Intensity of bands of the C≡C stretching modes in the IR spectra and conjugation in silylacetylenes

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A comparative study of the integrated extinction coefficients (A) of the C≡C stretching bands in the IR spectra of acetylene derivatives $Me_3SiC{\equiv}CR$, $HC{\equiv}CR$, and $Me_3CC{\equiv}CR$ was carried out. The resonance interactions of substituents with a triple bond are the main cause of the changes in the values of A. The total resonance effect of the Me_3Si fragment involves both acceptor (d,π-conjugation) and donor (σ,π-conjugation) components; d,π-conjugation dominates in the silylacetylenes studied. The $\sigma_R{}^0$ resonance constant of the Me_3Si substituent in compounds $Me_3SiC{\equiv}CR$ is 0.17±0.02.

Key words: acetylene, derivatives, silylacetylenes; integrated extinction coefficient; d,π-conjugation; σ,π-conjugation.

According to current concepts,[1–6] the Alk_3M substituent in compounds of group IV elements Alk_3MR_π (M = Si, Ge, Sn, and Pb; R_π is phenyl, vinyl, ethynyl, furyl, thienyl, and the like) is both a resonance acceptor of the −M-type and a resonance donor of the +M-type[7] with respect to the reaction (indicator) center R_π. The acceptor properties (d,π-conjugation) of the Alk_3M fragment are due to the joint effect of the vacant nd-orbitals of the M atom and antibonding σ*-orbitals of the M−C bonds, whereas the donor properties (σ,π-conjugation) are due to mixing of the σ-orbitals of the M−C bonds with the π-orbitals of R_π.

The relative contribution of d,π- and σ,π-conjugation to the total resonance effect in molecules Alk_3MR depends on the type of metal and group R_π as well as on the value of the negative effective charge on R_π. A strong change in this charge (caused by specific solvation, ionization, and chemical reactions) results in inversion of the donor-acceptor properties of substituents Alk_3M.[8] Therefore, one fails to define a universal (invariant with respect to both the type and the charge of R_π) scale of the resonance parameters quantitatively characterizing the conjugation between Alk_3M and R_π fragments, even for fixed substituents Alk_3M (for instance, Me_3Si, Et_3Sn, and the like). Resonance parameters $\sigma_R{}^0$ as a measure of R'_3M conjugation (R′ are organic groups) with R_π in the individual molecules R'_3MR_π, whose electronic structure is not perturbed by interaction with the medium, have only been systematically investigated for R_π = Ph.[1,3]

In this work, the conjugation effects in compounds $Me_3SiC{\equiv}CR$ (R are various organic groups) were studied by IR spectroscopy, and the $\sigma_R{}^0$ parameters, characterizing the resonance interactions between the Me_3Si substituent and the indicator center C≡CR, were determined. Carbon tetrachloride, which weakly solvates the Si atom[9] as well as the indicator center (according to the data for compounds HC≡CR and $Me_3CC{\equiv}CR$),[10,11] was used as a solvent.

Experimental

The studied compounds were synthesized according to previously published procedures.[12,13] The purity of the compounds was monitored by GLC. Freshly distilled CCl_4 of spectroscopic grade in the UV and IR spectral regions was used as the solvent.

The IR spectra of solutions of the compounds under study (0.08−0.30 mol L^{-1}) in CCl_4 were recorded on an UR-20 spectrophotometer in the region from 2000 to 2300 cm^{-1}. The values of the integrated extinction coefficients (A) of the C≡C stretching bands were determined following a previously described procedure[14] and expressed in IUPAC practical units (L mol^{-1} cm^{-2}).[10,11]

The data were processed by the least squares method using the standard STATGRAPHICS 3.0 program package on an IBM PC AT personal computer.

The previously determined[10,11] values of the $\sigma_R{}^0$ constants of organic substituents as well as those we calculated following the procedure described in Refs. 10 and 11 were used.

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Results and Discussion

It is known[15] that integrated extinction coefficient A is proportional to the squared derivative of the dipole moment (μ) of the molecule with respect to the ith normal coordinate (Q_i).

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

If vibration of a certain bond A—B in a polyatomic molecule is characterized by its eigenvector, then expression (1) transforms to

$$A \sim (\partial\mu_{A-B}/\partial q_{A-B})_0^2, \quad (2)$$

where μ_{A-B} is the dipole moment of the A—B bond, and q_{A-B} is the stretching coordinate of the bond. Since the stretching vibration of the A—B bond is characterized by its eigenvector, this bond can be considered to a good approximation as a diatomic molecule A—B, for which (according to the published data[15])

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

where r_0 is the interatomic distance A—B. Thus,

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

It follows from relation (4) that the reason for the change in extinction coefficient A of well-localized vibrations of the A—B bond is the electronic effects of molecular fragments, leading to a change in the dipole moment μ_{A-B}.

Three approaches based on relation (4) were used to study conjugation of Me_3Si and R substituents with the π-system in compounds $Me_3SiC{\equiv}CR$. The first one is based on a comparison between the values of $A^{1/2}$ and those of $\Delta\nu_R$ (Table 1) considering them as independent characteristics of the resonance interactions in $Me_3SiC{\equiv}CR$ molecules. A linear dependence was established

$$A^{1/2} = -1.10\Delta\nu_R - 22.0, \quad (5)$$

$S_a = 0.12$, $S_b = 3.1$, $S_y = 8.0$, $r = 0.953$, $n = 11$.

Equation (5) relates the $A^{1/2}$ values to the $\Delta\nu_R$ values, characterizing the conjugation effects of Me_3Si and R substituents with the triple bond not in the isolated $Me_3SiC{\equiv}CR$ molecules, but in their H-complexes with phenol.[16] Since a small positive charge δ^+ (0.01 e) is induced on the triple bond in H-complexation, the degree of conjugation in the molecules and in their H-complexes can be somewhat different. The $\Delta\nu_R$ parameters were systematically studied for a series of benzene,[21] ethylene,[4] thiophene,[22] furan,[23] and acetylene[16] derivatives. It was shown that the following relation is valid for each of the series of the above H-complexes

$$\Delta\nu = a\Sigma\sigma_I + b\Sigma\sigma_R + c, \quad (6)$$

where $\Delta\nu$ is the shift of the phenol ν(OH) frequency in the IR spectrum due to formation of a H-complex between phenol and the π-base; $\Sigma\sigma_I$ and $\Sigma\sigma_R$ are the sums of the inductive and the resonance constants of substituents at the π-donor center, bearing the charge δ^+, respectively. The numerical values of coefficients a, b, and c depend on the type of the π-base (benzene, acetylene derivatives, *etc.*). In a number of publications, the $b\Sigma\sigma_R$ value is denoted as $\Delta\nu_R$,[4,16,21–23] and it was also shown that the

Table 1. Integrated extinction coefficients A, values of $\Delta\nu_R$, and σ_R^0 constants of substituents R for compounds $Me_3SiC{\equiv}CR$

Compound	R	A /L mol^{-1} cm^{-2}	$-A^{1/2}$ /L$^{1/2}$ mol$^{-1/2}$ cm^{-1}	$\Delta\nu_R$ /cm^{-1}	σ_R^0
1	$CH_2SnBu^t_3$	4150	64.4	+44	−0.22
2	CH_2GeMe_3	4060	63.7	+38	−0.18
3	CH_2SiMe_3	4290	65.5	+35	−0.18
4	Bu^t_3	1590	39.9	+19	−0.13
5	SC_6F_5	2600	51.0	—	−0.12
6	CH_2Ph	2630	51.3	+19	−0.11
7	Ph	2700	52.0	+16	−0.10
8	$CH_2C_6F_5$	1700	41.2	+21	−0.08
9	CH_2SPh	1290	35.9	+24	−0.08
10	CH_2OMe	820	28.6	+7	−0.07
11	$CH_2SC_6F_5$	1100	33.2	—	−0.02
12	C_6F_5	640	25.4	−4	−0.01
13	CHO	490	−22.1	−34	+0.24

Note. The value of A for compound **4** was taken from Ref. 11. The values of $\Delta\nu_R$ were calculated following the previously described procedure;[16] the appropriate values of σ_R were taken from Refs. 16—18. The values of σ_R^0 for substituents R in molecules **1**—**3** were taken from Ref. 19, those in molecules **5**—**9**, **11**, and **12** we obtained following the previously described procedure;[10] the average value of two values (one taken from Ref. 10 and the other we measured) is given for compound **10**; the values of σ_R^0 for compounds **4** and **13** were taken from Refs. 10, 20.

π-electron-donor ability Δν, as well as its resonance component $\Delta\nu_R$, only depend on the electronic effects of the substituents bound to the π-donor center in accordance with Eq. (6). This conclusion and the satisfactory correlation coefficient of Eq. (5) point to the fact that the electronic effects of the substituents predominantly affect the values of integrated extinction coefficients A in compounds $Me_3SiC{\equiv}CR$.

The second approach (more rigorous than the first one) to the analysis of conjugation of substituents (Me_3Si and R) with the π-system in $Me_3SiC{\equiv}CR$ molecules is based on the results of normal coordinate analysis[10,11,15,24—26] of the stretching vibrations ν(C≡C) in the IR spectra of acetylene derivatives. According to these data, a change in the C≡C bond length corresponds in the main to ν(C≡C) stretch (whereas the mass of the substituents has no effect on ν(C≡C)) for any monosubstituted derivatives HC≡CR and $Me_3CC{\equiv}CR$. Insignificant and virtually equal mixing of the ν(C≡C) stretching vibration with the ν(CC≡) and ν(SiC≡) vibrations was established by the example of $Me_3CC{\equiv}CH$ and $Me_3SiC{\equiv}CH$. This mixing results in a small and approximately equal decrease in the degree of localization of the normal vibration ν(C≡C) for both compounds.[24—26] At the same time, the degree of localization of ν(C≡C) remains reasonably high, which is in particular confirmed by the existence of the relations[10,11]

$$A^{1/2} = 217(\sigma_R{}^0 + 0.05),\ r = 0.992 \qquad (7)$$

for 18 compounds HC≡CR and

$$A^{1/2} = 213[\sigma_R{}^0 - \sigma_R{}^0(\mathrm{Bu^t}) + 0.05],\ r = 0.995 \qquad (8)$$

for 17 compounds $Me_3CC{\equiv}CR$, where $\sigma_R{}^0$ are the resonance constants of substituents R.

The high values of the correlation coefficients in Eqs. (7) and (8) point to the fact that the values of $A^{1/2}$ in the series HC≡CR and $Me_3CC{\equiv}CR$ only change due to the resonance interactions between the substituents and the triple bond.

Two peculiarities of relations (7) and (8) should be emphasized. On the one hand, since $\sigma_R{}^0 = 0$ for the unsubstituted acetylene, the value of A must also be zero. However, because of the different eigenvectors of the ν(C≡C) normal vibration in HC≡CH and HC≡CR molecules (see Ref. 10), the line corresponding to Eq. (7) does not pass through the origin. On the other hand, Eq. (8) only differs from Eq. (7) in the constant ($\sigma_R{}^0(\mathrm{Bu^t}) = 0.13$), which is consistent with a nearly equal degree of localization of ν(C≡C) for compounds HC≡CR and $Me_3CC{\equiv}CR$.

On the basis of the above data on the degree of localization of the ν(C≡C) vibration, dependences of type (7) and (8) can be expected to exist for compounds $Me_3SiC{\equiv}CR$.

It is convenient to express Eqs. (7) and (8) in the form of dependences (9) and (10), respectively.

$$A^{1/2} = 217\sigma_R{}^0 + 10.8 \qquad (9)$$

$$A^{1/2} = 213\sigma_R{}^0 + 38.3 \qquad (10)$$

For compounds $Me_3SiC{\equiv}CR$ (see Table 1), the following relation is valid:

$$A^{1/2} = 197\sigma_R{}^0 - 24.7, \qquad (11)$$

$$S_a = 15,\ S_b = 2.1,\ S_y = 6.0,\ r = 0.969,\ n = 13.$$

To calculate the $\sigma_R{}^0$ values of substituents R in some silylacetylenes $Me_3SiC{\equiv}CR$ (see Table 1, compounds **5—12**), we measured the A values for compounds HC≡CR containing the same groups R. The $\sigma_R{}^0$ values were calculated using Eq. (7). The values of A/L mol^{-1} cm^{-2} for compounds HC≡CR are listed below.

R	CH_2Ph	Ph	$CH_2C_6F_5$	CH_2SPh	CH_2OMe	$CH_2SC_6F_5$	C_6F_5
A	150	180	40	40	90	35	70

The value of $\sigma_R{}^0$ for substituent SC_6F_5 was calculated by Eq. (8) using the value of A (130 L mol^{-1} cm^{-2}) for $Me_3CC{\equiv}CSC_6F_5$.

Comparing relations (9), (10), and (11), we can draw the following conclusions. The integrated extinction coefficient A of the ν(C≡C) bands in the IR spectra in the series of compounds HC≡CR, $Me_3CC{\equiv}CR$, and $Me_3SiC{\equiv}CR$ almost entirely depends on the conjugation of the substituents with the π-system.

As to their resonance properties, the Me_3C and Me_3Si groups are the +M-donor and the −M-acceptor, respectively. This unambiguously follows from the shift of line *2* in Fig. 1 toward smaller $\sigma_R{}^0$ values and that of line *3* toward larger $\sigma_R{}^0$ values with respect to line *1* (see Fig. 1).

The average value of the shift between lines *3* and *1* along the $\sigma_R{}^0$ axis in the region of the change in $A^{1/2}$ from −65 to +22 (see Table 1) is 0.17±0.02; it is the value of the $\sigma_R{}^0$ parameter of the Me_3Si substituent in the isolated molecules $Me_3SiC{\equiv}CR$. The positive sign of $\sigma_R{}^0$ points to the fact that d,π-conjugation dominates over σ,π-conjugation in these molecules.

A limited number of the studied compounds $Me_3SiC{\equiv}CR$ hampers (due to inadequate sample size and/or the possible effect of direct polar conjugation) detection of second-order effects, resulting in a difference between the slope of Eq. (9) and that of Eq. (11).

The third approach we used is based on the direct justification test of Eq. (4) using the $A^{1/2}$ values for compounds $Me_3SiC{\equiv}CR$ and the values proportional to the π-components of the dipole moments of C≡C bonds.

As is known,[27] the electric dipole moment μ is the product of the charge (q) and the distance (l) between the center of gravity of the positive charge and the negative charge. If only the π-component of the dipole moment (μ_π) is considered, then

$$\mu_\pi = q_\pi l, \qquad (12)$$

where q_π are the effective π-electron charges on the atoms of a given bond. Previously in this work for three series of acetylene derivatives (HC≡CR, $Me_3CC{\equiv}CR$, and $Me_3SiC{\equiv}CR$), the conclusions were drawn that the ν(C≡C) vibration is a well-localized vibration and the

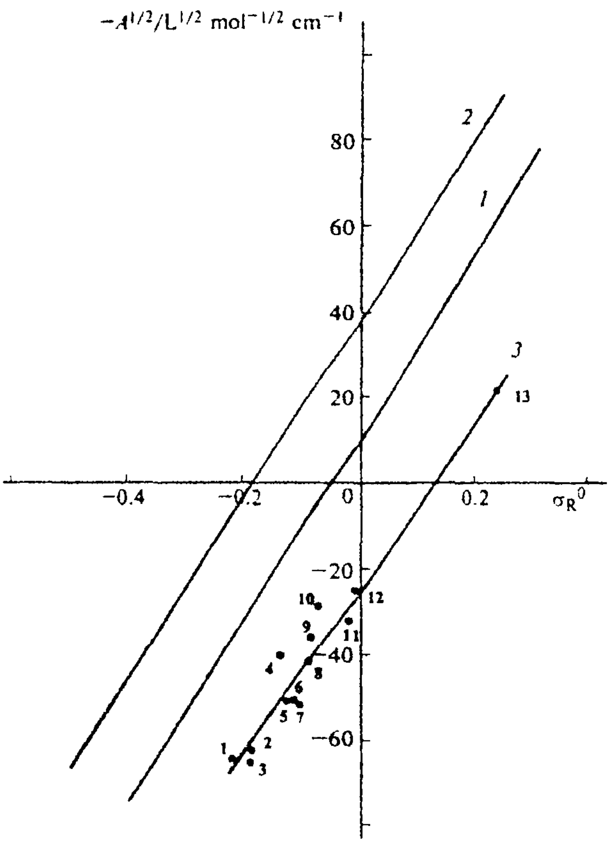

Fig. 1. Correlation between the $A^{1/2}$ and σ_R^0 values for compounds HC≡CR (*1*), Me_3CC≡CR (*2*), and Me_3SiC≡CR (*3*). The numbering of the points on line *3* corresponds to that of the compounds in Table 1.

value of the integrated extinction coefficient *A* of the ν(C≡C) band in the IR spectrum is predominantly affected by the resonance interactions between the substituents and the triple bond. If these conclusions are true and the length of the C≡C bond (*l*) is kept constant at least for each of the series, then it follows from relations (4) and (12) that

$$A^{1/2} \sim q_\pi(\mathrm{C{\equiv}C}), \tag{13}$$

where q_π(C≡C) are the effective π-electron charges on the atoms of the C≡C bond.

To verify relation (13), the Δq_π values for compounds HC≡CR (R = NH_2, OMe, OH, F, Me, CH=CH_2, CF_3, CN, COH, COMe, NO_2, and NO)[28] were taken as the q_π(C≡C) values. The Δq_π values, calculated by nonempirical quantum-chemical methods in the 4-31G basis set,[28] quantitatively characterize the π-electron exchange between substituent R and the triple bond in HC≡CR molecules, *i.e.*, that part of the change in the effective charge on the carbon atoms of the triple bond which is due to the conjugation effect between the R groups and the π-system (Table 2).

Table 2. Values of $A^{1/2}$ and Δq_π for compounds HC≡CR, Me_3CC≡CR, and Me_3SiC≡CR

R	$-A^{1/2}$ /L$^{1/2}$ mol$^{-1/2}$ cm^{-1}			$\Delta q_\pi/e$
	HC≡CR	Me_3CC≡CR	Me_3SiC≡CR	
NH_2	−91.2	−61.8	−117.3	−0.117
OMe	−82.5	−53.3	−109.4	−0.089
OH	−76.0	−46.9	−103.5	−0.087
F	−63.0	−34.1	−91.7	−0.062
Me	−10.9	+17.0	−44.4	−0.012
CH=CH_2	0	+27.6	−34.6	−0.010
H	+10.8	+38.3	−24.7	0
CF_3	+32.5	+59.6	−5.0	+0.005
CN	+30.3	+57.5	−7.0	+0.021
COH	+62.9	+89.4	+22.6	+0.042
COMe	+58.5	+85.2	+18.6	+0.043
NO_2	+47.7	+74.5	+8.8	+0.061
NO	+65.0	+91.6	+24.6	+0.077

Note. The values of $A^{1/2}$ were calculated by Eqs. (9), (10), and (11) using the values of σ_R^0 for the substituents taken from Refs. 10, 20. The values of Δq_π were taken from Ref. 28. The negative (positive) values of Δq_π correspond to an increase (decrease) in the π-electron transfer from substituent R to the triple bond as compared to that for acetylene.

The values $A^{1/2}$ and Δq_π are related by a linear dependence (Fig. 2), which is described by the following equations:

$$A^{1/2} = 930\Delta q_\pi + 7.9, \tag{14}$$

$S_a = 52$, $S_b = 3.1$, $S_y = 11.1$, $r = 0.983$, $n = 13$

for compounds HC≡CR,

$$A^{1/2} = 913\Delta q_\pi + 35.5, \tag{15}$$

$S_a = 51$, $S_b = 3.1$, $S_y = 10.9$, $r = 0.983$, $n = 13$

for compounds Me_3CC≡CR, and

$$A^{1/2} = 845\Delta q_\pi - 27.3, \tag{16}$$

$S_a = 47$, $S_b = 2.8$, $S_y = 10.1$, $r = 0.983$, $n = 13$

for compounds Me_3SiC≡CR.

Lines *1* and *2* in Fig. 2 are almost parallel. Line *2* is shifted toward smaller Δq_π values by -0.031 ± 0.002 *e* with respect to line *1*. π-Electron transfer from the substituents to the π-system increases by that value on going from HC≡CR to Me_3CC≡CR, which can be explained by the approximately constant (*i.e.*, independent of the R type) resonance contribution (the +M-effect) of the *tert*-butyl fragment.

The difference between the slope of Eq. (14) and that of Eq. (16) is due to the same causes considered above in discussing Fig. 1 and Eqs. (9) and (11). At the same time, the shift along the Δq_π axis between line *1* and line *3* in Fig. 2 varies within relatively narrow limits, from ~0.029 *e* (for $A^{1/2} = -115$, the case of typical resonance donors R in Me_3SiC≡CR) to ~0.043 *e*

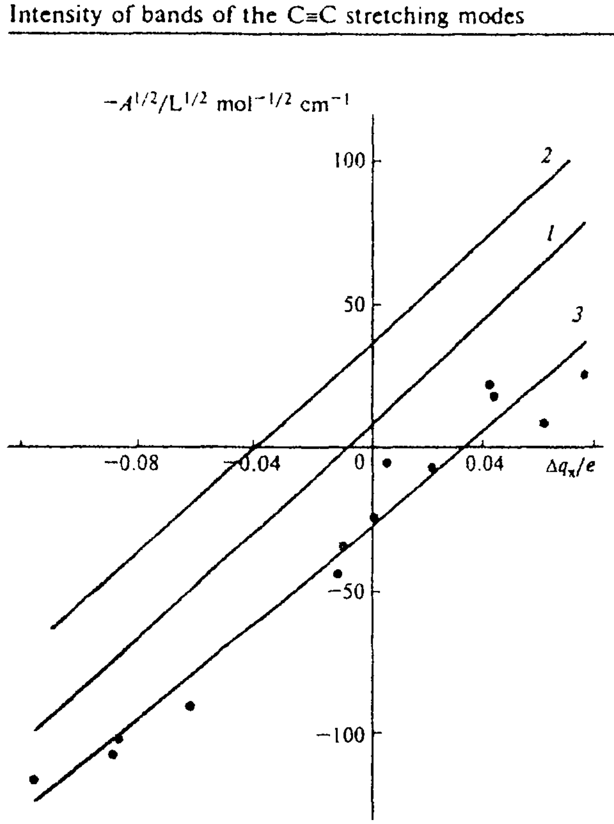

Fig. 2. Correlation between $A^{1/2}$ and Δq_x values for compounds HC≡CR (*1*), Me_3CC≡CR (*2*), and Me_3SiC≡CR (*3*).

(for $A^{1/2}$ = +25, the case of typical resonance acceptors R), in the studied range of the change in the $A^{1/2}$ values. The average value of the shift (+0.036±0.007 *e*) is the value of π-electron transfer from the triple bond to the Me_3Si substituent in isolated Me_3SiC≡CR molecules.

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References

1. A. N. Egorochkin, *Usp. Khim.*, 1992, **61**, 1092 [*Russ. Chem. Rev.*, 1992, **61** (Engl. Transl.)].
2. A. N. Egorochkin, G. A. Razuvaev, and M. A. Lopatin, *J. Organomet. Chem.*, 1988, **344**, 49.
3. A. N. Egorochkin and G. A. Razuvaev, *Usp. Khim.*, 1987, **56**, 1480 [*Russ. Chem. Rev.*, 1987, **56**, 846 (Engl. Transl.)].
4. A. N. Egorochkin, S. E. Skobeleva, and V. L. Tsvetkova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1383 [*Russ. Chem. Bull.*, 1993, **42**, 1316 (Engl. Transl.)].
5. A. N. Egorochkin, S. E. Skobeleva, V. L. Tsvetkova, E. T. Bogoradovsky, and V. S. Zavgorodny, *Metalloorg. Khim.*, 1991, **4**, 362 [*Organomet. Chem. USSR*, 1991, **4**, 171 (Engl. Transl.)].
6. A. N. Egorochkin, S. E. Skobeleva, E. T. Bogoradovsky, and T. P. Zubova, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1041 [*Russ. Chem. Bull.*, 1994, **43**, 976 (Engl. Transl.)].
7. C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell Univ. Press, Ithaca, 1969, Ch. 2.
8. A. N. Egorochkin and S. E. Skobeleva, in *Tez. dokl. VI Vseros. konf. po metalloorganicheskoi khimii* [*Abstracts VIth All-Russian Conf. on Organometallic Chemistry*], Nizhnii Novgorod, 1995, 257 (in Russian).
9. S. Ya. Khorshev, V. L. Tsvetkova, and A. N. Egorochkin, *J. Organomet. Chem.*, 1984, **264**, 169.
10. T. B. Grindley, K. F. Johnson, A. R. Katritzky, H. J. Keogh, C. Thirkettle, R. T. C. Brownlee, J. A. Munday, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 1974, 276.
11. T. B. Grindley, K. F. Johnson, A. R. Katritzky, H. J. Keogh, C. Thirkettle, and R. D. Topsom, *J. Chem. Soc., Perkin Trans. 2*, 1974, 282.
12. *Chemistry of Acetylenes*, Ed. H. G. Viehe, M. Dekker, New York, 1969.
13. V. Jager, M. Murray, U. Niedballa, and H. G. Viehe, *Methoden der organischen Chemie (Houben-Weil)*, Ed. E. Muller, Georg Thieme Verlag, Stuttgart, 1977, 5/2a.
14. R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Am. Chem. Soc.*, 1966, **88**, 1413.
15. M. V. Vol'kenshtein, L. A. Gribov, M. A. El'yashevich, and B. I. Stepanov, *Kolebaniya molekul* [*Molecular Vibrations*], Nauka, Moscow, 1972 (in Russian).
16. A. N. Egorochkin, S. E. Skobeleva, V. L. Tsvetkova, E. T. Bogoradovsky, and V. S. Zavgorodny, *Metalloorg. Khim.*, 1992, **5**, 818 [*Organomet. Chem. USSR*, 1992, **5**, 394 (Engl. Transl.)].
17. O. Exner, in *Correlation Analysis in Chemistry. Recent Advances*, Eds. A. Chapman and J. Shorter, Plenum Press, New York, 1978, 439.
18. C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
19. A. N. Egorochkin, S. E. Skobeleva, V. L. Tsvetkova, E. T. Bogoradovsky, and V. S. Zavgorodny, *Metalloorg. Khim.*, 1991, **4**, 992 [*Organomet. Chem. USSR*, 1991, **4**, 483 (Engl. Transl.)].
20. A. R. Katritzky and R. D. Topsom, *Chem. Rev.*, 1977, **77**, 639.
21. A. N. Egorochkin, S. E. Skobeleva, and V. L. Tsvetkova, *Metalloorg. Khim.*, 1993, **6**, 131 [*Organomet. Chem. USSR*, 1993, **6** (Engl. Transl.)].
22. A. N. Egorochkin and S. E. Skobeleva, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 2163 [*Russ. Chem. Bull.*, 1994, **43**, 2043 (Engl. Transl.)].
23. A. N. Egorochkin, S. E. Skobeleva, and T. G. Mushtina, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 289 [*Russ. Chem. Bull.*, 1995, **44**, 280 (Engl. Transl.)].
24. A. V. Belyakov, V. S. Nikitin, and M. V. Polyakova, *Zh. Obshch. Khim.*, 1995, **65**, 81 [*Russ. J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
25. V. S. Nikitin, M. V. Polyakova, A. V. Belyakov, E. T. Bogoradovsky, and V. S. Zavgorodny, *Zh. Fiz. Khim.*, 1993, **67**, 979 [*Russ. J. Phys. Chem.*, 1993, **67** (Engl. Transl.)].
26. V. S. Nikitin, M. V. Polyakova, I. I. Baburina, A. V. Belyakov, E. T. Bogoradovsky, and V. S. Zavgorodny, *Spectrochim. Acta A*, 1990, **46**, 1669.
27. V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov, *Dipol'nye momenty v organicheskoi khimii* [*Dipole Moments in Organic Chemistry*], Khimiya, Leningrad, 1968 (in Russian).
28. S. Marriott and R. D. Topsom, *J. Mol. Struct.*, 1984, **106**, 277.

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