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SPECTROSCOPIC STUDY OF SUBSTITUENT EFFECTS OF MAIN GROUP IV ELEMENTS IN ACETYLENIDES

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Summary

Shifts of frequencies ($\Delta\nu$) of the O—H stretching modes in the IR spectra of phenol (acceptor) when hydrogen-bonded to acetylenides of Main group IV elements, $R_3MC{\equiv}CX$ and $R_3MC{\equiv}CM'R_3$ (M, M' = C, Si, Ge, Sn; R = Alk; X = various substituents) have been measured. These shifts are a quantitative measure of the electron-donor properties of the acetylenides. The $\Delta\nu$ parameter has been shown for $R_3MC{\equiv}CX$ compounds to correlate linearly with the σ_p-constants of the substituents X. The σ_p-constants of some organometallic R_3M substituents have been determined from this correlation. The electron-donor properties of acetylenides have been estimated by means of electronic absorption spectroscopy of charge-transfer (CT) complexes of $R_3MC{\equiv}CX$ (M = C, Si, Ge) compounds (donors) with iodine (acceptor). The charge-transfer frequencies (ν_{CT}) were a quantitative measure of these properties in the CT state. The correlation between $\Delta\nu$ and ν_{CT} has been analysed. The effects of d_π—p_π interaction and of σ,π conjugation have been shown to be practically unchanged while π,π and p,π conjugations increase in the CT state. The significant role of direct resonance interaction was established in both the ground and CT states.

Introduction

Acetylenides of the $R_3MC{\equiv}CX$ type (M = Si, Ge, Sn; X = various substituents) have been studied by many workers using a variety of physical methods. In order to obtain information on the electronic effects of the organometallic substituents MR_3 and the nature of the chemical bonding in the —M—C≡C— fragment, IR spectroscopy (analysis of frequencies and intensities of ν(C≡C), ν(C—H), ν(M—C) stretching modes and hydrogen bonding by acetylene hydrogen atoms) [1—10],

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NMR spectroscopy (analysis of ^{1}H, ^{13}C, ^{19}F, ^{29}Si, ^{117,119}Sn chemical shifts, and a variety of spin-spin coupling constants of individual compounds, as well as of their donor acceptor complexes) [5,11,15], Mössbauer spectroscopy [16,17], electronic absorption spectroscopy [18—22] and dipole moments analysis [22—24] have been used.

It has also been repeatedly claimed that as well as donor properties ($+I$ effect), R_3M groups (M = Si, Ge, Sn) in $R_3M{-}C{\equiv}C$-fragments may exhibit acceptor properties ($d_\pi{-}p_\pi$ interaction). In addition, in a series of alkynes and their derivatives the role of π,π-; p,π conjugation effects was found to be substantial [25]; organometallic acetylenides were not very well understood in this respect. The effects of the substituents in the transition from the ground to the excited state were also unknown. It was thus interesting to investigate these properties of acetylenides with the aim of obtaining new data on Hammett-Taft type σ-constants, making allowance for the electronic effects of the organometallic substituents.

The aim of this work was to investigate trends in the electronic structure changes of organometallic acetylenides influenced by substituents, in order to obtain data on the poorly understood problems of electronic shift mechanisms.

Results and discussion

In this work we have studied the influence of substituents on the π-donating properties of acetylenides in the ground electronic state by IR spectroscopy. Frequency shifts ($\Delta\nu$) of O—H stretching modes of phenol when hydrogen bonded $(\overset{\mathrm{C}}{\underset{\mathrm{C}}{|||}}\cdots \mathrm{H{-}O{-}Ph})$ to acetylenes were measured. The parameter $\Delta\nu$ for a wide range of electron-donors on the acetylenes were related to the enthalpy of formation of hydrogen bonds by an approximately linear relationship [27]. For a few compounds with similar structure the linear relationship between $\Delta\nu$ and ΔH was followed fairly precisely [28]. The $\Delta\nu$ parameter gives information about specific details of the influence of the substituents on the electron-donating properties of the compounds. The influence of substituents on $\Delta\nu$ can be described in terms of Hammett-Taft σ constants [29].

Table 1 presents frequency shifts $\Delta\nu$ for phenol dissolved in the organometallic compounds. It should be noted that organometallic acetylenides are known to take part in donor-acceptor interaction with electron-donating compounds, of which phenol is an example. This interaction is most pronounced in tin derivatives, the $Sn{-}C_{sp}$ bond being cleaved in the presence of phenol. By virtue of the fact that the tin derivatives are stable under the conditions we have chosen (when the phenol concentration is significantly lower than the concentration of the organometallic compound) it may be assumed that under these conditions the degree of association with the tin atom is small and its influence on the π-donor properties of the compounds studied may be ignored. This applies to a greater degree to acetylenides of silicon and germanium.

The compounds we studied (Table 1) are represented by four series, i.e. carbon, silicon, germanium and tin derivatives, each of them including fixed (R_3C, R_3Si, R_3Ge, R_3Sn) and variable substituents bound to the triple bond. It should be noted, that the influence of R_3M on the $\Delta\nu$ parameter depends much more on

Number	Compound	M = C		M = Si		M = Ge		M = Si		$\sigma_p(X)$
		$\Delta\nu(OH)$	$\dot{\nu}_{CT} \times 10^{-3}$	$\Delta\nu(OH)$	$\nu_{CT} \times 10^{-3}$	$\Delta\nu(OH)$	$\nu_{CT} \times 10^{-3}$	$\Delta\nu(OH)$	$\nu_{CT} \times 10^{-3}$	
1	$(CH_3)_3MC\equiv CSn(CH_3)_3$	170	—	147	—	165	—	178	—	
2	$(CH_3)_3MC\equiv CSn(C_2H_5)_3$	172	—	154	—	169	—	—	—	
3	$(C_2H_5)_3MC\equiv CSn(CH_3)_3$	—	—	149	—	170 [a]	—	—	—	
4	$(C_2H_5)_3MC\equiv CSn(C_2H_5)_3$	—	—	158 [a]	—	—	—	190	—	
5	$(CH_3)_3MC\equiv CGe(CH_3)_3$	153	34.3	135	35.7	149	35.0	165	—	
6	$(C_2H_5)_3MC\equiv CGe(CH_3)_3$	—	—	135, 141 [a]	35.5	154, 155 [a]	34.2	169	—	
7	$(CH_3)_3MC\equiv CGeC_2H_5)_3$	155	33.7	137, 142 [a]	35.3	—	—	170 [a]	—	
8	$(C_2H_5)_3MC\equiv CGe(C_2H_5)_3$	—	—	—	—	168 [a]	—	—	—	
9	$(n\text{-}C_4H_9)_3MC\equiv CGe(C_4H_9)_3$	—	—	—	—	159 [a]	—	—	—	
10	$(CH_3)_3MC\equiv CSi(CH_3)_3$	131	35.0	121	36.1	135	35.7	147	—	
11	$(CH_3)_3MC\equiv CSi(C_2H_5)_3$	135	34.6	123	35.3	135	35.5	149	—	
12	$(C_2H_5)_3MC\equiv CSi(C_2H_5)_3$	—	—	130, 130 [a]	35.1	142 [a]	—	154	—	
13	$(CH_3)_3MC\equiv CC(CH_3)_3$	140	34.0	131	35.0	153	34.3	170	—	−0.197
14	$(C_2H_5)_3MC\equiv CC(CH_3)_3$	—	—	135	34.6	155	33.7	172	—	−0.197
15	$(CH_3)_3MC\equiv CCH_2Si(CH_3)_3$	—	—	139	35.1	158	34.2	190	—	
16	$(CH_3)_3MC\equiv COCH_3$	—	—	144	31.8	—	—	—	—	−0.268
17	$(CH_3)_3MC\equiv COC_2H_5$	—	—	150	32.3	—	—	—	—	−0.250
18	$(CH_3)_3MC\equiv CCH_3$	129	34.5	122	35.9	144, 143 [b]	34.3	154	—	−0.170
19	$(C_2H_5)_3MC\equiv CCH_3$	—	—	—	—	—	—	165	—	−0.170
20	$(CH_3)_3MC\equiv CC_2H_5$	137	34.8	—	—	148	—	160	—	−0.151
21	$(CH_3)_3MC\equiv CCH_2N(C_2H_5)_2$	—	—	125	—	150	—	160	—	−0.150
22	$(CH_3)_3MC\equiv CCH\equiv CH_2$	104	—	105	—	116 [b]	—	—	—	−0.020
23	$(C_2H_5)_3MC\equiv CCH=CH_2$	—	—	—	—	122, 121 [b]	—	—	—	−0.020
24	$(CH_3)_3MC\equiv CCH_2OC_2H_5$	—	—	—	—	—	—	140	—	−0.010
25	$(CH_3)_3MC\equiv CPh$ [c]	100	34.5	106	34.5	119	34.5	140	—	−0.010
26	$(CH_3)_3MC\equiv CSCH_3$	105	28.6	107	29.2	127	28.8	135	—	0
27	$(CH_3)_3MC\equiv CSC_2H_5$	106	28.6	109	29.1	129	28.7	136	—	0
28	$(C_2H_5)_3MC\equiv CSC_2H_5$	—	—	—	—	—	—	140	—	0
29	$(CH_3)_3MC\equiv CCH_2Br$ [d]	—	—	84	36.8	95	36.2	110	—	+0.150
30	$(CH_3)_3MC\equiv CCH_2Cl$ [d]	78	37.0	80	37.3	90, 90 [b]	36.5	111	—	+0.180
31	$(C_2H_5)_3MC\equiv CCH_2Cl$ d	—	—	—	—	—	—	119	—	+0.180
32	$(CH_3)_3MC\equiv CI$	79	33.9	79	34.5	94	32.3	—	—	+0.180
33	$(CH_3)_3MC\equiv CBr$	64	34.0	75	35.0	84	35.7	99	—	+0.230
34	$(CH_3)_3MC\equiv CCl$	59	34.5	70	35.7	79	36.0	—	—	+0.230
35	$(C_2H_5)_3MC\equiv CCl$	—	—	—	—	—	—	90	—	+0.230
36	$(CH_3)_3MC\equiv CC_6F_5$	50	—	49	—	64	—	74	—	+0.350

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[a] Ref. 10, [b] Ref. 8, [c] The $\Delta\nu$ values of phenol when hydrogen bonds are formed with the π-system of the aromatic ring are within 30—40 cm^{-1}, [d] $\Delta\nu$ = 40—60 cm^{-1} when phenol forms hydrogen bonds with halogens.

the nature of M than on the alkyl radical R (CH_3, C_2H_5, n-C_4H_9). Therefore, comparing $\Delta\nu$ values we used fixed Alk_3M substituents and various Alk substituents with unchanged M.

The electronic effects of the variable substituents change over a sufficiently wide range and apart from an inductive component, they may include a resonance one. It is known that the influence of such substituents on spectral parameters of derivatives of benzene [30], naphthalene [31], furan and thiophene [32] and ethylene [33] is brought about both by inductive and resonance mechanisms.

Treatment of the data obtained by the least squares method disclosed that $\Delta\nu$ values of the compounds studied are connected with the Hammett σ_p constants of the varying substituents (Fig. 1) by a linear correlation for each series of organometallic acetylenides, as well as for the carbon derivatives.

$$\Delta\nu_C = -(167 \pm 8)\,\sigma_p + (105 \pm 2) \qquad r = 0.988 \qquad n = 12 \tag{1}$$

(M = C, compounds 13, 18, 20, 22, 25, 27, 30, 32, 33, 34, 36)

$$\Delta\nu_{Si} = -(148 \pm 5)\,\sigma_p + (105 \pm 1) \qquad r = 0.992 \qquad n = 17 \tag{2}$$

(M = Si, compounds 13—18, 21, 22, 25—27, 29, 30, 32—34, 36)

$$\Delta\nu_{Ge} = -(166 \pm 6)\,\sigma_p + (121 \pm 1) \qquad r = 0.989 \qquad n = 17 \tag{3}$$

(M = Ge, compounds 13—15, 18, 20—23, 25—27, 30, 32—34, 29, 36)

$$\Delta\nu_{Sn} = -(164 \pm 8)\,\sigma_p + (136 \pm 1) \qquad r = 0.985 \qquad n = 18 \tag{4}$$

(M = Sn, compounds 13—15, 18—21, 24—31, 33, 35, 36)

From correlation analysis data it follows that the π-donor properties of acetylenides in each series (M = Si, Ge, Sn) increase with increasing electron-donating properties of the substituents on the opposite positions of the triple bond, as well as on transition from silicon to germanium and further to tin derivatives. The latter agree with the increase of donor properties of organometallic substituents in the series $R_3Si < R_3Ge < R_3Sn$.

When allowance was made for the significally higher electronegativity (in brackets) of the carbon (2.55) and germanium (2.01) atoms compared to silicon (1.90) in the absence of d_π—p_π interaction [34], it was hoped that $\Delta\nu$ values for silicon derivatives would be not lower than those for germanium derivatives, and markedly higher than for carbon compounds. This was, however, not supported by the experimental results. Along with the donor properties of the Alk_3M group these groups in acetylenides show acceptor properties, decreasing in the series $R_3Si > R_3Ge > R_3Sn$, due to d_π—p_π interaction.

Thus, $\Delta\nu$ values in the compounds $R_3M{-}C{\equiv}C{-}X$ depend upon inductive and resonance effects of the X substituents, as well as upon inductive and resonance effects of the R_3M groups (d_π—p_π interaction). Yet the influence of the substituents on the ground state parameter $\Delta\nu$ is not exhausted by these electronic effects. Really, the analysis of $\Delta\nu$ has shown that the change in their values with varying element M and with fixed substituent X depends on the character of X. So, for compounds 13 and 18 where, X is a typical electron donor, $C(CH_3)_3$ ($\sigma_p = -0.197$) or CH_3 ($\sigma_p = 0.17$), $\Delta\nu$ values increase with changing M in the series

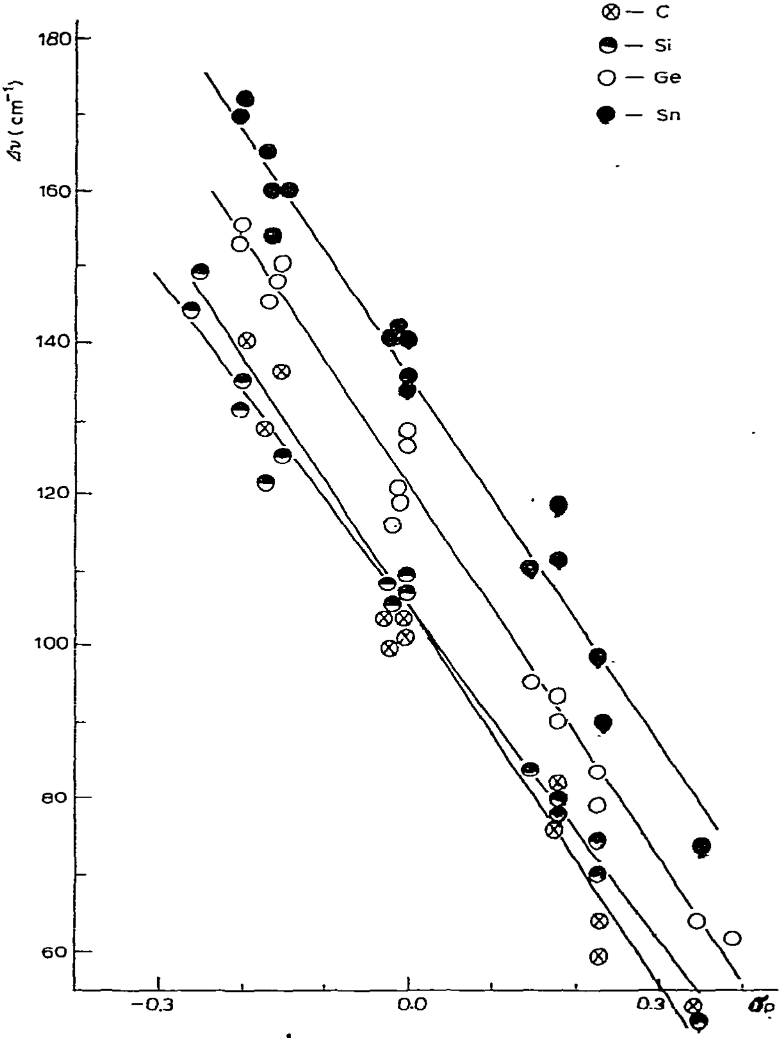
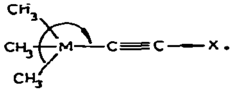


Fig. 1. Correlation Δν (cm^{-1}) vs. σ_p for acetylene derivatives (⊗-carbon, ⊖-silicon, ○-germanium, ●-tin)

Si < C < Ge. The minimum value of Δν for M = Si corresponds to maximum d_π—p_π interaction in the ⩾Si—C≡C fragment.

For compounds 25—27 and 32—34 substituents X (C_6H_5, SCH_3, SC_2H_5, I, Cl, Br) represent acceptors relative to the $(CH_3)_3M$ groups located on the opposite positions of the triple bond; their σ_p constants change in the —0.01 to 0.23 range. Values for these compounds increase with M in the series C < Si < Ge, in which the silicon atom position differs from that in the corresponding series for compounds 13 and 18. This results from the effect of direct resonance interaction between substituents located at the opposite positions of the triple bond



$(CH_3)_3M—C\equiv C—X$. This effect increases firstly with increasing atomic number of M in the series C < Si < Ge < Sn due to increasing polarizability of

M—CH_3 bonds in the series [35,36] and, secondly, with the increase of acceptor properties of the substituent X. In the event that the donor-acceptor properties of the conjugated substituents $(CH_3)_3M$ and X are similar, as is the case for compounds **13** and **18**, then direct resonance interaction is absent or is negligible. With increasing difference in donor-acceptor properties between $(CH_3)_3M$ and X for compounds **25**—**27** and **32**—**34** the influence of this effect increases. Clearly, d_π—p_π-interaction and direct resonance interaction act in opposite directions; therefore an increase in the second effect masks the activity of the first one. It should be noted that the pronounced effect of resonance interaction even in the ground electronic state confirms the [25] finding on the role of conjugation effects in acetylene derivatives. This means that for the acetylene derivatives studied, the $\Delta\nu$ parameter depends also upon direct resonance interaction between the substituents $(CH_3)_3M$ and X as well as the above quoted inductive and resonance effects.

From the above it will be obvious that contributions from the resonance interaction are alternating even for the series with the invariable M atom. Therefore, equations 1—4 derived by assumption of the absence or constant contributions to direct resonance interaction should be considered approximate relations. In general, in each of four series with an invariable substituent $(CH_3)_3M$ (i.e. with constant $+I$ effect and d_π—p_π interaction with M = Si, Ge, Sn), the dominating effect on $\Delta\nu$ is influenced by electronic effects of the substituent X, characterized by the σ_p constant. In this case, as a first approximation, the influence of the direct resonance interaction may be neglected, considering that the main manifestation of its influence on $\Delta\nu$ is the reduced accuracy of eqs. 1—4 in correlation analysis. Strictly speaking, the σ_p constants of one and the same substituent calculated from eqs. 1—4 should depend on the extent of direct resonance interaction in the series used for calculation of σ_p values. We obtained evidence for this in calculations according to eqs. 1—4 of σ_p constants for organometallic substituents in compounds **1**—**12** (Table 1) of $R_3MC{\equiv}CM'R_3$ type, using $\Delta\nu$ values for these compounds. (The compounds given, containing two organometallic substituents, were not used for obtaining the correlation relationships of eqs. 1—4, since the data in the literature on their σ_p constants are not reliable.)

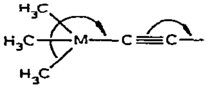
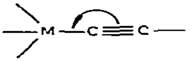
As can be seen from Table 2, all the substituents $MAlk_3$ bound to the triple bond exhibit an electron-donor effect, increasing in the series $Alk_3Si < Alk_3Ge < Alk_3Sn$, as well as on transition from methyl to ethyl derivatives. A characteristic property of σ_p constants of $MAlk_3$ substituents is their dependence on the

TABLE 2

CALCULATED σ_p VALUES OF ORGANOMETALLIC SUBSTITUENTS $MAlk_3$ IN UNSYMMETRICAL ORGANOMETALLIC COMPOUNDS $Alk_3MC{\equiv}CM'Alk_3$

$MAlk_3$	M' = C	M' = Si	M' = Ge	M' = Sn
$Si(CH_3)_3$	—0.16	—0.11	—0.08	—0.07
$Ge(CH_3)_3$	—0.29	—0.21	—0.18	—0.19
$Sn(CH_3)_3$	—0.39	—0.29	—0.28	—0.26
$Si(C_2H_5)_3$	—0.18	—0.14	—0.10	—0.09
$Ge(C_2H_5)_3$	—0.30	—0.24	—0.20	—0.21
$Sn(C_2H_5)_3$	—0.40	—0.34	—0.29	—0.33

nature of the second $M'Alk_3$ substituent in the molecule. σ_p constant values of $MAlk_3$ increase with the increasing atomic number of the element M.

Hyperconjugation effects (σ,π-conjugation  increase with the increasing atomic number of M; in the series $(CH_3)_3M'C{\equiv}CMAlk_3$ an increase in the σ_p constants of the $MAlk_3$ groups is seen. The latter is associated with decreasing donor properties of $MAlk_3$ groups under the influence of $M'(CH_3)_3$ substituents. Due to hyperconjugation effects and d_π—p_π interaction,  , acting in the opposite direction, the highest occupied molecular orbital (HOMO) becomes more delocalized, while the π-system becomes more sensitive to the influence of substituents. Therefore, despite the relatively small difference in donor-acceptor properties of organometallic substituents in the studied $Alk_3MC{\equiv}CM'Alk_3$ type compounds, these substituents, even in ground electronic state, interact efficiently with each other, and enter into direct resonance interaction. This means that σ_p constants of organometallic substituents for compounds **1**—**12** are estimated. Such features of σ_p constants of organometallic substituents, noted earlier [35], are due to the high polarizability of elements M of the silicon subgroup and of organometallic compounds as a whole, as well as to the significant role of conjugation effects of σ,π-; σ,σ-type involving M—C bonds in these compounds [36].

The σ_p constants for symmetrical compounds $R_3MC{\equiv}CMR_3$ (where M is fixed and R are the same radicals) are fairly close to the true value, since direct resonance interaction effects are cancelled out in these compounds. The σ_p constants for $MAlk_3$ substituents in symmetrical compounds, calculated from $\Delta\nu$ values, are given in Table 3.

The σ_p constant is the sum of two components; $\sigma_p = \sigma_I + \sigma_R$. The values of inductive σ_I constants for organometallic substituents given in literature [39] allow estimation of σ_R constants, characterizing the role of resonance interactions involving $MAlk_3$ substituents. It follows from the σ_R constants obtained, that in accordance with literature data [e.g., 2, 7, 8], in the ground electronic state of substituted acetylenes, the Alk_3Si group shows M type acceptor properties towards the triple bond, attributed to d_π—p_π interaction. It is known [29] that

TABLE 3

CALCULATED σ_p AND σ_R VALUES OF SUBSTITUENTS $MAlk_3$ IN SYMMETRICAL ORGANOMETALLIC COMPOUNDS $Alk_3MC{\equiv}CMAlk_3$

Substituent	σ_p	σ_I [a]	σ_R
$C(CH_3)_3$	−0.20	−0.05	−0.15
$Si(CH_3)_3$	−0.11	−0.15	+0.04
$Si(C_2H_5)_3$	−0.14	−0.18	+0.04
$Ge(CH_3)_3$	−0.18	−0.12	−0.06
$Ge(C_2H_5)_3$	−0.20	−0.13	−0.07
$Sn(CH_3)_3$	−0.26	−0.13	−0.13

[a] Ref. 39.

TABLE 4

CALCULATED σ_p VALUES OF SOME ORGANOMETALLIC SUBSTITUENTS

Compounds	$\Delta\nu$(cm^{-1})	Substituent	σ_p
$(CH_3)_2Sn[C{\equiv}CC(CH_3)_3]_2$	152	$Sn(CH_3)_2[C{\equiv}CC(CH_3)_3]$	—0.28
$(CH_3)_2Sn[C{\equiv}CSi(CH_3)_3]_2$	132	$Sn(CH_3)_2[C{\equiv}CSi(CH_3)_3]$	—0.18
$(CH_3)_2Sn[C{\equiv}CSi(C_2H_5)_3]_2$	128	$Sn(CH_3)_2[C{\equiv}CSi(C_2H_5)_3]$	—0.16
$CH_3Sn[C{\equiv}CSi(C_2H_5)_3]_3$	114	$Sn(CH_3)[C{\equiv}CSi(C_2H_5)_3]_2$	—0.06
$CH_3Sn[C{\equiv}CGe(C_2H_5)_3]_3$	129	$Sn(CH_3)[C{\equiv}CGe(C_2H_5)_3]_2$	—0.05

with increasing atomic number of the silicon subgroup element, its tendency to d_π—p_π interaction decreases. This is one of the reasons for decreasing σ_R constants on going from Alk_3Si to Alk_3Ge and further to Alk_3Sn. The second reason is apparently the strengthening of hyperconjugation (σ,π conjugation) in the $Alk_3MC{\equiv}C$ fragment with increasing atomic number of M, leading to increasing donor properties of this fragment. Simultaneously, values of σ_R constants of organometallic substituents are higher than the σ_R constant for the tert-butyl group (—0.15) for any M. Taking into account the approximative values of σ_p and hence of σ_R constants, this suggests that there is some acceptor effect of the tin atom towards the triple bond (d_π—p_π interaction). In the absence of this effect due to increasing hyperconjugation with increasing M atomic number increasing of negative values of σ_R constants would be observed in the series $C < Si < Ge < Sn$, in contradiction with experiment. Equations 1—4 allow for the calculation of σ_p constants of organometallic substituents with more complex structure, on the basis of $\Delta\nu$ values (Table 4). The σ_p constant values for organometallic substituents containing acetylene groups are appreciably higher than the values of σ_p constants of Alk_3M-type substituents (Tables 2—4). This points to pronounced acceptor properties of alkynyl fragments attached to the M atom.

The $Alk_3MC{\equiv}CH$-type acetylenides investigated earlier [7,37] do not obey eqs. 1—4. For M = C, Si, Ge and Sn experimental $\Delta\nu$ values equal 92, 84, 99 and 115—120 cm^{-1} whereas $\Delta\nu$ values calculated on the basis of eqs. 1—4 [$\sigma_p(H) = 0$] equal 105, 105, 121 and 136 cm^{-1}, respectively. The lower observed $\Delta\nu$ values compared to those calculated are probably a result of the lower π-donating properties of $Alk_3MC{\equiv}CH$-type acetylenes due to self-association attributed to the formation of hydrogen bonds of $C{-}H\cdots\overset{C}{\underset{C}{|||}}$ type. Thus, the $\Delta\nu$ parameter reflects the influence of the substituents on the ground electronic state of organometallic derivatives of acetylene.

We now consider the change of substituent electronic effects on transition of the compounds studied from the ground state to the charge-transfer (CT) state. For this purpose we analyse the relationship between $\Delta\nu$ and the frequencies of the CT bands (ν_{CT}) in electronic absorption spectra of CT complexes of the studied compounds with iodine. Organotin compounds react with iodine, therefore their CT complexes have not been studied.

Acetylene derivatives (π-donors, D) form CT complexes with iodine (σ-acceptor, A) of π,σ type: a new CT band (ν_{CT}) appears in the electronic absorption spectrum. As this takes place electron transfer from D to A occurs, and a positive charge arises on molecule D, the presence of which may lead to a change in the interaction mechanism of substituents with the electron-deficient center [30,33]. It was found for derivatives of benzene [30], furan and thiophene [32], cyclopropane [40] and ethylene [33] that the frequency ν_{CT} decreases with the increasing donor properties of the substituents in the molecule. A linear correlation has been found between ν_{CT} and σ_p^+ constants of substituents on the ring for benzene derivatives [41]. This demonstrated that the substituents exhibit an electronic $+E$ effect in the CT state (positive charge on molecule D), while in the ground state they exhibit a mesomeric $+M$ effect. Therefore the points corresponding to compounds with substituents of $+M$ type deviate markedly from the $\Delta\nu$ vs. ν_{CT} correlations in the benzene and ethylene [33] series.

The relationship between $\Delta\nu$ and ν_{CT} for acetylenes is also of a complicated nature (Fig. 2). Yet for the group of points corresponding to compounds **5—7**, **10—15**, **18**, **20**, **29** and **30** the values of $\Delta\nu$ and ν_{CT} are connected by the linear equation

$$\Delta\nu = -(0.022 \pm 0.002)\,\nu_{CT} + (918 \pm 67) \qquad r = 0.935, \qquad n = 22 \qquad (5)$$

For the compounds that obey eq. 5, a decrease in values (i.e. decrease of π-donor properties while forming a hydrogen bond with phenol in the ground state) is accompanied by a regular increase in ν_{CT} values (i.e. with decrease of π-donor properties of the compounds formation of CT complex with iodine). The decrease of $\Delta\nu$ and the increase of ν_{CT} is due to an increase of acceptor properties of the substituents bound to the triple bond. Equation 5 denotes that both in the ground and in CT state the influence of substituents either

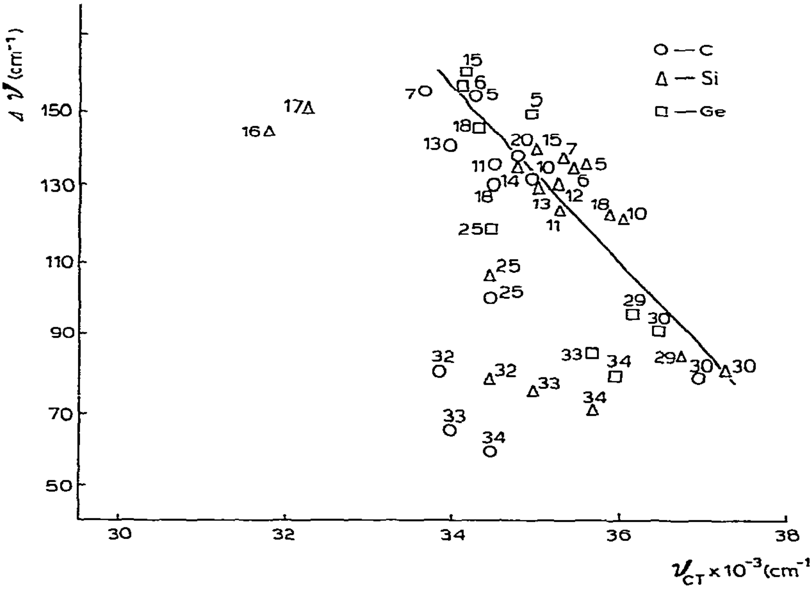
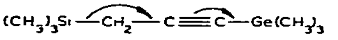


Fig. 2. Correlation $\Delta\nu$ (cm^{-1}) vs. ν_{CT} (cm^{-1}) for acetylene derivatives (o-carbon, △-silicon, □-germanium)

remains invariable or is connected by a linear relationship. It is characteristic that the point corresponding to compound **15** obeys eq. 5. This indicates that the effect of σ,π conjugation of the $(CH_3)_3SiCH_2$ fragment with the triple bond in  does not change appreciably on transition of the molecule from the ground state to the CT state. An analogous phenomenon is observed [33] for allyl derivatives of silicon subgroup elements. However, for benzene derivatives a significant increase of the σ,π conjugation effect on transition of the molecule to the CT state is observed [30]. Apparently, electronic effects in a conjugated system of bonds do not increase sufficiently in acetylene derivatives in the CT state. The compounds that obey eq. 5 do not contain substituents of $+M$ type bound to the triple bond. It is probably the main reason for the fact that electronic effects of substituents in the ground and CT states of these compounds differ slightly.

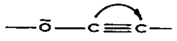
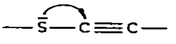
Points corresponding to compounds containing substituents of $+M$ type (OCH_3, SAlk, Cl, Br, I) deviate drastically from the correlation eq. 5 to lower ν_{CT} values. The deviations are given in Table 5, $\Delta\nu_{CT} = \nu_{CT}^{calcd.} - \nu_{CT}^{obs.}$, where $\nu_{CT}^{calcd.}$ is ν_{CT} calculated according to eq. 5 on the basis of $\Delta\nu$ values in IR spectra. The analysis of $\Delta\nu_{CT}$ values demonstrates that the conjugation effect of $+M$-type substituents with the triple bond is similar to the conjugation effect of these substituents with a benzene ring and a double bond. Actually, much as is observed for benzene derivatives [30], p,π conjugation effects in  and  fragments already appearing in the ground state, sharply increase in the CT state. Therefore, for compounds **16**, **17**, **26** and **27** high $\Delta\nu_{CT}$ values are observed (Table 5). As with benzene derivatives, higher $\Delta\nu_{CT}$

TABLE 5

VALUES OF ν_{CT} AND $\Delta\nu_{CT}$ IN THE ELECTRONIC ABSORPTION SPECTRA OF THE CT COMPLEX COMPLEXES STUDIED

Number	Compounds	$\nu_{CT}^{obs.} \times 10^{-3}$ (cm^{-1})	$\nu_{CT}^{calcd.} \times 10^{-3}$ (cm^{-1})	$\Delta\nu_{CT} \times 10^{-3}$ (cm^{-1})
16	$(CH_3)_3SiC{\equiv}COCH_3$	31.8	33.7	1.9
17	$(CH_3)_3SiC{\equiv}COC_2H_5$	32.3	33.4	1.1
26	$(CH_3)_3CC{\equiv}CSCH_3$	28.6	35.4	6.8
26	$(CH_3)_3SiC{\equiv}CSCH_3$	29.2	35.3	6.1
26	$(CH_3)_3GeC{\equiv}CSCH_3$	28.6	34.4	5.6
27	$(CH_3)_3CC{\equiv}CSC_2H_5$	28.6	35.3	6.7
27	$(CH_3)_3SiC{\equiv}CSC_2H_5$	29.1	35.2	6.1
27	$(CH_3)_3GeC{\equiv}CSC_2H_5$	28.7	34.3	5.6
25	$(CH_3)_3C{\equiv}CPh$	34.5	35.6	1.1
25	$(CH_3)_3SiC{\equiv}CPh$	34.5	35.3	0.8
25	$(CH_3)_3GeC{\equiv}CPh$	34.5	34.7	0.2
34	$(CH_3)_3CC{\equiv}CCl$	34.5	37.4	2.9
34	$(CH_3)_3SiC{\equiv}CCl$	35.7	36.9	1.2
34	$(CH_3)_3GeC{\equiv}CCl$	36.0	36.5	0.5
33	$(CH_3)_3CC{\equiv}CBr$	34.0	37.1	3.1
33	$(CH_3)_3SiC{\equiv}CBr$	35.0	36.7	1.7
33	$(CH_3)_3GeC{\equiv}CBr$	35.7	36.3	0.6
32	$(CH_3)_3CC{\equiv}CJ$	33.9	36.5	2.6
32	$(CH_3)_3SiC{\equiv}CJ$	34.5	36.5	2.0

values are observed for sulphur compounds (**16** and **26**, **17** and **27**). The sulphur atom possesses higher polarizability compared to oxygen. It is likely that this is the main reason for the fact that in the CT state donor properties (electromeric $+E$ effect) of AlkS groups increase to a greater degree than of CH_3O group. So the differences between values of σ_p constant and σ_p^+ constant (characterizing the influence of substituents in the CT state) for substituents SMe and OMe are equal to 0.6 and 0.5, respectively.

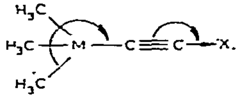
Halides are also substituents of $+M$ type, therefore the points corresponding to halogen derivatives (compounds **32**—**34**) deviate from the linear correlation (eq. 5) (Fig. 2, Table 5). The deviation $\Delta\nu_{CT}$ is increased in the order $Cl < Br < I$. Thus, an additional donation of electron density from the halides to the triple bond in the CT state (an increase of p,π conjugation in this state) increases with rising polarizability of the halide atom with increasing atomic number. A similar phenomenon is also observed for ethylene derivatives, but practically does not show up in the CT state of benzene derivatives [30,33]. Increase of π,π conjugation in phenyl acetylenes (**25**) in the CT state takes place, manifesting itself in a deviation of corresponding points from the linear correlation eq. 5.

There are other peculiarities in the change of substituent influence on transition of acetylene derivatives from the ground state to the CT state. It is worthwhile considering these features after comparing general trends in the influence of the substituent in the CT state of benzene, ethylene and acetylene derivatives. This has been partly considered [33]. The change of substituent influence is a result from perturbation of the π-electronic system in the transition to the CT state. This perturbation varies for benzene, ethylene and acetylene derivatives. Actually, in the electronically excited state produced due to electron transfer from the π HOMO to the lowest unoccupied molecular orbital (LUMO) of π^* type one of the six bonding electrons is transferred in benzene derivatives, one of two in ethylene derivatives and one of four in acetylene derivatives. As a consequence, perturbation is a maximum for ethylene and a minimum for benzene. When the π electron transfers from the HOMO of the donor to σ^* LUMO of acceptor (iodine), the amount of perturbation decreases compared to that in the electronically excited state, but their relative role in the series of benzene, acetylene and ethylene derivatives remains constant. Therefore, the positive charge arises on the aromatic ring or on the multiple bond in the CT state and simultaneously the conjugation system breaks (partially). These factors cause dissimilar effects in the three series of compounds studied. In benzene derivatives the positive charge is delocalized along the ring, and aromaticity in the CT state is reduced to a small degree. Therefore, in the CT state conjugation effects in the conjugated system of bonds remain: the presence of the positive charge increases conjugation with substituents of $+M$ type moderately.

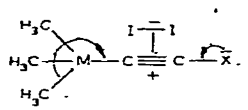
In ethylene derivatives the positive charge is localized on the C=C bond, the π-character of which is partially disturbed in the CT state. Therefore, in the CT state the conjugation effects in the conjugated system of bonds are weakening. The positive charge stimulates an increase in conjugation with $+M$ -type substituents possessing lone electron pairs.

Acetylene derivatives in the CT state exhibit properties of intermediate character between benzene and ethylene derivatives. This conclusion is most likely true only in general view. Detailed investigations are essential to study the properties of particular substituents in the CT state.

A characteristic feature of acetylene derivatives, that does not obey eq. 5, is the decrease of deviation values $\Delta\nu_{CT}$ in the series C > Si > Ge with the X substituent remaining fixed. This follows from a comparison of $\Delta\nu_{CT}$ values in compounds 25—27 and 32—34 (Table 5, Fig. 2). It was demonstrated above, that in the ground state the direct resonance interaction takes place for these compounds in accordance with the scheme



This effect is strengthening (i.e. donor properties of the $(CH_3)M$ group increase) with the increase in the atomic number of M. In the CT state this effect is probably, as in the ground state, most prominent for organometallic compounds. At the same time as opposed to the ground state, in the CT state the influence of p,π or π,π conjugation of lone electron pairs or π-electrons of X substituents with the multiple bond increases due to appearance on the latter of the positive charge in CT state



The two resonance effects, i.e. direct resonance interaction and p,π conjugation increased in the CT state, have opposite effects. Therefore, the total effect is not an additive sum of the two individual effects, but may be substantially weaker. So-called "dissipation" of the influence of the acceptor fragment, if this fragment is bound to two donor groups conjugated with it is a well known fact [e.g. 43]. The "dissipation" represents a decrease of acceptor fragment influence on donor groups in comparison with the influence it could exert on each group in the absence of another. In our case the acceptor fragment is the multiple bond with which $(CH_3)_3M$ and X groups come into conjugation.

With the X substituent remaining unchanged, the weakening of conjugation of both donor groups with the multiple bond will be larger, the more donating the group $(CH_3)_3M$ is. Hence, the weakening of conjugation must increase in the series Ge > Si > C, which repeats the series of increasing susceptibility of the $(CH_3)_3M$ groups to direct resonance interaction. As far as the conjugation weakening considered must lead to lowering $\Delta\nu_{CT}$ values, with X unchanged the lowest $\Delta\nu_{CT}$ values may be expected for organogermanium compounds; for silicon and carbon derivatives $\Delta\nu_{CT}$ values must increase. Such a nature of the dependence of $\Delta\nu_{CT}$ values on the nature of substituent X is the case for compounds 25—27 and 32—34.

Experimental

The IR spectra were recorded on a Zeiss UR-20 spectrometer, in the 3 000—3 600 cm^{-1} region (LiF prism) using 0.1 cm thick CaF_2 cells. In studies of hydrogen bonding with phenol, the concentration of the phenol in CCl_4 (spectral grade) was 0.02 mol/l, those of the organometallic compounds was 0.5—1.5 mol/l. Some organotin compounds reacted with the phenol. In this case for studies of the hydrogen bonding pyrrole was used. Concentration of pyrrole in

CCl_4 was 0.02 mol/l and those of organometallic compounds were 0.5—1.0 mol/l. The frequency shift $\Delta\nu$(N—H) was recalculated in $\Delta\nu$(O—H) values for phenol. All measurements were referred to solutions of organometallic compounds in CCl_4.

The electronic absorption spectra of CT complexes of the studied compounds with iodine in CCl_4 were recorded on a Perkin-Elmer 402 spectrophotometer in the 25 000—40 000 cm^{-1} region. The cells were 1 cm thick. Donor concentrations were about 0.02 mol/1; that of iodine was about 0.002 mol/1. All measurements were referred to iodine solutions in CCl_4. CT complexes of organotin compounds were not studied, as these compounds reacted with iodine.

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