [1, 2]. As with MMe_3 , the effect increases in the M series $C < Si < Ge < Sn$.

Weak and poorly studied [1] acceptor resonance effect of CH_2MMe_3 substituents originates from σ^*,π (or σ^*,n) conjugation, i.e., interaction between antibonding σ^* orbitals of the CH_2 –M bond and R_π (or X). It will be shown below that effects of σ^*,π and σ^*,n conjugation in DCH_2MMe_3 , despite their lesser importance as compared to donor σ,π and σ,n conjugation, are not negligible. Of the two opposite constituents of the overall resonance effect (acceptor and donor), only σ,π conjugation (and probably σ,n) depends on the charge on D [1, 2]. As the positive charge on D rises, donor resonance effects in $DMMe_3$ and DCH_2MMe_3 become stronger the more so as the atomic number of element M is larger. This relation was studied most thoroughly for substituted benzenes (D = Ph).

In keeping with available data [1, 2], the greater the atomic number of M and the positive charge on D, the

Table 1. Resonance parameters σ_R^+ of MMe_3 , CH_2MMe_3 , and $\text{C}(\text{SiMe}_3)_3$ substituents in Me_3MD^+ , $\text{Me}_3\text{MCH}_2\text{D}^+$, and $(\text{Me}_3\text{Si})_3\text{CD}^+$ radical cations^a

D	SiMe ₃	GeMe ₃	SnMe ₃	CH ₂ SiMe ₃	C(SiMe ₃) ₃	CH ₂ GeMe ₃	CH ₂ SnMe ₃
Phenyl [1, 2]	0.02	-0.11	-0.21	-0.49	-0.63	-0.59	-0.76
2-Furyl [3]	0.17	0.05	-0.05	-0.25	-	-	-
2-Thienyl [3]	0.25	0.01	-0.01	-0.27	-	-	-
H ₂ C=CH [4]	-0.03	-0.15	-0.30 ^b	-0.65	-0.89 ^b	-0.83	-1.00
HC≡C [5]	0.00	-0.22	-0.33 ^b	-0.74	-0.98 ^b	-0.92	-1.19
-N< [6]	2.79 (0.93)	-	-0.16 (-0.05)	-0.23 (-0.08)	-	-	-
-P< [7]	0.54 (0.18)	-	-0.33 (-0.11)	-0.60 (-0.20)	-	-	-
CH ₃ S [8]	0.15	-0.10	-0.16	-0.37	-0.43	-0.86 ^b	-1.16 ^b
-Se- [8]	-	-	-0.20 (-0.10)	-	-	-	-
Cl [9]	0.05	-0.47	-0.58	-	-1.13 ^b	-2.01 ^b	-2.61 ^b
Br [9]	0.08	-0.44	-0.57	-0.46 ^b	-1.09 ^b	-1.97 ^b	-2.56 ^b
I [9]	-	-	-0.37	-	-	-	-

^a Hereinafter, the sum of σ_R^+ of three or two substituents attached to D is given. The σ_R^+ value of a single substituent is given in parentheses.

^b Calculated by Eqs. (1)–(5).

less general should be the resonance parameters of MMe_3 and CH_2MMe_3 . We are now capable of studying donor resonance effect in derivatives with D other than Ph. This is favored by accumulation of data (though poorly analyzed) on resonance effects in radical cations Me_3MD^+ and $\text{Me}_3\text{MCH}_2\text{D}^+$ [3–9] having a large positive charge on various D centers. We anticipated that study of such radical cations will make it possible to analyze donor effects of σ, π and σ, n conjugation (which are the main factor responsible for nongeneral character of resonance parameters of organometallic substituents) provided that acceptor effects of d, π and d, n conjugation (in Me_3SnD^+) or σ^*, π and σ^*, n conjugation (in $\text{Me}_3\text{MCH}_2\text{D}^+$) are less important.

The goal of the present work was to study general relations holding in conjugation in radical cations Me_3MD^+ and $\text{Me}_3\text{MCH}_2\text{D}^+$, depending on the nature of D and M (M = Si, Ge, Sn), and estimate the energies of σ, π and σ, n conjugation in systems where these effects clearly predominate over acceptor d, π , d, n , σ^*, π , and σ^*, n conjugation effects.

In order to estimate the energy of σ, π and σ, n conjugation we used the molecular orbital perturbation method. We modified the traditional procedure based on the Koopmans approximation [10]. The procedure considered in detail below is free from the above approximation, so that it makes it possible for the first time to take into account not only inductive but also

polarization effect on the energy of initial orbitals. The correlation equations were calculated using standard Statgraphics 3.0 software on a PC AT-286. The data were processed by the least-squares procedure to a confidence probability of 95%.

Conjugation in molecules like DMMe_3 and DCH_2MMe_3 (M = Si, Ge, Sn) which possess a large positive charge on the D center (e.g., in radical cations Me_3MD^+ and $\text{Me}_3\text{MCH}_2\text{D}^+$) is quantitatively characterized by electrophilic resonance parameters σ_R^+ of MMe_3 and CH_2MMe_3 substituents [1–9]. Until recently, σ_R^+ values for organometallic substituents (which are arbitrarily referred to as primary) were known only for phenyl and benzyl derivatives (D = Ph, Table 1) which were extensively studied by chemical and spectral methods [1, 2]. The corresponding values for other D became accessible only as a result of our studies [3–9] (Table 1). Let us consider general relations holding in variation of σ_R^+ for MMe_3 and CH_2MMe_3 , depending on the nature of M and D.

First of all, it should be emphasized that, due to the presence of a large positive charge on D, the parameters σ_R^+ characterize conjugation under the conditions which (as noted above) are the most favorable for donor resonance effects (σ, π and σ, n conjugation). Here, acceptor resonance effects (d, π , d, n , σ^*, π , and σ^*, n conjugation) do not change appreciably relative to those in neutral molecules, i.e., when no charge is present on D [1, 2].

As follows from the data in Table 1, variation of D leads to deviation of σ_R^\pm from the corresponding primary values in both directions (toward smaller and larger values) for each of the seven series, DSiMe_3 , DGeMe_3 , DSnMe_3 , $\text{DCH}_2\text{SiMe}_3$, $\text{DC}(\text{SiMe}_3)_3$, $\text{DCH}_2\text{GeMe}_3$, and $\text{DCH}_2\text{SnMe}_3$. This pattern is typical of all σ_R^\pm , including the data in Table 1 marked with note ^b. The latter were calculated from the primary $\sigma_R^\pm(\text{Ph})$ values using correlations (1)–(5) (σ_R^\pm is followed by indication of D in parentheses).

$$\sigma_R^\pm(\text{H}_2\text{C}=\text{CH}) = 1.41\sigma_R^\pm(\text{Ph}), r = 0.988 [4]; \quad (1)$$

$$\sigma_R^\pm(\text{HC}\equiv\text{C}) = 1.56\sigma_R^\pm(\text{Ph}), r = 0.985 [5]; \quad (2)$$

$$\sigma_R^\pm(\text{S}) = 1.68\sigma_R^\pm(\text{Ph}), r = 0.975 [8]; \quad (3)$$

$$\sigma_R^\pm(\text{Cl}) = -0.25 + 2.04\sigma_R^\pm(\text{S}), r = 0.999 [9]; \quad (4)$$

$$\sigma_R^\pm(\text{Br}) = -0.22 + 2.02\sigma_R^\pm(\text{S}), r = 0.997 [9]. \quad (5)$$

It is seen that σ_R^\pm for MMe_3 substituents takes both positive and negative values. Positive values are typical of most members of the DSiMe_3 series; they indicate prevalence of acceptor resonance effect (d,π and d,n conjugation) over donor (σ,π and σ,n conjugation). In going from $M = \text{Si}$ to $M = \text{Ge}$ and Sn within the DMMe_3 series, σ_R^\pm values decrease, and at $M = \text{Sn}$ all σ_R^\pm values are negative. This means that within the DSnMe_3 series σ,π and σ,n conjugation predominates over d,π and d,n conjugation. Donor resonance effect also predominates over acceptor effect for most members of the DGeMe_3 series, but in two cases (small positive σ_R^\pm values) donor and acceptor effects are almost equal in absolute value.

Thus there are both similarity and difference between conjugation effects in neutral DMMe_3 molecules [1, 2] and systems with a large positive charge on the D center, e.g., in $\text{Me}_3\text{MD}^{++}$ radical cations. The similarity implies weakening of acceptor resonance effect (d,π and d,n conjugation) and strengthening of donor resonance effect (σ,π and σ,n conjugation) as the atomic number of M increases. The difference consists of sharp enhancement of σ,π and σ,n conjugation in going from DMMe_3 to $\text{Me}_3\text{MD}^{++}$. For instance, the donor resonance effect in $\text{Me}_3\text{SnD}^{++}$ clearly predominates over acceptor (the σ_R^\pm values are negative at any D; Table 1).

Radical cations $\text{Me}_3\text{MCH}_2\text{D}^{++}$ ($M = \text{Si}, \text{Ge}, \text{Sn}$) and $(\text{Me}_3\text{Si})_3\text{CD}^{++}$ are characterized by only negative σ_R^\pm values. This means that donor resonance effect (σ,π and σ,n conjugation) predominates over acceptor (σ^*,π and σ^*,n conjugation). As with neutral molecules, σ,π and σ,n conjugation becomes stronger as the atomic

number of M rises, and σ_R^\pm values increase in absolute value. In going from neutral molecules (where the conjugation is quantitatively characterized by substituent σ_R^\pm constants) to radical cations, donor resonance effect also strengthens. The σ_R^\pm [1] and σ_R^\pm values (in parentheses) for $\text{PhCH}_2\text{MMe}_3$ are equal to -0.20 (-0.49), -0.21 (-0.59), and -0.24 (-0.76) at $M = \text{Si}, \text{Ge},$ and Sn , respectively. The larger the atomic number of M, the greater the strengthening of donor resonance effect (i.e., the difference $\sigma_R^\pm - \sigma_R^\pm$). This effect also increases in going from $\text{Me}_3\text{SiCH}_2\text{D}^{++}$ to $(\text{Me}_3\text{Si})_3\text{CD}^{++}$ (Table 1) due to increase in the number of C–Si bonds which are more capable of σ,π and σ,n conjugation than C–H bonds.

In order to study nongeneral character of σ_R^\pm parameters of substituents due to their dependence on the nature of the D center, we selected two series of radical cations, $\text{Me}_3\text{SiCH}_2\text{D}^{++}$ and $\text{Me}_3\text{SnD}^{++}$. Our choice was based on the following considerations. First, in the two series donor resonance effect (σ,π and σ,n conjugation) *a priori* predominates over acceptor (σ^*,π , σ^*,n , d,π , and d,n conjugation). Second, the D centers and parameters σ_R^\pm of CH_2SiMe_3 and SnMe_3 substituents vary over a fairly wide range (Table 1). Initially (as a first approximation) we did not take into account acceptor effect to simplify the application of the molecular orbital perturbation method (PMO) [10] to the study of donor σ,π and σ,n conjugation effects.

Let us consider specific properties of the highest occupied molecular orbitals (HOMO) of $\text{DCH}_2\text{SiMe}_3$ and DSnMe_3 molecules. The HOMO in $\text{R}_\pi\text{CH}_2\text{SiMe}_3$ and $\text{R}_\pi\text{SnMe}_3$ is a π -MO which is perturbed via electronic interactions with CH_2SiMe_3 or SnMe_3 [3–9]. In terms of the PMO approach [10], the HOMOs are formed by mixing of unperturbed initial π -MOs [$E^k(\pi)$] with σ -MOs of the C–Si or Sn–C bonds [$E^k(\text{M}-\text{C})$]. Mixing of π and σ orbitals in $\text{R}_\pi\text{CH}_2\text{SiMe}_3$ and $\text{R}_\pi\text{SnMe}_3$ is characterized by the perturbation energy $\delta E^k(\pi,\sigma)$ [Eq. (6)].

$$\delta E^k(\pi,\sigma) = E(\text{HOMO}) - E^k(\pi). \quad (6)$$

The HOMO in $\text{XCH}_2\text{SiMe}_3$ and XSnMe_3 is the unshared electron pair on the X atom (N, P, S, Cl, Br, I), which is perturbed by electronic interactions with CH_2SiMe_3 and SnMe_3 [3–9].

According to the PMO method, HOMO is considered to be formed by mixing of initial unperturbed n orbitals of the X atom [$E(n)$] and σ orbitals [$E(\text{M}-\text{C})$]. n,σ -Orbital mixing in $\text{XCH}_2\text{SiMe}_3$ and XSnMe_3 is

characterized by the perturbation energy $\delta E^k(n, \sigma)$ given by Eq. (7).

$$\delta E^k(n, \sigma) = E(\text{HOMO}) - E^k(n). \quad (7)$$

The traditional PMO version is based on the Koopmans approximation [10], according to which the first ionization potential I of a neutral molecule, e.g., $R_\pi\text{CH}_2\text{SiMe}_3$, is equal to the energy of its highest occupied molecular orbital taken with the opposite sign.

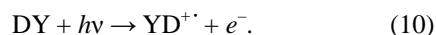
$$I = -E(\text{HOMO}). \quad (8)$$

Here, the energy $E^k(\pi)$, which is necessary for the calculation of π, σ -mixing in $R_\pi\text{CH}_2\text{SiMe}_3$ by Eq. (6), is a difference [Eq. (9)].

$$E^k[\pi(R_\pi\text{CH}_2\text{SiMe}_3)] = E[\pi(R_\pi\text{H})] + \text{Ind}. \quad (9)$$

Here, $E[\pi(R_\pi\text{H})]$ is the energy of π -MO of unsubstituted molecule $R_\pi\text{H}$, and Ind is a correction to $E[\pi(R_\pi\text{H})]$ for purely inductive effect of the CH_2SiMe_3 substituent on E . The energy $E(n)$ in Eq. (7) is calculated in a similar way.

Despite extensive use [10], calculations of the perturbation energies $\delta E^k(\pi, \sigma)$ and $\delta E^k(n, \sigma)$ on the basis of the Koopmans approximation (8) are quite rough. In order to prove this statement, let us consider in general photoionization of DY molecules in the gas phase.



Here, D is a reaction center given in Table 1, and Y is any substituent, including MMe_3 , CH_2MMe_3 , and $\text{C}(\text{SiMe}_3)_3$. By definition [11], the ionization potential I is the difference in the total energies of radical cation and neutral molecule [Eq. (11)]; it also can be expressed by Eq. (12).

$$I = E(\text{YD}^{+\cdot}) - E(\text{YD}); \quad (11)$$

$$I = I^\circ - R + C. \quad (12)$$

The energies of relaxation R and correlation C characterize variation of the wave function of a neutral molecule as a result of its transformation into radical cation. The Koopmans "frozen orbital" approximation (8) neglects the contributions of R and C to I ; i.e., it unreasonably ignores the difference between electronic systems of neutral molecule and radical cation. Therefore, it is not valid [3–9] for the DY series.

It is known [6] that ionization potential is the Gibbs standard energy of reaction (10) [Eq. (13)].

$$I = \Delta_r G^0(T). \quad (13)$$

It follows from Eq. (13) that substituent-dependent variation of I in each of the 12 DY series (Table 1) conforms to the linear Gibbs energy relationship principle (for details, see [6]). The application of that principle in the form of Hammett–Taft correlation equations [3–9] leads to Eq. (14) which is general for all DY series.

$$I = I(\text{DH}) + a\sigma_I + b\sigma_R^+ + c\sigma_a. \quad (14)$$

Here, $I(\text{DH})$ is the ionization potential of unsubstituted molecule DH; σ_I , σ_R^+ , and σ_a are parameters characterizing, respectively, inductive, resonance, and so-called polarization effect of substituent Y (if several substituents are attached to D, the sum of these parameters $\Sigma\sigma$ must be used); and a , b , and c are coefficients depending on the nature of D.

According to [3–9], the universal (independent of D) polarization constant σ_a in Eq. (14) quantitatively characterizes stabilizing electrostatic attraction between the positive charge q in radical cation $\text{YD}^{+\cdot}$ and dipole moment induced by that charge on the Y substituent. In keeping with classical electrostatic relations, the energy of such stabilization is given by Eq. (15).

$$E_{\text{st}} = -q^2\alpha/(2\epsilon r^4). \quad (15)$$

Here, α is the polarizability of Y, ϵ is dielectric constant, and r is the distance between the charge and induced dipole.

Equation (14) can be rewritten as (16).

$$I = I(\text{DH}) + \text{Ind} + \text{Res} + \text{Pol}. \quad (16)$$

As shown in [3–9], the inductive ($\text{Ind} = a\sigma_I$), resonance ($\text{Res} = b\sigma_R^+$), and polarization ($\text{Pol} = c\sigma_a$) contributions are comparable. However, the Koopmans approximation [Eq. (8)] unreasonably neglects the polarization contribution. From the above stated it follows that ionization potentials I contain information on not only inductive and resonance effects but also polarization effect of substituent Y in radical cations $\text{YD}^{+\cdot}$. Therefore, the traditional PMO version [10] based on the rough Koopmans approximation (8) was modified so as to take into account polarization contribution (Pol) to I . According to the modified PMO version, the energies of initial unperturbed π -MOs [$E(\pi)$] in radical cations $\text{Me}_3\text{SiCH}_2\text{R}_\pi^{+\cdot}$ and $\text{Me}_3\text{SnR}_\pi^{+\cdot}$ and of n -MOs [$E(n)$] in $\text{Me}_3\text{SiCH}_2\text{X}^{+\cdot}$ and $\text{Me}_3\text{SnX}^{+\cdot}$

Table 2. First vertical ionization potentials of $\text{Me}_3\text{SiCH}_2\text{D}$ (I) and DH molecules [$I(\text{DH})$], contributions Ind and Pol , energies of initial unperturbed orbitals $E(\pi)$ and $E(n)$, energy of perturbation δE in $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$ radical cations, and its donor δE^d and acceptor δE^a constituents

D	I , eV	$I(\text{DH})$, eV	Ind , eV	Pol , eV	$E(\pi)$ or $E(n)$, eV	δE , eV	δE^d , eV	δE^a , eV
Phenyl	8.42 [1, 2]	9.24	-0.05	-0.28	-8.91	0.49	0.84 (0.65)	-0.35 (-0.16)
2-Furyl	8.15 [3]	8.89	-0.08	-0.46	-8.35	0.20	0.55 (0.45)	-0.35 (-0.25)
2-Thienyl	8.26 [3]	8.87	-0.05	-0.36	-8.46	0.20	0.55 (0.44)	-0.35 (-0.24)
$\text{H}_2\text{C}=\text{CH}$	9.10 [4]	10.51	-0.06	-0.46	-9.99	0.89	1.24 (0.89)	-0.35 (~0)
$\text{HC}\equiv\text{C}$	9.04 [5]	11.40	-0.06	-1.00	-10.34	1.30	1.65 (1.30)	-0.35 (~0)
$-\text{N}$ / \	7.66 [6]	11.08	-0.26	-3.03	-7.79	0.13	0.48 (0.39)	-0.35 (-0.26)
$-\text{P}$ / \	7.85 [7]	10.60	-0.24	-1.76	-8.60	0.75	1.10 (0.86)	-0.35 (-0.11)
HS	8.96 [8]	10.47	-0.12	-0.90	-9.45	0.49	0.84 (0.49)	-0.35 (~0)
CH_3S	8.35 [8]	9.46	-0.07	-0.71	-8.68	0.33	0.68 (0.53)	-0.35 (-0.20)

include three constituents which are denoted as in Eqs. (14) and (16).

$$E(\pi) = I(\text{DH}) + Ind + Pol; \quad (17)$$

$$E(n) = I(\text{DH}) + Ind + Pol. \quad (18)$$

The perturbation energies are calculated according to Eqs. (19) and (20).

$$\delta E(\pi, \sigma) = -I - E(\pi); \quad (19)$$

$$\delta E(n, \sigma) = -I - E(n). \quad (20)$$

Here, I is the first ionization potential of $\text{R}_\pi\text{CH}_2\text{SiMe}_3$ and $\text{R}_\pi\text{SnMe}_3$ molecules [Eq. (19)] or $\text{XCH}_2\text{SiMe}_3$ and XSnMe_3 [Eq. (20)]. In the calculations by Eqs. (17)–(20) (Tables 2, 3) we used I values and expressions like (14) which were taken from [3–9]. The data in Tables 2 and 3 show that the contribution Pol (which is neglected in the traditional PMO version) is in fact fairly large and that its magnitude strongly depends on the nature of D.

Let us consider the energies of perturbation δE (Tables 2, 3) as parameters characterizing conjugation of the CH_2SiMe_3 and SnMe_3 substituents with the electron-deficient centers $\text{D}^{+\cdot}$ in radical cations $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$ and $\text{Me}_3\text{SnD}^{+\cdot}$. The values of δE vary over a wide range, depending on the nature of $\text{D}^{+\cdot}$ for both types of radical cations. This confirms once more that the ability of CH_2SiMe_3 and SnMe_3 to be involved in conjugation is not their persistent property but is determined by the nature of the reaction center. Thus the parameter δE may be regarded as the first objective estimate of the energy of resonance interaction between the substituent and reaction center in $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$ and $\text{Me}_3\text{SnD}^{+\cdot}$ radical cations.

As noted above, another parameter characterizing such interactions is the resonance constant σ_R^+ of CH_2SiMe_3 or SnMe_3 substituent. Therefore, 9 radical cations $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$ fit linear relation (21), and 10 radical cations $\text{Me}_3\text{SnD}^{+\cdot}$ fit correlation (22).

$$\delta E = -1.99\sigma_R^+(\text{CH}_2\text{SiMe}_3) - 0.35; \quad (21)$$

$$S_a = 0.20, S_b = 0.10, S_Y = 0.11, r = 0.966, n = 9;$$

$$\delta E = -1.79\sigma_R^+(\text{SnMe}_3) - 0.15; \quad (22)$$

$$S_a = 0.14, S_b = 0.04, S_Y = 0.08, r = 0.977, n = 10.$$

Equations (21) and (22) include a free term. As we already noted, in the calculation of δE by the modified PMO method in the first approximation we took into account mainly donor effects of σ, π and π, n conjugation, temporarily setting aside acceptor effects of $\sigma^*, \pi, \sigma^*, n, d, \sigma$, and d, n conjugation in $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$ and $\text{Me}_3\text{SnD}^{+\cdot}$ radical cations. In the real case, both resonance substituent constants σ_R^+ and perturbation energies δE characterize the overall resonance effect (donor and acceptor) in the radical cations under study. The quantity σ_R^+ is such a parameter by definition [1–9], while the energy δE is calculated by Eq. (19) or (20) from the ionization potential I which contains information on all types of resonance interactions in $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$ and $\text{Me}_3\text{SnD}^{+\cdot}$.

Let us consider first the interactions in $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$. The overall resonance effect δE includes donor δE^d (σ, π and σ, n conjugation) and acceptor δE^a constituents (σ^*, π and σ^*, n conjugation) which have opposite signs.

$$\delta E = \delta E^d + \delta E^a. \quad (23)$$

If only donor resonance effect were operative in $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$, the straight line described by Eq. (21)

Table 3. First vertical ionization potentials of Me₃SnD (*I*) and DH molecules [*I*(DH)], contributions *Ind* and *Pol*, energies of initial unperturbed orbitals *E*(π) and *E*(*n*), energy of perturbation δE in Me₃SnD⁺ radical cations, and its donor δE^d and acceptor δE^a constituents

D	<i>I</i> , eV	<i>I</i> (DH), eV	<i>Ind</i> , eV	<i>Pol</i> , eV	<i>E</i> (π) or <i>E</i> (<i>n</i>), eV	δE , eV	δE^d , eV	δE^a , eV
Phenyl	8.75 [1, 2]	9.24	-0.13	-0.25	-8.86	0.11	0.26	-0.15
2-Furyl	8.33 [3]	8.89	-0.20	-0.42	-8.27	-0.06	0.09	-0.15
2-Thienyl	8.49 [3]	8.87	-0.13	-0.33	-8.41	-0.08	0.07	-0.15
-N \diagup	7.59 [6]	11.08	-0.67	-2.75	-7.66	0.09	0.24	-0.15
-P \diagup	7.81 [7]	10.60	-0.60	-1.69	-8.31	0.50	0.65	-0.15
CH ₃ S	8.37 [8]	9.46	-0.19	-0.64	-8.63	0.26	0.41	-0.15
-Se-	8.00 [8]	9.88	-0.40	-1.36	-8.12	0.12	0.27	-0.15
Cl	10.16 [9]	12.79	-0.15	-1.54	-11.10	0.94	1.09	-0.15
Br	9.72 [9]	11.81	-0.21	-1.06	-10.54	0.82	0.97	-0.15
I	9.14 [9]	10.72	-0.22	-0.82	-9.68	0.54	0.69	-0.15

would pass through the origin, for $\sigma_R^+(\text{CH}_2\text{SiMe}_3) = 0$ means the absence of σ, π and σ, n conjugation, i.e., $\delta E = 0$. By excluding the free term from Eq. (21) we obtain hypothetical dependence (24) which (in some approximation) could be valid for Me₃SiCH₂D⁺ radical cations provided that acceptor resonance effects (σ^*, π and σ^*, n conjugation) were absent.

$$\delta E^d = -1.99\sigma_R^+(\text{CH}_2\text{SiMe}_3). \quad (24)$$

An approximate energy estimate ($\delta E^a = -0.35$ eV) of σ^*, π and σ^*, n conjugation effects (Table 2) was obtained as the distance between straight lines (21) and (24) along the δE axis (see figure). The energy of σ, π and σ, n conjugation (δE^d , Table 2) was calculated by Eq. (23). According to the above procedure for separation of the overall resonance effect δE into constituents δE^d and δE^a , the acceptor resonance effect δE^a (-0.35 eV) in Me₃SiCH₂D⁺ does not depend on D. However, this approximation seems to be fairly rough.

Another approach, which is free from such approximation, is based on the energies of initial unperturbed σ^* orbitals of CH₂-Si bonds and π or *n* orbitals of R _{π} or X groups involved in σ^*, π or σ^*, n conjugation. The energies *E*(σ^*) and *E*(π) in the C₆H₅CH₂SiMe₃ molecule are 2.8 [12] and -8.91 eV, respectively (Table 3), and the difference $\Delta E = E(\sigma^*) - E(\pi)$ is about 11.7 eV. In the HC \equiv CCH₂SiMe₃ molecule, *E*(σ^*) = 4.1 eV [13] {assuming that *E*(σ^*) values for ethylene and acetylene derivatives are similar [1, 13, 14]}, *E*(σ) = -10.34 eV, and $\Delta E \approx 14.4$ eV. Apart from Eqs. (6), (7), (19), and (20), the energy of perturbation (PMO) can also be determined by Eq. (25) [10].

$$\delta E = P^2/\Delta E. \quad (25)$$

Here, *P* is the perturbation integral which is related to the overlap integral of interacting orbitals (e.g., overlap of σ^* orbitals with π or *n* orbitals), and ΔE is the energy difference between the interacting orbitals.

On the basis of the data in [1, 10] we assume the following. First, the energy difference ΔE in Eq. (25) affects the perturbation energy δE more strongly than does *P*² in the same equation. Second, at large ΔE values, the energy δE^a in Me₃SiCH₂D⁺ tends to zero. This situation is observed when D = HC \equiv C- ($\Delta E = 14.4$ eV) and, probably, when D = H₂C=CH- or HS- [here, *E*(π) and *E*(*n*) have large negative values, and hence ΔE is also large].

Hypothetical straight line described by Eq. (26) was passed through the origin ($\sigma_R^+ = \delta E^d = \delta E^a = 0$) and the point corresponding to HC \equiv C⁺-CH₂SiMe₃ { $\sigma_R^+ = -0.74$, $\delta E^d = 1.17$ eV [calculated by Eq. (21)], $\delta E^a = 0$ }.

$$\delta E^d = -1.59\sigma_R^+(\text{CH}_2\text{SiMe}_3). \quad (26)$$

This dependence would be valid for Me₃SiCH₂D⁺ radical cations provided that acceptor resonance effects (σ^*, π and σ^*, n conjugation) were absent. Thus, in terms of the second approach, the energy δE^a of σ^*, π and σ^*, n conjugation (Table 2) can be estimated by the distance between straight lines (21) and (26) along the δE axis (see figure). The energy of donor resonance effects δE^d (σ, π and σ, n conjugation; Table 2) is calculated by Eq. (23).

Both the above approaches to separation of the overall resonance effect δE in Me₃SiCH₂D⁺ into donor

δE^d and acceptor δE^a constituents are approximate. Therefore, the corresponding values given in Table 2 (the data obtained in terms of the second approach are given in parentheses) differ from each other.

Our results convincingly demonstrate a complex character of resonance interactions in $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$ radical cations. The substituent CH_2SiMe_3 exert not only strong donor resonance effect (σ, π and σ, n conjugation) on the reaction center $\text{D}^{+\cdot}$ but also relatively weak acceptor effect (σ^*, π and σ^*, n conjugation).

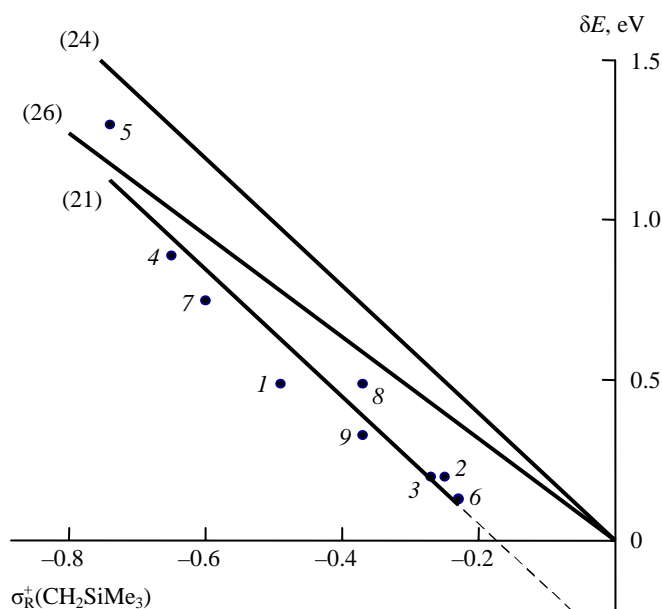
Now let us consider resonance interactions in $\text{Me}_3\text{SnD}^{+\cdot}$ radical cations. They also fit general Eq. (23) where the donor component δE^d reflects (as in $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$) σ, π and σ, n conjugation, and the acceptor component δE^a , d, π and d, n conjugation. Let us assume temporarily that SnMe_3 substituent possesses no acceptor resonance properties, i.e., $\delta E^a = 0$. In this case, the straight line defined by Eq. (22) would pass through the origin since no σ, π and σ, n conjugation exists at $\sigma_R^+(\text{SnMe}_3) = 0$ and hence $\delta E^d = 0$. Furthermore, the relation between δE^d and $\sigma_R^+(\text{SnMe}_3)$ could be described by Eq. (27) which, unlike (22), has no free term.

$$\delta E^d = -1.79\sigma_R^+(\text{SnMe}_3). \quad (27)$$

In fact, the overall resonance effect in $\text{Me}_3\text{SnD}^{+\cdot}$ includes both donor δE^d and acceptor δE^a constituents. An approximate estimate of $\delta E^a = -0.15$ eV (d, π and d, n conjugation; Table 3) was obtained from the distance between straight lines (22) and (27) along the δE axis. The δE^d values were calculated by Eq. (23) from δE (Table 3).

From the above stated it follows that δE^d is greater than δE^a in absolute value for the whole series of $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$ and for most members of the $\text{Me}_3\text{SnD}^{+\cdot}$ series. Exception are radical cations in which $\text{D} = 2\text{-furyl}$ and 2-thienyl ; in these cases acceptor effect (d, π conjugation) predominates over donor effect (σ, π conjugation; Table 3). This pattern is even more distinct for silyl- and germyl-substituted derivatives of furan and thiophene (Table 1).

To conclude, it should be emphasized that Eq. (21) may be useful in rough estimation of strengthening



Correlation between δE and σ_R^+ for $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$ radical cations: (1) $\text{D} = \text{Ph}$, (2) $\text{D} = 2\text{-furyl}$, (3) $\text{D} = 2\text{-thienyl}$, (4) $\text{D} = \text{H}_2\text{C}=\text{CH}$, (5) $\text{D} = \text{HC}\equiv\text{C}$, (6) $\text{D} = -\text{N}^{\langle}$, (7) $\text{D} = -\text{P}^{\langle}$, (8) $\text{D} = \text{HS}$, (9) $\text{D} = \text{CH}_3\text{S}$; the numbers on the straight lines refer to the corresponding equations.

of donor resonance effect (increase in the energy of σ, π and σ, n conjugation) with increase of the positive charge on D , i.e., in going from systems like $\text{Me}_3\text{SiCH}_2\text{D}^{\delta+}$ with a small positive charge $\delta+$ (where the conjugation is characterized by substituent parameters σ_R) to radical cations $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$. Let us assume that Eq. (21) is valid not only for radical cations but also for $\text{Me}_3\text{SiCH}_2\text{D}^{\delta+}$ systems. From the parameters σ_R we can calculate the energy δE_1 in $\text{Me}_3\text{SiCH}_2\text{D}^{\delta+}$ and the difference $\Delta = \delta E - \delta E_1$, where δE is the energy of perturbation in $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$ (Table 4). Acceptor resonance effect (d, π conjugation) almost does not depend on the charge on D [1, 2]. Therefore, the parameter Δ characterizes the gain in the energy of σ, π conjugation due to increase of the positive charge on D in going from $\text{Me}_3\text{SiCH}_2\text{D}^{\delta+}$ to

Table 4. Energies of perturbation δE and resonance constants σ_R^+ for $\text{Me}_3\text{SiCH}_2\text{D}^{+\cdot}$ radical cations, resonance constants σ_R and calculated δE_1 values for $\text{Me}_3\text{SiCH}_2\text{D}$ molecules, and differences Δ

Molecule	δE , eV	$\sigma_R^+(\text{CH}_2\text{SiMe}_3)$	$\sigma_R(\text{CH}_2\text{SiMe}_3)$ [1]	δE_1 , eV	$\Delta = \delta E - \delta E_1$, eV
$\text{PhCH}_2\text{SiMe}_3$	0.49	-0.49	-0.20	0.02	0.47
$\text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$	0.89	-0.65	-0.24	0.11	0.78
$\text{HC}\equiv\text{CCH}_2\text{SiMe}_3$	1.30	-0.74	-0.24	0.11	1.19

$\text{Me}_3\text{SiCH}_2\text{D}^+$. The larger the absolute value of σ_{R}^+ of CH_2SiMe_3 (i.e., its donor resonance effect with respect to D^+), the greater the gain in the energy of σ, π conjugation (Table 4).

REFERENCES

1. Egorochkin, A.N. and Voronkov, M.G., *Elektronnoe stroenie organicheskikh soedinenii kremniya, germaniya i olova* (Electronic Structure of Organic Silicon, Germanium, and Tin Compounds), Novosibirsk: Sib. Otd. Ross. Akad. Nauk, 2000, p. 615.
2. Voronkov, M.G. and Egorochkin, A.N., *The Chemistry of Organic Germanium, Tin, and Lead Compounds*, Chichester: Wiley, 2002, vol. 1, p. 131.
3. Egorochkin, A.N., Skobeleva, S.E., and Mushtina, T.G., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, p. 2434.
4. Egorochkin, A.N., Skobeleva, S.E., and Mushtina, T.G., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1997, p. 1626.
5. Egorochkin, A.N., Skobeleva, S.E., and Mushtina, T.G., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, p. 1481.
6. Egorochkin, A.N., Voronkov, M.G., Zderenova, O.V., and Skobeleva, S.E., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2001, p. 41.
7. Egorochkin, A.N., Voronkov, M.G., Skobeleva, S.E., and Zderenova, O.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2001, p. 34.
8. Egorochkin, A.N., Voronkov, M.G., Skobeleva, S.E., Mushtina, T.G., and Zderenova, O.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2000, p. 25.
9. Egorochkin, A.N. and Kuznetsova, O.V., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2003, p. 298.
10. Pitt, C.G., *J. Organomet. Chem.*, 1973, vol. 61, p. 49.
11. Nefedov, V.I. and Vovna, V.I., *Elektronnaya struktura khimicheskikh soedinenii* (Electronic Structure of Chemical Compounds), Moscow: Nauka, 1987, p. 347.
12. Distefano, G., Modelli, A., Guerra, M., Jones, D., and Rossini, S., *J. Mol. Struct.*, 1988, vol. 174, p. 177.
13. Giordan, J.C., *J. Am. Chem. Soc.*, 1983, vol. 105, p. 6544.
14. Modelli, A., Jones, D., and Distefano, G., *Chem. Phys. Lett.*, 1982, vol. 86, p. 434.