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Intensity of the ν(C≡C) Bands in the IR Spectra of Acetylene Derivatives and σ_R^0 Constants of Organosilicon, Organogermanium, and Organotin Substituents

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Abstract—The integral absorptivities of shape-characteristic ν(C≡C) bands in the IR spectra of 66 acetylene derivatives RC≡CX (R = H, Me_3M; X are inorganic and organic substituents) are related by a common linear equation to the σ_R^0 constants of the R and X substituents. The σ_R^0 constants of 10 Alk_3M substituents were calculated. The σ_R^0, σ_R, and σ_R^+ constants of Me_3M substituents were analyzed. The positive σ_R^0 values (0.12, 0.06, and 0.04 for R = Si, Ge, and Sn, respectively) suggest that in the ground electronic state of $Me_3MC{\equiv}CX$ molecules the resonance acceptor effect of the Me_3M substituents (*d*,π conjugation) prevails over donor (σ,π conjugation). The first effect attenuates and the second enhances as the atomic number of M increases.

The modern view of conjugation in organometallic compounds Alk_3MR_π (M = Si, Ge, Sn; $R_\pi = C_6H_5$, $H_2C{=}CH$, $HC{\equiv}C$, etc.) is based on the hypothesis of dual (acceptor and simultaneously donor) resonance properties of the Alk_3M substituent with respect to the reaction center R_π (see, for example, [1]). The resonance acceptor properties of the Alk_3M substituent (*d*,π conjugation) result from interaction of *nd* orbitals of M, as well as σ^* orbitals of M–C with the π system of R_π. The resonance donor properties of Alk_3M (σ,π conjugation) result from interaction of σ orbitals of M–C with the π system of R_π. In organometallic compounds $Alk_3MCH_2R_\pi$, no other effect that the donor σ,π conjugation is operative.

At present the regularities of conjugation in organometallic compounds have thoroughly been studied on a qualitative level only. Thus, in particular, as the atomic number of M increases in the Si–Ge–Sn series, *d*,π conjugation attenuates, whereas σ,π conjugation enhances. The *d*,π-conjugation effect depends both on the type of R_π and the partial positive charge δ^+ induced on R_π by complex formation, ionization, and chemical reactions. A general tendency is observed: The higher δ^+ and the atomic number of M, the stronger enhancement of σ,π conjugation in Alk_3MR_π and $Alk_3MCH_2R_\pi$ systems [1]. Therefore, Alk_3M and Alk_3MCH_2 substituents are impossible to characterize by universal resonance constants.

In physical organometallic chemistry, conjugation is quantitatively measured by the resonance parameters σ_R^0 (ground electronic state of Alk_3MR_π and $Alk_3MCH_2R_\pi$ molecules; $\delta^+ = n\ 0.01\ e$), σ_R ($\delta^+ = n\ 0.01\ e$), and σ_R^+ ($\delta^+ = n\ 0.1\ e$) of Alk_3M and Alk_3MCH_2 substituents. Regardless of the fact that quantitative characteristics of conjugation are exceptionally important for the theoretical chemistry of organometallic compounds, a sufficiently full set of resonance parameters is available for $R_\pi = C_6H_5$ only [1, 2].

The aim of the present work was to compare the resonance parameters σ_R^0 of Me_3M (M = Si, Ge, Sn) substituents, to correlate conjugation with the charge δ^+ on R_π in acetylene derivatives, and to develop a procedure for estimating σ_R^0 for R_3M (R is any group) substituents at the triple bond from the integral absorptivities of the ν(C≡C) bands in the IR spectra.

The integral absorptivities *A* of the ν(C≡C) bands in the IR spectra of $Me_3SnC{\equiv}CX$ compounds vary with varied X substituent (Table 1). Correlation between *A* and donor–acceptor properties of X can be established on the basis of the general theory of intensities [3], according to which the integral absorptivity *A* is proportional to the squared derivative of the dipole moment μ of the molecule by the *i*th normal coordinate Q_i [Eq. (1)].

$$A \sim (\partial\mu/\partial Q_i)_0^2. \qquad (1)$$

When applied to the shape-characteristic A–B stretching vibration in a polyatomic molecule, Eq. (1) is simplified to Eq. (2).

Table 1. Integral absorptivities *A* of the ν(C≡C) bands and σ_R^0 constants of the X substituents in $Me_3SnC{\equiv}CX$ compounds

X	ν(C≡C), cm^{-1}	*A*, $l\ mol^{-1}\ cm^{-1}$	$A^{1/2}$, $l^{1/2}\ mol^{-1/2}\ cm^{-1}$	$\sigma_R^0(X)$
CH_2SnMe_3	2140	3670	–60.6	–0.21
CH_2SiMe_3	2132	2680	–51.8	–0.18
CH_2Ph	2156	1240	–35.2	–0.11
Ph	2139	1180	–34.4	–0.10
CH_2CMe_3	2151	1110	–33.3	–0.09
CH_2SPh	2154	680	–26.1	–0.08
$CH_2C_6F_5$	2160	680	–26.1	–0.08
$CH_2SC_6F_5$	2156	300	–17.5	–0.02
C_6F_5	2154	70	–8.4	–0.01
H	2012	18	–4.2	0.00

$$A \sim (\partial\mu_{A-B}/\partial q_{A-B})_2^0. \quad (2)$$

Here μ_{A-B} and q_{A-B} are the dipole moment and stretching coordinate of the A–B bond. The fact that the A–B vibration is shape-characteristic allows this bond to be represented as a diatomic molecule for which Eq. (3) is valid [3].

$$\partial\mu_{A-B}/\partial q_{A-B} \sim \mu_{A-B}/r_0. \quad (3)$$

Here r_0 is the A–B interatomic distance. If r_0 = const, then Eq. (4) is valid.

$$A^{1/2} \sim \mu_{A-B}. \quad (4)$$

Thus, the *A* value for the highly shape-characteristic A–B stretching vibrations depends exclusively on the electronic effects of groups surrounding this bond and thus affecting μ_{A-B}.

The dipole moment μ_{A-B} of the A–B bond as a diatomic molecule is related to the difference of the effective atomic charges (Δ*q*) on A and B by Eq. (5) [4].

$$\mu_{A-B} = \Delta q r_0. \quad (5)$$

There is an important particular case, when μ_{A-B} is affected exclusively by conjugation of the A–B bond with other groups in the molecule (see, for example, [5–7]). Therewith, the integral absorptivity *A* depends exclusively on π components of the dipole moment (μ^{π}_{A-B}) and on the difference in the effective atomic charges (Δ*q*π) on A and B, and Eqs. (5) and (4) transform into Eqs. (6) and (7).

$$\mu^{\pi}_{A-B} = \Delta q r_0, \quad (6)$$

$$A^{1/2} \sim \Delta q_{\pi}. \quad (7)$$

Thus, Eqs. (3)–(7) hold rigorously for the highly shape-characteristic ν(A–B) stretching vibrations of A–B bonds. Unlike ν(A–B), the ν(C≡C) stretching vibrations of the C≡C bond in acetylene derivatives are in general not ideally characteristic. Nevertheless, we suggested that they can be treated similarly to ν(A–B). This suggestion is supported by the following three conclusions drawn from a combined analysis of published theoretical calculations of shape characteristicity of ν(C≡C) vibrations [3, 5, 8–10] and our correlations.

1. Both in monosubstituted HC≡CX (Table 2, compounds **I**–**XVIII**) and in disubstituted RC≡CX (compounds **XIX**–**LXVI**; R = Me_3C, Me_3Si, Me_3Ge, Me_3Sn) acetylenes, the ν(C≡C) stretching vibration is largely due to changing C≡C bond length [3, 5, 8–10]. At the same time, according to the calculations [3, 5–10], the shape characteristicity of ν(C≡C) in RC≡CX depends on the type of substituent R and increases in going from H≡CX and $Me_3CC{\equiv}CX$ to organometallic derivatives $Me_3MC{\equiv}CX$ (M = Si, Ge, Sn). Therefore, one might expect in HC≡CX and $Me_3CC{\equiv}CX$ a stronger (compared with $Me_3MC{\equiv}CX$) deviation of the shape of the ν(C≡C) stretching vibration from the ideal characteristicity inherent in ν(A–B). Nevertheless, as shown in [5–8], ν(C≡C) is sufficiently shape-characteristic, even though ν(C≡C) and ν(CC≡) vibrations in HC≡CX and $Me_3CC{\equiv}CX$ are mixed with each other to a certain extent. Illustrative evidence for this statement comes from correlation analysis. As follows from *ab initio* quantum-chemical calculations for HC≡CX molecules [11], the π components of the effective atomic charges in the C≡C (Δ*q*π) fragment are proportional to the σ_R^0 constants of the X substituents [Eq. (8)].

$$\Delta q_{\pi} \sim \sigma_R^0. \quad (8)$$

On the assumption that ν(C≡C) is completely shape-characteristic, then, in view of Eq. (8), we can

Table 2. Experimental $A^{1/2}$ values in RC≡CX compounds (R = H,[a] Me_3C,[b] Me_3Si,[c] Me_3Ge,[d] Me_3Sn[e]) and σ_R^0 constants of substituents R and X

Comp. no.	R	X	$A^{1/2}$, $l^{1/2}\,mol^{-1/2}\,cm^{-1}$	$\sigma_R^0(R)$	$\sigma_R^0(X)$	$\sigma_R^0(X) - \sigma_R^0(R)$	$[\sigma_R^0(X) - \sigma_R^0(R)]_{calc}$[f]	Δ[g]
I	H	OEt	–87.2	–0.05	–0.44	–0.39	–0.39	0
II	H	*t*-Bu	–16.7	–0.05	–0.13	–0.08	–0.08	0
III	H	Bu	–14.4	–0.05	–0.11	–0.06	–0.06	0
IV	H	CH_2OH	–12.4	–0.05	–0.06	–0.01	–0.06	–0.05
V	H	Ph	–11.7	–0.05	–0.10	–0.05	–0.05	0
VI	H	CH(OH)Ph	–10.8	–0.05	–0.08	–0.03	–0.05	–0.02
VII	H	CH_2NMe_2	–9.8	–0.05	–0.10	–0.05	–0.04	0.01
VIII	H	CH(OH)Me	–9.7	–0.05	–0.08	–0.03	–0.04	–0.01
IX	H	CH_2Cl	10.9	–0.05	–0.04	0.01	0.05	0.04
X	H	CH_2Br	11.0	–0.05	–0.02	0.03	0.05	0.02
XI	H	$CH_2N^+H_3Cl^-$, H_2O	16.2	–0.05	0.00	0.05	0.07	0.02
XII	H	$CH_2N^+Me_3Br^-$	23.1	–0.05	0.03	0.08	0.10	0.02
XIII	H	CO_2Et	49.8	–0.05	0.18	0.23	0.22	–0.01
XIV	H	COPh	50.1	–0.05	0.19	0.24	0.22	–0.02
XV	H	CO_2Me	51.2	–0.05	0.16	0.21	0.23	0.02
XVI	H	COMe	54.1	–0.05	0.22	0.27	0.24	–0.03
XVII	H	COCl	59.6	–0.05	0.21	0.26	0.27	0.01
XVIII	H	CO_2H	64.9	–0.05	0.29	0.34	0.29	–0.05
XIX	Me_3C	NMe_2	–71.0	–0.18	–0.53	–0.35	–0.32	0.03
XX	Me_3C	NMePh	–70.3	–0.18	–0.50	–0.32	–0.32	0
XXI	Me_3C	SEt	–9.8	–0.18	–0.25	–0.07	–0.04	0.03
XXII	Me_3C	Br	–7.9	–0.18	–0.23	–0.05	–0.04	0.01
XXIII	Me_3C	I	–7.5	–0.18	–0.22	–0.04	–0.03	0.01
XXIV	Me_3C	Cl	–7.7	–0.18	–0.22	–0.04	–0.04	0
XXV	Me_3C	Me	5.2	–0.18	–0.10	0.08	0.02	–0.06
XXVI	Me_3C	Ph	16.3	–0.18	–0.10	0.08	0.07	–0.01
XXVII	Me_3C	CH_2OH	23.0	–0.18	–0.06	0.12	0.10	–0.02
XXVIII	Me_3C	CH_2NMe_2	14.8	–0.18	–0.10	0.08	0.07	–0.01
XXIX	Me_3C	CO_2Me	79.3	–0.18	0.16	0.34	0.36	0.02
XXX	Me_3C	COCl	93.2	–0.18	0.21	0.39	0.42	0.03
XXXI	Me_3C	CO_2H	94.8	–0.18	0.29	0.47	0.43	–0.04
XXXII	Me_3Si	CH_2SiMe_3	–65.5	0.12	–0.18	–0.30	–0.30	0
XXXIII	Me_3Si	$CH_2Sn(t\text{-}Bu)_3$	–64.4	0.12	–0.22	–0.34	–0.29	0.05
XXXIV	Me_3Si	CH_2GeMe_3	–63.7	0.12	–0.18	–0.30	–0.29	0.01
XXXV	Me_3Si	Ph	–52.0	0.12	–0.10	–0.22	–0.23	–0.01
XXXVI	Me_3Si	CH_2Ph	–51.3	0.12	–0.11	–0.23	–0.23	0
XXXVII	Me_3Si	SC_6F_5	–51.0	0.12	–0.12	–0.24	–0.23	0.01
XXXVIII	Me_3Si	$CH_2C_6F_5$	–41.2	0.12	–0.08	–0.20	–0.19	0.01
XXXIX	Me_3Si	*t*-Bu	–39.9	0.12	–0.13	–0.25	–0.18	0.07
XL	Me_3Si	CH_2SPh	–35.9	0.12	–0.08	–0.20	–0.16	0.04
XLI	Me_3Si	$CH_2SC_6F_5$	–33.2	0.12	–0.02	–0.14	–0.15	–0.01
XLII	Me_3Si	CH_2OMe	–28.6	0.12	–0.07	–0.19	–0.13	0.06
XLIII	Me_3Si	C_6F_5	–25.4	0.12	–0.01	–0.13	–0.11	0.02
XLIV	Me_3Si	CHO	22.1	0.12	0.24	0.12	0.10	–0.02
XLV	Me_3Ge	CH_2GeMe_3	–67.2	0.06	–0.18	–0.24	–0.30	–0.06
XLVI	Me_3Ge	CH_2SiMe_3	–65.6	0.06	–0.18	–0.24	–0.29	–0.05
XLVII	Me_3Ge	CH_2Ph	–40.2	0.06	–0.11	–0.17	–0.18	–0.01
XLVIII	Me_3Ge	SC_6F_5	–38.7	0.06	–0.12	–0.18	–0.17	0.01

Table 2. (Contd.)

Comp. no.	R	X	$A^{1/2}$, $l^{1/2}\,mol^{-1/2}\,cm^{-1}$	$\sigma_R^0(R)$	$\sigma_R^0(X)$	$\sigma_R^0(X) - \sigma_R^0(R)$	$[\sigma_R^0(X) - \sigma_R^0(R)]_{calc}$[f]	Δ[g]
XLIX	Me_3Ge	Ph	–37.7	0.06	–0.10	–0.16	–0.17	–0.01
L	Me_3Ge	$CH_2C_6F_5$	–29.1	0.06	–0.08	–0.14	–0.13	0.01
LI	Me_3Ge	CH_2SPh	–28.8	0.06	–0.08	–0.14	–0.13	0.01
LII	Me_3Ge	CH_2OMe	–24.5	0.06	–0.07	–0.13	–0.11	0.02
LIII	Me_3Ge	H	–20.5	0.06	0.00	–0.06	–0.09	–0.03
LIV	Me_3Ge	$CH_2SC_6F_5$	–19.2	0.06	–0.02	–0.08	–0.09	–0.01
LV	Me_3Ge	CH_2Br	–11.4	0.06	–0.02	–0.08	–0.05	0.03
LVI	Me_3Ge	CHO	44.2	0.06	0.24	0.18	0.20	0.02
LVII	Me_3Sn	CH_2SnMe_3	–60.6	0.04	–0.21	–0.25	–0.27	–0.02
LVIII	Me_3Sn	CH_2SiMe_3	–51.8	0.04	–0.18	–0.22	–0.23	–0.01
LIX	Me_3Sn	CH_2Ph	–35.2	0.04	–0.11	–0.15	–0.16	–0.01
LX	Me_3Sn	Ph	–34.4	0.04	–0.10	–0.15	–0.15	0
LXI	Me_3Sn	$CH_2Bu\text{-}t$	–33.3	0.04	–0.09	–0.13	–0.15	–0.02
LXII	Me_3Sn	CH_2SPh	–26.1	0.04	–0.08	–0.12	–0.12	0
LXIII	Me_3Sn	$CH_2C_6F_5$	–26.1	0.04	–0.08	–0.12	–0.12	0
LXIV	Me_3Sn	$CH_2SC_6F_5$	–17.5	0.04	–0.02	–0.06	–0.08	–0.02
LXV	Me_3Sn	C_6F_5	–8.4	0.04	–0.01	–0.05	–0.04	0.01
LXVI	Me_3Sn	H	–4.2	0.04	0.00	–0.04	–0.02	0.02

[a] [8], [b] [5], [c] [6], [d] [7]. [e] Present work. [f] The $[\sigma_R^0(X) - \sigma_R^0(R)]_{calc}$ values were obtained by Eq. (17). [g] $\Delta = [\sigma_R^0(X) - \sigma_R^0(R)]_{calc} - [\sigma_R^0(X) - \sigma_R^0(R)]$.

Table 3. Linear equations $A^{1/2} = a\sigma_R^0(X) + b$, standard deviations S_a and S_b, standard approximation errors S_Y, correlation coefficients r, point numbers n, and calculated $\sigma_R^0(R)$ constants for RC≡CX series

Series	Equation no.	Equation	R	$\sigma_R^0(R)$	S_a	S_b	S_Y	r	n
HC≡CX [8]	10-1	$A^{1/2} = 217\sigma_R^0(X) + 10.8$	H	–0.05	–	–	–	0.992	18
$Me_3CC≡CX$ [5]	11-1	$A^{1/2} = 213\sigma_R^0(X) + 38.3$	Me_3C	–0.18	–	–	–	0.995	17
$Me_3SiC≡CX$ [6]	12	$A^{1/2} = 197\sigma_R^0(X) - 24.7$	Me_3Si	0.12 ± 0.02	15	2.1	6.0	0.969	13
$Me_3GeC≡CX$ [7]	13	$A^{1/2} = 253\sigma_R^0(X) - 13.0$	Me_3Ge	0.06 ± 0.03	16	2.0	5.8	0.981	12
$Me_3SnC≡CX$	14	$A^{1/2} = 253\sigma_R^0(X) - 7.5$	Me_3Sn	0.04 ± 0.02	13	1.4	2.7	0.990	10

write Eq. (7) for the HC≡CX series in the form of Eq. (9).

$$A^{1/2} \sim \sigma_R^0(X). \qquad (9)$$

Correlation analysis of experimental $A^{1/2}$ values for HC≡CX and $Me_3MC≡CX$ (M = C, Si, Ge, Sn) gave linear equations (10-1), (11-1), and (12)–(14) of the type $A^{1/2} = a\sigma_R^0(X) + b$ (Table 3, Fig. 1), whose slopes a compare with each other, whereas free terms b much differ in value and sign.

Had ν(C≡C) been not sufficiently highly shape-characteristic, no linear correlations (10)–(14) would have been found. At the same time, as will be shown below, the free terms b in Eqs. (10-1) and (11-1) bear information about deviation of the ν(C≡C) stretching vibration in HC≡CX and $Me_3CC≡CX$ from the ideal characteristicity inherent in ν(A–B).

2. For the HC≡CX and $Me_3CC≡CX$ series, b values are positive. If ν(C≡C) in HC≡CX were completely characteristic, Eq. (10) would contain no free term, since at X = H, the $A^{1/2}$, σR(H), as well as Δq_π [11] are equal to zero. The fact that ν(C≡C) in HC≡CX are not completely characteristic (see also [6–8]) can formally be taken into account, assuming that the σ_R constant of the hydrogen atom as substituent is –0.05 rather than 0. Then Eq. (10-1) trans-

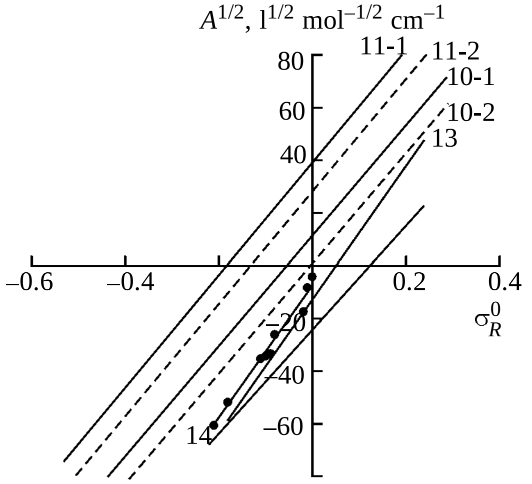

Fig. 1. Plot of $A^{1/2}$ vs. resonance constants σ_R^0 of the X substituents in RC≡CX series. Plot numbers correspond to equation numbers in the text. Points belonging to plot 14 are shown ($Me_3SnC{\equiv}CX$ series).

forms into Eq. (10-2) that corresponds a hypothetical case when the stretching vibration of the C≡C bond in HC≡CX is completely characteristic.

$$A^{1/2} = 217\sigma_R^0(X). \qquad (10\text{-}2)$$

Introduction of the same correction (–0.05) for the incomplete characteristicity of ν(C≡C) in Me_3CC–CX transforms Eq. (11-1) into Eq. (11-2).

$$A^{1/2} = 213\sigma_R^0(X) + 27.6 = 213[\sigma_R^0(X) + 0.13]. \qquad (11\text{-}2)$$

Here 0.13 is the negative difference for the σ_R^0 constant of the Me_3C group. The slopes of Eqs. (10-2) and (11-2) are quite close to each other. The almost parallel shift of plot 11-2 to lower $\sigma_R^0(X)$ values by –0.13 (Fig. 1) can be explained in terms of conjugation of the Me_3C group with the triple bond.

Thus, if the ν(C≡C) vibration in disubstituted acetylenes RC≡CX would be completely characteristic, correlations of type (15) would contain a free term [Eq. (15)]. This arises because of the conjugation of substituents *R* with the triple bond.

$$A^{1/2} = a\sigma_R^0(X) + b. \qquad (15)$$

3. As noted above, data in [3, 5–10], including results of normal coordinate analysis [9, 10], show that the shape characteristicity of ν(C≡C) increases in going from HC≡CX and Me_3CC–CX to $Me_3MC{\equiv}CX$ (M = Si, Ge, Sn) and with increasing atomic number of M in Me3MC≡CX. It will be remembered that to account for the slight deviation from complete characterisicity of the ν(C≡C) vibration in the HC≡CX and $Me_3CC{\equiv}CX$ series, only slight corrections in the σ_R^0 constants of the invariable substituents H and Me_3C will suffice (see item 2). This reasoning gives us grounds to suggests that deviations of ν(C≡C) from ideal characteristicity, if ever occur in the $Me_3MC{\equiv}CX$ (M = Si, Ge, Sn) series, most probably at M = Si, are negligible. It view of the aforesaid, let us dwell on equations of type (15) for the $Me_3MC{\equiv}CX$ (M = Si, Ge, Sn) series (Table 3). Equations (12)–(14) for these series have negative free terms *b*, which sharply distinguishes them from Eqs. (10-1) and (11-1) with positive *b* values for HC≡CX and $Me_3CC{\equiv}CX$. The negative *b* values are unambiguous evidence showing that Me_3M substituents (M = Si, Ge, Sn) exhibit resonance acceptor properties with respect to the triple bond. An illustration of this conclusion can be found in Fig. 1, where plots 12–14 are shifted to higher $\sigma_R^0(X)$ values with respect to plot 10-2.

From these shifts we could estimate σ_R^0 for Me_3M substituents. Above we dealt with the simplest case when plots 10-2 and 11-2 are almost parallel to each other, and the σ_R^0 constant of the Me_3C substituent is given directly by the free term *b* of Eq. (11-2). In a more general case, plots 10-2 and 12–14 are not strictly parallel to each other. Therefore, one can only calculate a mean distance between the plots. The $A^{1/2}$ values in the $Me_3SnC{\equiv}CX$ series (Table 1) vary from –60.6 (X = CH_2SnMe_3) to –4.2 $l^{1/2}$ $mol^{-1/2}$ cm^{-1} (X = H). In this range, the distance between plots 10-2 and 14 varies from 0.07 to 0.02. The mean distance (0.04–0.02) is the σ_R^0 constant of the Me_3Sn substituent at the C≡C bond.

Similarly, using Eqs. (12) and (13), we obtained σ_R^0 values for Me_3Si and Me_3Ge [7] (Table 3). The $\sigma_R^0(Me_3M)$ values were calculated under the assumption that the ν(C≡C) vibration in $Me_3MC{\equiv}CX$ (M = Si, Ge, Sn) is sufficiently shape-characteristic. It should be emphasized once more that this assumption for M = Ge, Sn is fairly consistent with the results of normalcoordinate analysis of $Me_3MC{\equiv}CH$ (M = C, Si, Ge, Sn), which shows that ν(C≡C) gets more characteristic with increasing atomic number of M [10]. At M = C and, to a lesser extent, M = Si, the ν(C≡C) vibration is partly mixed with ν(MC≡) [10]. These results cast some doubts in the reliability of the estimate +0.12 for the σ_R^0 constant of Me_3Si (Table 3). As considered above, the incomplete characteristicity of ν(C≡C) in $Me_3MC{\equiv}CX$ reduces $\sigma_R^0(Me_3C)$ by 0.05. Consequently, even if $\sigma_R^0 = 0.12$ for Me_3Si is an underestimated value (methods for determination of true values have been still absent), this underestimation is no larger than 0.05.

Table 4. Experimental $A^{1/2}$ values and calculated σ_R^0 constants of the R_3M^a substituents in $R_3MC{\equiv}CX$ compounds

Compound	R_3M	X	$\sigma_R^0(R_3M)$	$\sigma_R^0(X)$	$\sigma_R^0(X)$ – $\sigma_R^0(R_3M)$	$A^{1/2}$, $l^{1/2}\,mol^{-1/2}\,cm^{-1}$
Me3SiC≡CMe	Me_3Si	Me	0.15	–0.10	–0.25	–56.5
$Me_3SiC{\equiv}CCH_2Br$	Me_3Si	CH_2Br	0.10	–0.02	–0.12	–26.1
$Me_3SiC{\equiv}CCH_2OSiMe_3$	Me_3Si	CH_2OSiMe_3	0.11	–0.02	–0.13	–29.5
$Et_3SiC{\equiv}CH$	Et3Si	H	0.11	0.00	–0.11	–23.5
i-$Pr_3SiC{\equiv}CH$	*i*-Pr_3Si	H	0.15	0.00	–0.15	–33.7
i-$Pr_3SiC{\equiv}CMe$	*i*-Pr_3Si	Me	0.15	–0.10	–0.25	–54.9
$Ph_3SiC{\equiv}CH$	Ph_3Si	H	0.19	0.00	–0.19	–41.7
$Et_3GeC{\equiv}CPh$	Et_3Ge	Ph	0.07	–0.10	–0.17	–37.7
$Et_3SnC{\equiv}CCH_2SiMe_3$	Et_3Sn	CH_2SiMe_3	0.05	–0.18	–0.23	–50.4
$Bu_3SnC{\equiv}CH$	Bu_3Sn	H	0.04	0.00	–0.04	–9.2
Me(*t*-Bu)$_2$SnC≡CH	Me(*t*-Bu)$_2$Sn	H	0.02	0.00	–0.02	–4.4
Me(*t*-Bu)$_2$SnC≡CBu-*t*	Me(*t*-Bu)$_2$Sn	*t*-Bu	0.04	–0.13	–0.17	–36.9
Me(*t*-Bu)$_2$SnC≡CCH$_2$SiMe$_3$	Me(*t*-Bu)$_2$Sn	CH_2SiMe_3	0.05	–0.18	–0.23	–51.7
t-Bu$_3$SnC≡CBu-*t*	*t*-Bu3Sn	*t*-Bu	0.04	–0.13	–0.17	–38.5

[a] The $\sigma_R^0(X) - \sigma_R^0(R_3M)$ values were calculated by Eq. (17) from the $A^{1/2}$ values.

In view of the aforesaid, the five equations of type (15) for RC≡CX series (R = H, Me_3C, Me_3Si, Me_3Ge, Me_3Sn) can be combined in one, provided the three following conditions are fulfilled. First, the fact that $A^{1/2}$ depends on the σ_R^0 constants of both X and R should be taken into account. Second, to account for the incomplete characteristicity of the ν(C≡C) vibration, the σ_R^0 values for R = H in the HC≡CX series and for R = Me_3M in the $Me_3MC{\equiv}CX$ series should be taken to be –0.05 and –0.18 (if X are organic substituents; see, for example, Table 2, compounds **I**–**XVIII** and **XIX**–**XXXI**). Third, with compounds like $Me_3MC{\equiv}CH$ and $Me_3MC{\equiv}CCMe_3$ (M = Si, Ge, Sn), conventional σ_R^0 constants for H (0.00) and Me_3C (–0.13) should be applied.

In terms of the above approach, Eq. (16) is valid for compounds **I**–**LXVI** (Table 2). The corresponding plot is a straight line that passes through the origin.

$$A^{1/2} = 216[\sigma_R^0(X) - \sigma_R^0(R)], \tag{16}$$

$$S_a\ 4,\ S_Y\ 5.7,\ r\ 0.990,\ n\ 66.$$

Using Eq. (16) written in form (17) and experimental $A^{1/2}$ values, we obtained $\sigma_R^0(R_3M)$ values for a series of trialkylsilyl, trialkylgermyl, and trialkylstannyl substituents (Table 4).

$$\sigma_R^0(X) - \sigma_R^0(R) = 0.0045A^{1/2}, \tag{17}$$

$$S_a\ 0.0001,\ S_Y\ 0.03,\ r\ 0.990,\ n\ 66.$$

According to Eq. (7), the $A^{1/2}$ values for RC≡CX series (R = H, Me_3C, Me_3Si, Me_3Ge, Me_3Sn) should be linearly related to the π components of the difference of the effective atomic charges in the C≡C fragment (Δq_π). Table 5 lists the input $A^{1/2}$ and Δq_π values for the three series and Table 6, the resulting correlation equations of type (18).

$$A^{1/2} = c\Delta q_\pi + d. \tag{18}$$

Let us consider briefly these equations. The Δq_π values were obtained by quantum-chemical calculations of HC≡CX molecules [11] (13 substituents X, Table 5). Using the $\sigma_R^0(X)$ constants, by Eqs. (10-2), (11-2), and (14), we obtained $A^{1/2}$ values for the HC≡CX and $Me_3MC{\equiv}CH$ (M = C, Sn) series, and the values for M = Si, Ge were taken from [7]. As noted above, Eqs. (10-2) and (11-2) involve corrections for incomplete characteristicity of the ν(C≡C) vibration. Therefore, in Eq. (18) for R = H, $d = 0$. The corresponding equations for R = Me_3M (M = C, Si, Ge, Sn) have a nonzero free term d (Table 6). This fact can be explained by that Δq_π for $Me_3MC{\equiv}CH$ comprises two components: $\Delta q_\pi(X)$ and $\Delta q_\pi(Me_3M)$. The first relates to the effect on Δq_π of substituents X, and the second, of substituents Me_3M. The $\Delta q_\pi(Me_3M)$ values were calculated from equations of type (18) (Table 6), much as the $\sigma_R^0(Me_3M)$ values were determined from equations of type (15). Graphically (Fig. 2), the $\Delta q_\pi(Me_3C)$ and $\Delta q_\pi(Me_3Sn)$ values are the mean distances along the $\Delta q_\pi(X)$ axis between plot *1* (HC≡CX) and plot *2* ($Me_3CC{\equiv}CX$) or plot *3* ($Me_3SnC{\equiv}CX$).

The $\Delta q_\pi(R)$ and $\sigma_R^0(R)$ values as quantitative characteristics of the conjugation of the R substituents

Table 5. Calculated $A^{1/2}$ values for HC≡CX,[a] $Me_3CC≡CX$,[b] and $Me_3SnC≡CX$[c] compounds and $\Delta q_\pi(X)$ values for HC≡CX[d] compounds

X	$\sigma_R^0(X)$	$A^{1/2}$, $l^{1/2}\,mol^{-1/2}\,cm^{-1}$			$\Delta q_\pi(X)$, *e*
		HC≡CX	$Me_3CC≡CX$	$Me_3SnC≡CX$	
NH_2	–0.47	–102.0	–72.5	–126.4	–0.117
OMe	–0.43	–93.3	–64.0	–116.3	–0.089
OH	–0.40	–86.8	–57.6	–108.7	–0.087
F	–0.34	–73.8	–44.8	–93.5	–0.062
Me	–0.10	–21.7	–6.3	–32.8	–0.012
$CH=CH_2$	–0.05	–10.8	17.0	–20.5	–0.010
H	0.00	0	27.6	–7.5	0.000
CN	0.09	19.5	46.8	15.3	0.021
CF_3	0.10	21.7	48.9	17.8	0.005
NO_2	0.17	36.9	63.8	35.5	0.061
COMe	0.22	47.7	74.5	48.2	0.043
CHO	0.24	52.1	78.7	53.2	0.042
NO	0.25	54.2	80.8	55.8	0.077

[a] Calculated by Eq. (10-2) with the $\sigma_R^0(X)$ values. [b] Calculated by Eq. (11-2) with the $\sigma_R^0(X)$ values. [c] Calculated by Eq. (14) with the $\sigma_R^0(X)$ values. [c] *Ab initio* quantum-chemical calculation (4-31G basis) [11].

(H, Me_3C, Me_3Si, Me_3Ge, Me_3Sn) with the triple bond in RC≡CX molecules are related to each other by Eq. (19).

$$\Delta q_\pi(R) = 0.23\sigma_R^0(R) + 0.004, \qquad (19)$$

$$S_a\ 0.02,\ S_b\ 0.002,\ S_Y\ 0.004,\ r\ 0.985,\ n\ 5.$$

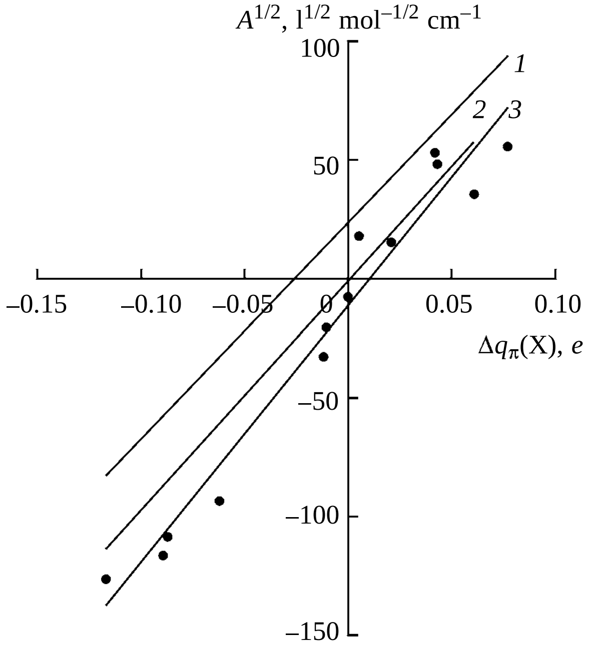

Fig. 2. Correlation between $A^{1/2}$ and $\Delta q_\pi(X)$ for the series (*1*) HC≡CX, (*2*) $Me_3CC≡CX$, and (*3*) $Me_3SnC≡CX$. Points belonging to plot *3* are shown.

Let us now consider how conjugation in $Me_3MC≡CX$ depends on the nature of M (C, Si, Ge, Sn) and on the partial atomic positive charges δ^+ on the triple bond (Table 7).

Owing to σ,p conjugation, Me_3C acts as resonance donor. This follows from the negative σ_R^0 and Δq_π values of this substituent. Unlike Me_3C, Me_3M substituents (M = Si, Ge, Sn) exhibit not only resonance donor (σ,π conjugation) but also acceptor (*d*,π conjugation) properties with respect to the triple bond [1, 6, 7, 12]. In the ground electronic state of $Me_3MC≡CX$ molecules (lack of δ^+ charges on the triple-bond atoms), *d*,π conjugation prevails over σ,π conjugation, attenuating as the atomic number of M increases. This follows from the positive σ_R^0 and Δq_π values which decrease in the series M = Si > Ge > Sn. Evidence for this conclusion also comes from the σ_R^0 values of R_3M substituents (R = Alk, Ph) (Table 4).

The constants σ_R and σ_R^+ measure the resonance properties of Me_3M substituents at the triple bond in cases where the letter bears a low (*n* 0.01 *e*) and a high (*n* 0.1 *e*) charge [1, 2]. The negative values of the resonance constants of Me_3C slightly increase in the series $\sigma_R^0 < \sigma_R < \sigma_R^+$, as a result of the enhancement of σ,π conjugation, produced by the δ^+ charge.

The effect of σ,π conjugation in $Me_3MC≡CX$ stronger depends on δ^+ at M = Si, Ge, Sn compared with M = C. Comparison of σ_R^0 and σ_R shows that Me_3Si does not longer acts as resonance acceptor

Table 6. Linear equations $A^{1/2} = c\Delta q_\pi(\mathrm{X}) + d$, standard deviations S_c and S_d, standard approximation errors S_Y, correlation coefficient r, point number n, and calculated $\sigma_R^0(\mathrm{R})$ values for RC≡CX series

Series	R	Equation no.	Equation	$\Delta q_\pi(\mathrm{X})$, e	S_a	S_b	S_Y	r	n
HC≡CX [8]	H	10-2	$A^{1/2} = 926\Delta q_\pi(\mathrm{X})$	0	58	–	12.3	0.979	13
$Me_3CC≡CX$ [5]	Me_3C	11-2	$A^{1/2} = 910\Delta q_\pi(\mathrm{X}) + 23.8$	–0.026±0.002	62	3.7	13.3	0.975	13
$Me_3SiC≡CX$ [6]	Me_3Si	12	$A^{1/2} = 845\Delta q_\pi(\mathrm{X}) - 27.3$	0.028±0.006	47	2.8	10.1	0.983	13
$Me_3GeC≡CX$ [7]	Me_3Ge	13	$A^{1/2} = 1081\Delta q_\pi(\mathrm{X}) - 16.3$	0.022±0.013	67	4.0	14.4	0.979	13
$Me_3SnC≡CX$	Me_3Sn	14	$A^{1/2} = 1080\Delta q_\pi(\mathrm{X}) - 10.9$	0.016±0.013	67	4.0	14.4	0.979	13

Table 7. Resonance constants σ_R^0, σ_R [12], and σ_R^+ [13] and parameters Δq_π of the Alk_3M substituents in $Alk_3MC≡CX$ compounds

Alk_3M	$\sigma_R^0(\Delta q_\pi,\ e)$	σ_R	σ_R^+
Me_3C	–0.13 (–0.026)	–0.15	–0.19
Me_3Si	0.12 (0.028)	0.00	0.00
Me_3Ge	0.06 (0.022)	–0.18	–0.22
Me_3Sn	0.04 (0.016)	–0.24	–
Et_3Sn	0.05 (0.019)	0.25	–0.36

already at low δ^+ ($\sigma_R = 0$ suggests equal d,π- and σ,π-conjugation effects in $Me_3SiC≡CX$). Therewith, Me_3Ge becomes resonance donor ($\sigma_R < 0$ suggests that σ,π prevails over d,π conjugation in $Me_3GeC≡CX$). In $Me_3SnC≡CX$, σ,π conjugation even stronger enhances.

The effect of further increase in δ^+ on σ,π conjugation manifests itself in differences in σ_R^+ and σ_R. As seen from Table 7, this effect is most pronounced when resonance donor properties obviously prevail over acceptor, i.e. in $Et_3SnC≡CX$.

EXPERIMENTAL

The compounds studied were synthesized as described above [14, 15]. Their purity was checked by ^{1}H NMR and GLC. The purity of the solvent (freshly distilled CCl_4) was checked by UV and IR spectroscopy.

The IR spectra of CCl_4 solutions (c 0.05–0.6 M) were measured on a UR-20 spectrometer at 2000–2300 cm^{-1}. The integral absorptivities A of the C≡C stretching vibration bands was performed by a procedure previously applied for HC≡CX [8] and $Me_3MC≡CX$ (M = C [5], Si [6], Ge [7]; X are inorganic, organic, and organometallic substituents). The A values were measured in practical IUPAC units [5–8] ($\mathrm{l\ mol^{-1}\ cm^{-2}}$).

The σ_R^0 constants for the Me_3M and X substituents were taken from [5–8].

The correlation equations were calculated by standard Statgraphics 3.0 programs. The least-squares treatment was performed at a 95% confidence level.

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