The conjugation and effective charges of the atoms at the triple bond in germylacetylenes

A. N. Egorochkin,[a]* *S. E. Skobeleva,*[a] *T. G. Mushtina,*[a] *and E. T. Bogoradovsky*[b]

[a]*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation. Fax: +7 (831 2) 66 1497. E-mail: imoc@infotel.msk.su*

[b]*St. Petersburg State Technological Institute, 26 Moskovsky prosp., 198013 St. Petersburg, Russian Federation. Fax: +7 (812) 110 6285*

The integrated extinction coefficients (A) of the C≡C stretching modes in the IR spectra of 12 germylacetylenes $Me_3GeC{\equiv}CR$ are determined by the resonance interactions of substituents with the triple bond. The $A^{1/2}$ values change linearly with change in the difference between the effective π-electron charges on the atoms at the triple bond and $\sigma^0{}_R$ constants of organic substituents R. The average value of the $\sigma^0{}_R$ constant of the Me_3Ge substituent in the compounds studied is +0.06. The resonance acceptor effect of the Me_3Ge substituent toward the triple bond (d,π-conjugation) is stronger than the donor effect (σ,π-conjugation).

Key words: germylacetylenes, integrated extinction coefficients, effective charge, d,π-conjugation, σ,π-conjugation.

Generally, the conjugation in compounds R_π—X is determined not only by the properties of organic (R) and organoelement (MR_3, M = Si, Ge, Sn, Pb) substituents X, but also by those of the reaction (indicator) center R_π (Ph—, $H_2C{=}CH$—, HC≡C—, *etc.*).[1-3] Therefore, it is impossible to characterize the capability of substituents X for conjugation by universal parameters, which are invariant toward R_π. The charge on the R_π fragment and its type (in the case of organoelement compounds with X = MR_3) are of great importance.[1-5] The $\sigma^0{}_R$-parameters of the substituents are a measure of resonance interactions in the ground electron state of isolated R_π—X molecules for any X (R and MR_3).[6] If a small (~0.01 e) or large (~0.1 e) positive charge is induced on the R_π fragment as a result of chemical or physical perturbations (*e.g.*, upon complexation or ionization of R_π—X molecules), then the conjugation is characterized[1-5] by σ_R and $\sigma_R{}^+$ parameters, respectively. In addition, the values of resonance parameters of a fixed substituent MR_3 (for instance, $GeMe_3$ in compounds R_π—MR_3) change when varying the type of R_π (in contrast to X = R).[1,2,5,7,8] The reasons for the lesser universality of the parameters of organoelement substituents as compared to those of organic substituents remain unclear, which is, in particular, due to fragmentary experimental data on the dependence of σ-parameters of MR_3 substituents on the R_π type in compounds R_π—MR_3. The solution of this problem, which is critical for physical organometallic chemistry, suggests a progressive increase in the number of studied series of R_π—MR_3 compounds.

The aim of this work is to study the resonance effects in trimethylgermylacetylene derivatives $Me_3GeC{\equiv}CR$ by analyzing the integrated extinction coefficients of the ν(C≡C) IR bands, to estimate changes in the effective charge on the indicator center in the case of conjugation with the Me_3Ge substituent, and to calculate the $\sigma^0{}_R$ parameter of this substituent.

Experimental

The studied compounds were synthesized following the known procedures.[9,10] The purity of the compounds was monitored by GLC.

The purity of freshly prepared solvent CCl_4 was monitored by UV and IR spectroscopy.

The integrated extinction coefficients (A) of the C≡C stretching bands in the IR spectra were measured on an UR-20 spectrophotometer in the wavelength range 2000—2300 cm^{-1} for solutions of the compounds under study (0.1—0.4 mol L^{-1}) in CCl_4.

The A values are given in IUPAC practical units (L^2 mol^{-1} cm^{-2}) and determined following a previously described procedure,[11] which was used earlier for the determination of A values in compounds HC≡CR,[12] $Me_3CC{\equiv}CR$,[13] and $Me_3SiC{\equiv}CR$.[14]

Correlation equations were calculated using the standard Statgraphics 3.0 program package on a PC AT 286 personal computer. The data were processed by the least squares method at a 95% confidence level.

The values of the $\sigma^0{}_R$ constants of organic substituents were taken from the literature.[12,14,15]

Results and Discussion

The integrated extinction coefficients A of the ν(C≡C) stretching bands in the IR spectra of the studied

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1569—1574, August, 1998.

1066-5285/98/4708-1526 $20.00

Table 1. Integrated extinction coefficients (A) and $\sigma^0{}_R$ constants of substituents R for compounds $Me_3GeC{\equiv}CR$

Compound	R	A /L^2 mol^{-1} cm^{-2}	$A^{1/2}$ [a] /L $mol^{-1/2}$ cm^{-1}	$\sigma^0{}_R$ [b]
1	CH_2GeMe_3	4520	−67.2	−0.18
2	CH_2SiMe_3	4300	−65.6	−0.18
3	SC_6F_5	~1500	−38.7	−0.12
4	CH_2Ph	1620	−40.2	−0.11
5	Ph	1420	−37.7	−0.10
6	$CH_2C_6F_5$	845	−29.1	−0.08
7	CH_2SPh	830	−28.8	−0.08
8	CH_2OMe	600	−24.5	−0.07
9	$CH_2SC_6F_5$	370	−19.2	−0.02
10	CH_2Br	130	−11.4	−0.02
11	H	420	−20.5	0
12 [c]	CHO	1955	44.2	0.24

[a] The $A^{1/2}$ values are alternating; according to the literature data,[12–14] they have the same sign as the $\sigma^0{}_R$ values for substituents R. [b] See Ref. 14. [c] See Ref. 16.

$Me_3GeC{\equiv}CR$ compounds change over a wide range depending on the organic substituents R (Table 1). As follows from the general theory of vibrational spectra,[17] the electronic effects of Me_3Ge and R substituents are the only reason for changes in the A values only if the $\nu(C{\equiv}C)$ vibration is characterized by its eigenvector. If this condition is fulfilled, then the C≡C fragment can be considered to a good approximation as a diatomic molecule C≡C. The following relationships are known to be valid for such molecules[17]

$$A \sim (\partial\mu_{C\equiv C}/\partial q_{C\equiv C})^2 \qquad (1)$$

and

$$\partial\mu_{C\equiv C}/\partial q_{C\equiv C} \approx \mu_{C\equiv C}/r_0, \qquad (2)$$

and, hence, at r_0 = const

$$A^{1/2} \sim \mu_{C\equiv C}. \qquad (3)$$

In these relationships $\mu_{C\equiv C}$ is the dipole moment of the C≡C bond, $q_{C\equiv C}$ is the stretching coordinate of the C≡C bond, and r_0 is the interatomic C≡C distance.

In turn, the dipole moment of the C≡C fragment considered as a diatomic molecule taking into account the limitations (see, for instance, Ref. 18) is defined by the formula

$$\mu_{C\equiv C} = Qr_0, \qquad (4)$$

where Q is the difference between the effective charges on the atoms of the C≡C fragment.

The π-component μ_π of the dipole moment of the C≡C bond and the difference between the effective π-electron charges on the atoms of the C≡C fragment q_π is of prime interest for studying the conjugation in $Me_3GeC{\equiv}CR$ molecules. In this case expression (4) takes the form

$$\mu_\pi = q_\pi r_0. \qquad (5)$$

The A values for HC≡CR, $Me_3CC{\equiv}CR$, and $Me_3SiC{\equiv}CR$ molecules are virtually dependent only on the resonance interactions between the substituents and the π-electron system.[12–14] If it is assumed to be also valid for $Me_3GeC{\equiv}CR$ molecules, then in the case of non-coupled $\nu(C{\equiv}C)$ vibration one can expect on the basis of relationships (3) and (4) that the following dependence is valid

$$A^{1/2} \sim q_\pi. \qquad (6)$$

The dependence (6) can be proved using a direct or indirect approach.

We consider first the second approach. To this end, let us discuss the problem of contribution of other modes to the $\nu(C{\equiv}C)$ stretching mode. In monosubstituted HC≡CR and disubstituted $Me_3CC{\equiv}CR$ and $Me_3SiC{\equiv}CR$ compounds, the mass of the substituent has no effect on the $\nu(C{\equiv}C)$ vibration, where the C≡C bond length is predominantly changed.[12–14,17,19] Though some mixing of $\nu(C{\equiv}C)$ stretching mode with the $\nu(CC{\equiv})$ and $\nu(SiC{\equiv})$ stretching modes (in $Me_3CC{\equiv}CH$ and $Me_3SiC{\equiv}CH$, respectively) has been established,[19] its contribution to the $\nu(C{\equiv}C)$ mode in acetylene derivatives is small. This is clearly supported by linear dependences between $A^{1/2}$ and $\sigma^0{}_R$ ($\sigma^0{}_R$ are the resonance constants of substituents R), which take the form

$$A^{1/2} = 217\sigma^0{}_R + 10.8 \ (r = 0.992), \qquad (7)$$

$$A^{1/2} = 213\ \sigma^0{}_R + 38.3 \ (r = 0.995), \qquad (8)$$

$$A^{1/2} = 197\sigma^0{}_R - 24.7 \ (r = 0.969). \qquad (9)$$

for compounds HC≡CR, $Me_3CC{\equiv}CR$, and $Me_3SiC{\equiv}CR$, respectively.[12–14]

The presence of the absolute term in Eq. (7) is the manifestation of slight coupling of the $\nu(C{\equiv}C)$ mode in HC≡CR molecules. If the $\nu(C{\equiv}C)$ mode is totally pure, the line (7) should pass through the origin.

According to the data of normal coordinate analysis,[19] an increase in the atomic number of the central element M (C, Si, Ge, and Sn) in $Me_3MC{\equiv}CH$ molecules is accompanied by the decrease in contribution of other modes to the $\nu(C{\equiv}C)$ mode. Therefore, it can be suggested that dependences of the type (7)—(9) will be all the more valid for germylacetylenes $Me_3GeC{\equiv}CR$.

Processing the data for compounds $Me_3GeC{\equiv}CR$ (see Table 1) by the least squares method following this hypothesis lead to the equation

$$A^{1/2} = 253\sigma^0{}_R - 13.0 \qquad (10)$$

$$(S_a = 16,\ S_b = 2.0,\ S_Y = 5.8,\ r = 0.981,\ n = 12).$$

Equation (10) serves as an indirect confirmation of dependence (6). In fact, the $\sigma^0{}_R$ constants in expressions (7)—(10) are quantitative characteristics of conjugation

Table 2. The $A^{1/2}$ values for compounds $Me_3GeC{\equiv}CR$, σ^0_R constants of substituents R, and Δq_π values calculated by the *ab initio* method[6] for compounds $HC{\equiv}CR$

R	σ^0_R	$A^{1/2}$ /L mol$^{-1/2}$ cm^{-1}	Δq_π/e
NH_2	−0.47	−131.9	−0.117
OMe	−0.43	−121.8	−0.089
OH	−0.40	−114.2	−0.087
F	−0.34	−99.0	−0.062
Me	−0.10	−38.3	−0.012
$CH{=}CH_2$	−0.05	−25.6	−0.010
H	0	−13.0	0
CF_3	0.10	12.3	0.005
CN	0.09	9.8	0.021
CHO	0.24	47.7	0.042
COMe	0.22	42.7	0.043
NO_2	0.17	30.3	0.061
NO	0.25	50.2	0.077

of the substituents R with the triple bond. At the same time, the difference between the effective π-electron charges on the atoms of the $C{\equiv}C$ fragment q_π in relationship (6) is, by definition, also changed only due to the effect of the resonance interactions of substituents with the π-system. According to the earlier studies,[6] both characteristics of the resonance effect, namely, σ^0_R and q_π, are closely related to each other.

It is also possible to obtain a direct confirmation of the fulfilment of relationship (6). In Table 2, the Δq_π parameters for compounds $HC{\equiv}CR$ calculated by the *ab initio* method (using the 4-31G basis set)[6] are listed. These parameters characterize the π-electron transfer in the case of resonance interactions between the $HC{\equiv}C$ indicator center and substituents R and hence are relative characteristics of the π-electron charge on the C atoms at the triple bond. For R = H, the Δq_π is equal to zero. The resonance electron donor and resonance electron acceptor substituents R in $HC{\equiv}CR$ are characterized by negative and positive values of Δq_π, respectively. Then, using the σ^0_R constants of substituents R and Eq. (10), we calculated the $A^{1/2}$ values for compounds $Me_3GeC{\equiv}CR$ containing the same R as compounds $HC{\equiv}CR$ with known Δq_π values (see Table 2). To increase the reliability of statistical processing, we, as well as the authors of Ref. 6, provided the maximum representative sample. Therefore, calculated values of $A^{1/2}$ and Δq_π[6] for compounds not reported in the literature are also listed in Table 2. The linear dependence is observed for $Me_3GeC{\equiv}CR$ derivatives

$$A^{1/2} = 1081\Delta q_\pi - 16.3 \quad (11)$$

$$(S_a = 67,\ S_b = 4.0,\ S_Y = 14.4,\ r = 0.979,\ n = 13).$$

Equation (11) serves as direct confirmation of the fulfilment of relationship (6).

It follows from the aforesaid that the $A^{1/2}$ values are justified characteristics of the conjugation in acetylene derivatives. Therefore, with the aim of studying the conjugation of the Me_3Ge substituent with the triple bond, let us analyze Eqs. (10) and (11) in more detail.

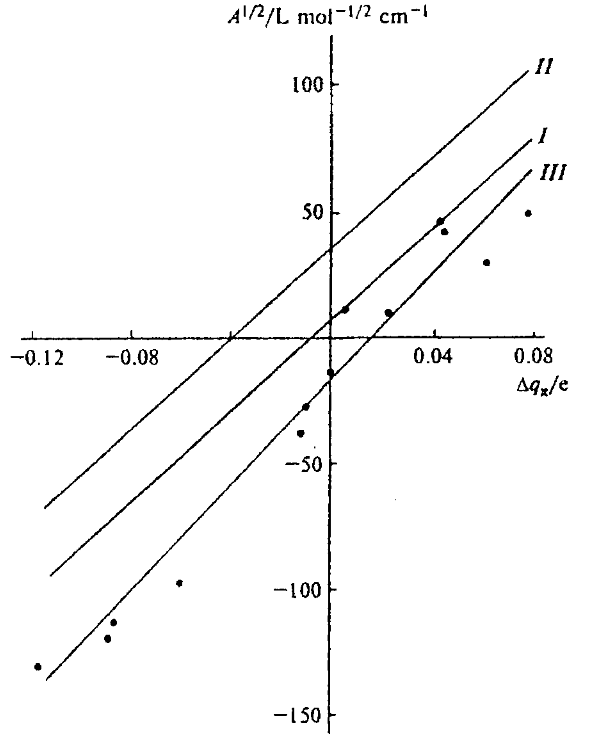

Fig. 1. Dependence of the $A^{1/2}$ values on the Δq_π parameters for compounds $HC{\equiv}CR$ (line *I*, Eq. (12)), $Me_3CC{\equiv}CR$ (line *II*, Eq. (13)), and $Me_3GeC{\equiv}CR$ (line *III*, Eq. (11)). The points corresponding to line *III* are shown.

For compounds $HC{\equiv}CR$ and $Me_3CC{\equiv}CR$ with standard sets of substituents R listed in Table 2, equations of the type (11) take the form[14]

$$A^{1/2} = 930\Delta q_\pi + 7.9\ (r = 0.983) \quad (12)$$

and

$$A^{1/2} = 913\Delta q_\pi + 35.5\ (r = 0.983), \quad (13)$$

respectively.

Lines *I*—*III* on the plot (Fig. 1) are approximately parallel. As was shown previously,[14] the shift of line *II* with respect to line *I* toward negative Δq_π values by −0.031 e is due to the resonance donor properties (the +M-effect) of the Me_3C group. In contrast to this, line *III* corresponding to compounds $Me_3GeC{\equiv}CR$ is shifted toward positive Δq_π values with respect to line *I* corresponding to compounds $HC{\equiv}CR$. This is unambiguous evidence for the resonance acceptor properties (the −M-effect) of the Me_3Ge substituent in trimethylgermylacetylene and its derivatives. Depending on the type of R, the magnitude of the considered shift between lines *III* and *I* (see Fig. 1) varies from +0.043 e (for NH_2, which is a typical electron donor substituent) to +0.017 e (for NO, which is a typical electron acceptor substituent). The average value of the shift (+0.030±0.013 e) characterizes the decrease in the negative effective charge of the atoms at the triple bond upon substitution of the H atom by the Me_3Ge group in monosubstituted acetylenes HC≡CR. Comparison of the value +0.03 e with the Δq_x values in Table 2 shows that the Me_3Ge substituent is comparable in its resonance acceptor properties toward the triple bond to typical organic electron-accepting substituents of the −M-type. The negative effective charge of the atoms at the triple bond decreases by 0.036 e upon substitution of the H atom in HC≡CR by the Me_3Si group.[14] This is in agreement with commonly accepted ideas on the decrease in the resonance acceptor effect of the elements of the silicon subgroup towards the π- and n-systems upon increasing their atomic numbers.[1]

The total resonance effect of the Me_3Ge substituent includes two components, the acceptor component (the d,π-conjugation, *i.e.*, the interaction of 4d orbitals of the Ge atom and σ*-orbitals of the Ge—C bond with the π-system) and the donor component (the σ,π-conjugation, *i.e.*, the interaction of σ-orbitals of the Ge—C bond with the π-system).[1] As was shown above, the total effect of this substituent is an acceptor effect. This means that for the $Me_3GeC{\equiv}CR$ molecules in the ground electron state the d,π-conjugation obviously dominates over σ,π-conjugation.

This conclusion is confirmed by the magnitude and sign of the σ^0_R constant of the Me_3Ge substituent in compounds $Me_3GeC{\equiv}CR$. Actually, lines *II* and *III* corresponding to compounds $Me_3CC{\equiv}CR$ and $Me_3GeC{\equiv}CR$, respectively, are on the opposite sides from line *I* corresponding to compounds HC≡CR on the plot in coordinates $A^{1/2}$—σ^0_R (Fig. 2). The parallel shift of line *II* along the σ^0_R axis toward negative σ^0_R values is due to the resonance donor +M-effect of the Me_3C group. The magnitude of the shift between lines *II* and *I* is the σ^0_R value of the Me_3C substituent and is equal to −0.13. Line *III* is shifted toward positive σ^0_R values with respect to line *I*. This is due to the resonance acceptor −M-effect of the Me_3Ge group, *i.e.*, to the domination of the d,π-conjugation over σ,π-conjugation in the total effect of the conjugation of the Me_3Ge group with the π-system of C≡CR. In the studied range of $A^{1/2}$ values, *i.e.*, from −67.2 (for a typical resonance donor CH_2GeMe_3) to +44.2 (for a typical resonance acceptor CHO), the average value of the shift between lines *I* and *III* along the σ^0_R axis is +0.11±0.03. This value is the σ^0_R constant of the Me_3Ge substituent in $Me_3GeC{\equiv}CR$ molecules, whose electronic structure was not changed due to ionization, strong specific solvation, and chemical reactions. The σ^0_R constant of the Me_3Si substituent in $Me_3SiC{\equiv}CR$ determined in such a way is equal to +0.17.[14] The decrease in the σ^0_R value of the Me_3M substituent on going from M = Si to M = Ge serves as one more confirmation of weakening of d,π-conjugation with increase in the atomic number of the central M atom.

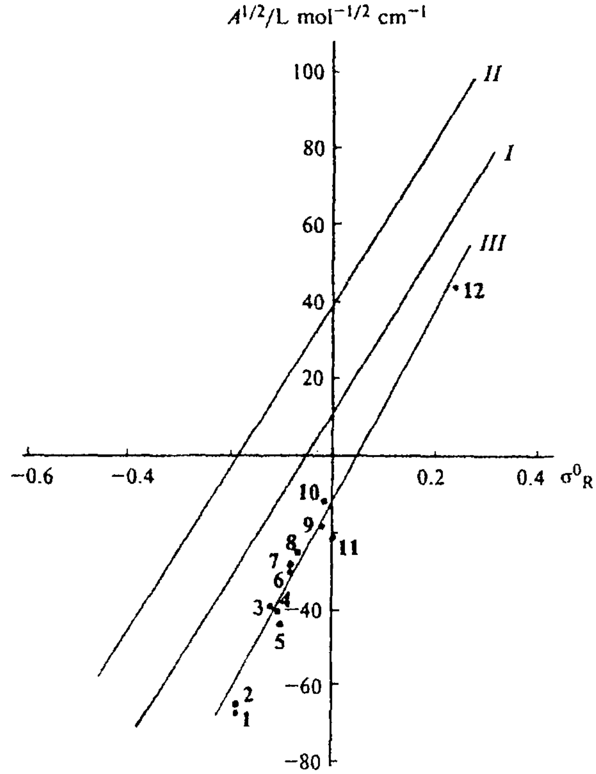

Fig. 2. Dependence of the $A^{1/2}$ values on the resonance σ^0_R constants of substituents R for compounds HC≡CR (line *I*, Eq. (7)), $Me_3CC{\equiv}CR$ (line *II*, Eq. (8)) and $Me_3C{\equiv}CR$ (line *III*, Eq. (10)). Points corresponding to line *III* are shown; their numbering corresponds to that of the compounds in Table 1.

It should be noted that difficulties, caused by the approximate character of the method of determination of σ^0_R used previously[14] and in this work, arise when estimating the accuracy of the obtained values of σ^0_R constants of the Me_3Ge and Me_3Si substituents (+0.11 and +0.17, respectively). In fact, as was shown above, this method is fairly rigorous only if the ν(C≡C) mode in the HC≡CR, $Me_3CC{\equiv}CR$, $Me_3SiC{\equiv}CR$, and $Me_3GeC{\equiv}CR$ series is totally pure. The fulfillment of this condition was considered in Refs. 12—14, 17, and 19; it follows from the results of these studies that the ν(C≡C) mode in compounds HC≡CR is most likely slightly coupled. Therefore, the line corresponding to the equation for compounds HC≡CR does not pass through the origin. After exclusion of the absolute term, Eq. (7) is transformed into the following relationship

$$A^{1/2} = 217\sigma^0_R. \qquad (14)$$

Formula (14) expresses the relationship between the $A^{1/2}$ and σ^0_R values for such a hypothetical situation when the contribution of other modes to the ν(C≡C) mode in compounds HC≡CR is small. In $Me_3MC{\equiv}CH$ molecules, the contribution of other modes to the ν(C≡C) mode decreases as the atomic number of M (C, Si, Ge, and Sn) increases.[19] Therefore, the complicated influence of coupled vibrations can be reduced to a minimum if the shifts along the σ^0_R axis of the lines described by Eqs. (10) and (9) with respect to the line calculated using Eq. (14) are used for the calculation of σ^0_R constants of the Me_3Ge and Me_3Si substituents. The σ^0_R values of the Me_3Ge and Me_3Si substituents (+0.06±0.03 and +0.12±0.02, respectively) determined in such a manner seem to be more reliable as compared to the values +0.11 and +0.17 calculated without taking account of contributions of other modes to the ν(C≡C) mode in HC≡CR molecules. Thus, in particular, the value +0.06 lies in the range of the change in the σ^0_R values for the Me_3Ge group (−0.1—+0.07) obtained using various physical methods.[20]

The contribution of other modes to the ν(C≡C) vibration in HC≡CR molecules can also be taken into account for a more precise estimate (as compared to that described above) of the change in the effective charge of the atoms of the C≡C fragment caused by the effect of resonance interactions between Me_3M substituents and the π-system in $Me_3MC{\equiv}CR$ compounds (M = Si and Ge). After exclusion of the absolute term, Eq. (12) is transformed into the following relationship

$$A^{1/2} = 930\Delta q_\pi. \qquad (15)$$

Formula (15) expresses the relationship between the $A^{1/2}$ and Δq_π values (change in the effective π-electron charge on the atoms of the C≡C fragment due to conjugation of the substituent R with the triple bond) for such a hypothetical situation when the contribution of other modes to the ν(C≡C) mode in molecules HC≡CR is small. In contrast to compounds HC≡CR, the $A^{1/2}$ and Δq_π values in compounds $Me_3GeC{\equiv}CR$ should be determined by resonance interactions of the π-system not only with the substituent R, but also with the Me_3Ge group. However, Eq. (11) was obtained assuming that the $A^{1/2}$ values for $Me_3GeC{\equiv}CR$ depend only on the resonance interactions involving R. Therefore, the line corresponding to Eq. (11) is shifted along the Δq_π axis with respect to the line corresponding to Eq. (15). The shift varies from +0.035 e (for R = NH_2) to +0.008 e (for R = NO). The average value of the shift (0.022±0.013 e) characterizes the decrease in the negative effective charge of the atoms of the C≡C fragment caused by resonance acceptor properties of the Me_3Ge substituent. Analogous calculations for $Me_3SiC{\equiv}CR$ compounds performed using the literature data[14] showed that the negative effective charge on the atoms of the C≡C fragment is decreased by 0.028±0.010 e due to resonance acceptor properties of the Me_3Si substituent.

Thus, both rough and more accurate estimates of σ^0_R constants of Me_3M substituents and changes in the effective π-electron charge on the atoms of the C≡C fragment in the case of resonance interactions of these substituents with the triple bond show that the d,π-conjugation in $Me_3MC{\equiv}CR$ molecules, first, dominates over σ,π-conjugation and, second, it becomes weaker on going from M = Si to M = Ge.

It should be noted that the increase in the slope of Eq. (10) as compared to those of Eqs. (7) and (8) as well as the increase in the slope of Eq. (11) as compared to those of Eqs. (12) and (13) can be due to several reasons, *e.g.*, to the effect of direct polar conjugation and the limited number of compounds studied. These problems will be considered elsewhere. Here we only note that a possible effect of direct polar conjugation between the Me_3Ge and R substituents in $Me_3GeC{\equiv}CR$ molecules on the integrated extinction coefficients *A* should be of secondary importance, which is indicated by the sharp decrease in the correlation coefficient *r* of the equation

$$A^{1/2} = 257\sigma_R - 4.7 \qquad (16)$$

$$(S_a = 50,\ S_b = 7.4,\ S_Y = 16.5,\ r = 0.901,\ n = 8)$$

as compared to that of Eq. (10).

Line (16) was obtained for eight compounds from Table 1, for which the values of σ_R constants of organic[21] and organometallic[22] substituents are known, namely, **1** (−0.27), **2** (−0.24), **4** (−0.05), **5** (−0.13), **8** (−0.12), **10** (0), **11** (0), and **12** (+0.09). If the resonance effects of substituents R in the same germylacetylenes $Me_3GeC{\equiv}CR$ are characterized by σ^0_R constants rather than by σ_R values, then Eq. (16) is transformed into the following equation:

$$A^{1/2} = 258\sigma^0_R - 14.3 \qquad (17)$$

$$(S_a = 18,\ S_b = 2.5,\ S_Y = 6.5,\ r = 0.985,\ n = 8).$$

The σ_R constants are quantitative characteristics of the resonance properties of substituents R in relation to the multiple bond in the case of direct polar conjugation in the molecule (see, for instance, Refs. 1—5). Therefore, the decrease in *r* and the increase in the standard error of approximation S_Y upon changing the σ^0_R variable by σ_R (the passage from Eq. (10) or Eq. (17) to Eq. (16)) indicates the insignificant effect of the direct polar conjugation on the *A* values of germylacetylenes $Me_3GeC{\equiv}CR$.

The spectral investigations were carried out at the Analytical Center of the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences with the financial support of the Russian Foundation for Basic Research (Project No. 96-03-40042).

References

1. A. N. Egorochkin, *Usp. Khim.*, 1992, **61**, 1092 [*Russ. Chem. Rev.*, 1992, **61** (Engl. Transl.)].
2. A. N. Egorochkin, S. E. Skobeleva, and T. G. Mushtina, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1626 [*Russ. Chem. Bull.*, 1997, **46**, 1549 (Engl. Transl.)].
3. A. N. Egorochkin, S. E. Skobeleva, and T. G. Mushtina, in *Tez. dokl. V Vseros. Simp. "Stroenie i reaktsionnaya sposobnost'*

kremnijorganicheskikh soedinenii" [*Abstracts Vth All-Russian Symp. "The Structure and Reactivity of Organosilicon Compounds"*], Irkutsk, 1996, 2 (in Russian).

4. A. N. Egorochkin, G. A. Razuvaev, and M. A. Lopatin, *J. Organomet. Chem.*, 1988, **344**, 49.
5. 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.)].
6. S. Marriott and R. D. Topsom, *J. Mol. Struct.*, 1984, **106**, 277.
7. 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.)].
8. 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.)].
9. *Chemistry of Acetylenes*, Ed. H. G. Viehe, M. Dekker, New York, 1969.
10. V. Jager, M. Murray, U. Niedballa, and H. G. Viehe, *Methoden der Organischen Chemie (Houben-Weil)*, Ed. E. Muller, Georg Thieme, 1977, 5/2a.
11. R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Am. Chem. Soc.*, 1966, **88**, 1413.
12. T. B. Gridley, 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.
13. 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.
14. A. N. Egorochkin, S. E. Skobeleva, T. G. Mushtina, and E. T. Bogoradovsky, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 76 [*Russ. Chem. Bull.*, 1997, **46**, 71 (Engl. Transl.)].
15. A. R. Katritzky and R. D. Topsom, *Chem. Rev.*, 1977, **77**, 639.
16. A. S. Medvedeva, O. I. Margorskaya, I. D. Kalikhman, N. I. Golovanova, N. I. Shergina, and N. S. Vyazankin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 321 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 246 (Engl. Transl.)].
17. M. V. Vol'kenshtein, L. A. Gribov, M. A. El'yashevich, and B. I. Stepanov, *Kolebaniya molekul* [*Molecular Vibrations*], Nauka, Moscow, 1972 (in Russian).
18. 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).
19. A. V. Belyakov, V. S. Nikitin, and M. V. Polyakova, *Zh. Obshch. Khim.*, 1995, **65**, 81 [*Russ. J. Gen. Chem.*, 1995, **65** (Engl. Transl.)].
20. A. N. Egorochkin and G. A. Razuvaev, *Usp. Khim.*, 1987, **56**, 1480 [*Russ. Chem. Rev.*, 1987, **56**, 846 (Engl. Transl.)].
21. C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
22. 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.].

Received May 22, 1997;
in revised form November 10, 1997