Electronic effects of Me_3SiOCR_2 substituents in acetylene derivatives

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The σ_R^0 and σ_p parameters of Me_3SiOCR_2 and $HOCR_2$ substituents at the triple bond were determined using the IR spectra of individual acetylene derivatives and their H-complexes. These parameters vary as the effective charge on the atoms of the C≡C fragment of terminal acetylenic alcohols and their trimethylsilyl ethers changes due to intermolecular interaction. The most reliable values of σ_R^0 and σ_p parameters (−0.02 and −0.03, respectively) for the Me_3SiOCH_2 substituent were established; they indicate a sharp decrease in σ,π-conjugation of the Me_3SiOCH_2 substituent with the triple bond as compared to the Me_3SiCH_2 substituent.

Key words: IR spectra; acetylenic alcohols, trimethylsilyl ethers, H-complexes; σ_R^0 and σ_p parameters; σ,π-conjugation.

Unlike compounds containing $Me_3SiC{\equiv}C$— and $Me_3SiCH_2C{\equiv}C$— groups, electronic interactions between the substituents and the triple bond in the molecules of silicon-containing acetylene derivatives with $Me_3SiOCR_2C{\equiv}C$— fragments (R = H, Alk) have long remained poorly studied.

As we have shown, trimethylsilyl ethers of acetylenic alcohols are promising synthons in the organic synthesis. *O*-Silylation of terminal acetylenic alcohols can substantially enhance the reactivity of Iotsitch reagents, determine previously unknown rearrangements involving a silyl group and the triple bond. Recently, it has been shown that the Si—O bond is stable to the Grignard reagent taking 1-trimethylsilyloxyprop-2-yne as an example. This makes it possible to efficiently use silyl ethers of ethynylcarbinols in reactions with electrophilic agents. For instance, the Iotsitch reagent obtained from trimethylsilyl ether of propargyl alcohol reacts with trialkylchlorosilanes and -germanes to give triorganylsilyl(germyl)propargyl alcohols in yields 85—87%,[1] which is almost twice as high as the yields of these compounds in the reactions with propargyl alcohol itself.[2,3] We have found the previously unknown 1,4- and 1,5-O→C(sp) migrations of the trimethylsilyl group in Iotsitch reagents obtained from trimethylsilyl ethers of α,β- and β,γ-acetylenic alcohols, which after hydrolysis result in corresponding trimethylsilylacetylenic alcohols.[4,5] It has also been shown that trimethylsilyl ethers of acetylenic alcohols are less toxic than the starting ethynylcarbinols.[6]

The estimation of electronic interactions between the Me_3SiOCR_2 substituents and the triple C≡C bond makes it possible to extend the available knowledge of the reactivity of trimethylsilyl ethers of acetylenic alcohols. Therefore, the aim of this work was to study individual compounds and their H-complexes by IR spectroscopy and to compare the Hammett σ_R^0 and σ_p parameters of Me_3SiOCR_2 substituents at the triple bond with analogous characteristics of $HOCR_2$ groups in the corresponding acetylenic alcohols.

Experimental

The IR spectra of individual acetylene derivatives and their H-complexes were recorded on an UR-20 spectrometer in the spectral region 2000—3600 cm^{-1}; freshly distilled solvents (THF and CCl_4) were used. The compounds studied were synthesized by reactions of acetylenic alcohols with hexamethyldisilazane in the presence of imide of *o*-sulfobenzoic acid (saccharin) (1 mol.%) as catalyst.[6]

To determine the σ_R^0 parameters of the substituents following the previously described procedure,[7] we measured the integrated extinction coefficients A(C≡C) of the ν(C≡C) stretching bands in the IR spectra of solutions of individual compounds **1—10** (Tables 1 and 2) in CCl_4 (0.2—1.0 mol L^{-1}). The σ_R^0 parameters of substituents X in the XC≡CH molecules (see Table 1) were calculated using Eq. (1).[8]

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

The σ_R^0 values for the Me_3SiOCH_2 substituent in compounds $Me_3SiC{\equiv}CCH_2OSiMe_3$ and $Et_3GeC{\equiv}CCH_2OSiMe_3$ were calculated using Eqs. (2) and (3), respectively.[8,9]

$$A^{1/2} = 197\sigma_R^0 - 24.7,\ r = 0.969 \qquad (2)$$

$$A^{1/2} = 251\sigma_R^0 - 13.8,\ r = 0.983 \qquad (3)$$

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Table 1. Experimental values of ν(C≡C), *A*(C≡C), and Δν(CH...THF) for XC≡CH compounds and their H-complexes with THF and calculated values of σ_R^0 and σ_p parameters of substituents X

Compound	X	ν(C≡C) /cm^{-1}	*A*(C≡C) /L mol^{-1} cm^{-2}	ν(CH, CCl_4) /cm^{-1}	Δν(CH...THF) /cm^{-1}	σ_R^0	σ_p
1	Me_3SiOCH_2	2124	70	3315	65	−0.09	−0.06
2	$HOCH_2$	2125	76	3315	59	−0.09	−0.14
3	$Me_3SiOCH(Me)$	2116	50	3314	65	−0.08	−0.06
4	HOCH(Me)	2117	50	3314	57	−0.08	−0.16
5	$Me_3SiOCMe_2$	2113	23	3311	66	−0.07	−0.05
6	$HOCMe_2$	2119	51	3312	58	−0.08	−0.15
7	$Me_3SiOCH(Me)CH_2$	2123	150	3316	60	−0.11	−0.12
8	$HOCH(Me)CH_2$	2122	151	3315	55	−0.11	−0.18

Table 2. Experimental values of ν(C≡C), *A*(C≡C), and Δν(OH) for individual compounds **9**, **10**, and their H-complexes with phenol and calculated values of σ_R^0 and σ_p parameters of Me_3SiOCH_2 substituent

Compound	ν(C≡C) /cm^{-1}	*A*(C≡C) /L mol^{-1} cm^{-2}	Δν(OH) /cm^{-1}	σ_R^0	σ_p
$Me_3SiC{\equiv}CCH_2OSiMe_3$ **9**	2178	870	100	−0.02	−0.02
$Et_3GeC{\equiv}CCH_2OSiMe_3$ **10**	2171	264	128	−0.01	−0.04

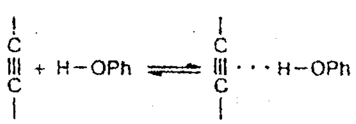
The σ_p parameters of the substituents for compounds **1**—**10** were determined using two procedures. The first procedure was applied to trimethylsilyl ethers of terminal acetylenic alcohols and compounds **1**—**8** and consisted in synthesizing corresponding H-complexes with THF (Eq. (4)), recording their IR spectra, and determining the Δν(CH...THF) = ν(CH, CCl_4) − ν(CH, THF) values, where ν(CH, CCl_4) is the frequency of the ν(≡C—H) stretching vibration of the complex in a solution of CCl_4 (0.02—0.05 mol L^{-1}) and ν(CH, THF) is the frequency of the ν(≡C—H) stretching vibration of the complex in a solution in neat THF or in a THF—CCl_4 mixture at a XC≡CH concentration of 0.1 to 0.5 mol L^{-1}.


(4)

The frequency shifts Δν(CH...THF) upon the formation of H-complexes are related to σ_p parameters of substituents X by the linear dependence (5).[11]

$$\Delta\nu(\mathrm{CH...THF}) = 81\sigma_p + 70,\ r = 0.949 \quad (5)$$

The second procedure was applied to 1-trimethylsilyloxy-3-trimethylsilylprop-2-yne (**9**) and 1-trimethylsilyloxy-3-triethylgermylprop-2-yne (**10**) and consisted in studying the IR spectra of their H-complexes with phenol obtained according to Eq. (6) (a solution in CCl_4; the concentration of phenol was ~0.2 mol L^{-1} and those of compounds **9** and **10** were in the range from 0.5 to 0.8 mol L^{-1}).


(6)

The frequency shift Δν(OH) of the ν(OH) stretching vibration of non-associated phenol upon the formation of H-complex is related to the sum of $\Delta\sigma_p$ parameters of two substituents at the triple bond ($\Sigma\sigma_p$) by the linear dependence (7).[12]

$$\Delta\nu(\mathrm{OH}) = -167\Sigma\sigma_p + 71,\ r = 0.986 \quad (7)$$

The σ_p values for the Me_3Si and Et_3Ge groups (−0.15 and −0.30, respectively) found in our previous study[12] were used.

It should be noted that phenol forms H-complexes with compounds **9** and **10** both at the triple bond (the Δν(OH) are listed in Table 2) and at the oxygen atom. No detailed studies of the second type of H-complexes (Δν(OH) = 230—235 cm^{-1}) were carried out.

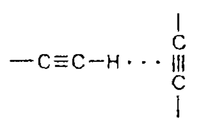
Results and Discussion

The values of the σ_R^0 and σ_p parameters of substituents X in the studied compounds **1**—**10** calculated using Eqs. (1)—(3), (5), and (7) are listed in Tables 1 and 2.

First, let us consider the σ_R^0 parameters. It follows from the data in Table 1 that they are negative and their values for Me_3SiOCR_2 and $HOCR_2$ substituents are virtually the same.

The signs and values of the σ_R^0 parameters indicate that the X groups (Me_3SiOCR_2 and $HOCR_2$) exhibit almost the same resonance donor properties toward the triple bond in terminal acetylene compounds **1**—**8**. Donor properties are due to σ,π-conjugation of substituents X with the multiple bond. Judging by the close values of σ_R^0 parameters for all X in molecules **1**—**8** (see Table 1), the effect of σ,π-conjugation with the participation of $YOCR_2$ substituents is only slightly dependent on the type of R (H, Me) and Y (H, $SiMe_3$). If the functional group ($OSiMe_3$, OH) is in β-position to the triple bond (the passage from compound **3** to compound **7** and that from compound **4** to compound **8**, respectively), the effect of σ,π-conjugation exhibits a tendency to be increased. However, it can be seen that on the average the $\sigma_R{}^0$ values for all acetylene derivatives considered in Table 1 are approximately constant (-0.09 ± 0.02). This indicates that the C—H, C—O, and C—C bonds have a comparable capability for σ,π-conjugation with the triple bond in the molecules of individual compounds **1**—**8**.

In fact, strictly speaking, terminal acetylene derivatives **1**—**8** cannot be considered as true individual compounds under conditions of measuring the A values needed for the calculations of $\sigma_R{}^0$ parameters (0.2—1.0 M solutions in CCl_4). It is likely that compounds **1**—**8** form self-associates due to the formation of H-bonds under these conditions.



Previously,[13] it has been established that the self-association is accompanied by the appearance of a partial positive charge δ^+ on the triple bond. The δ^+ charge is compensated by a shift of the electron density from substituent X to the C≡C bond by the mechanism of σ,π-conjugation. Therefore, there are reasons to assume that the $\sigma_R{}^0$ values characterize the effect of σ,π-conjugation in self-associated compounds **1**—**8** rather than in individual ones. Hence, one can expect a weakening of the σ,π-conjugation when passing from terminal acetylene compounds **1**—**8** to disubstituted derivatives **9** and **10** (see Table 2) incapable of forming self-associates of the considered type.

This assumption is confirmed by comparing the $\sigma_R{}^0$ parameters of the Me_3SiOCH_2 substituent in molecules **1**, **9**, and **10**. The negative $\sigma_R{}^0$ values for the last two mentioned compounds are much smaller than that for the first compound. Therefore, an $\sigma_R{}^0$ value equal to -0.02 is the most reliable quantitative characteristic of σ,π-conjugation of the Me_3SiOCH_2 substituent with the triple bond in individual acetylene derivatives.

Let us consider now the σ_p parameters. As in the case of $\sigma_R{}^0$ parameters, it is reasonable to analyze the σ_p values of the substituents separately for compounds **1**—**8** and **9**, and **10**. If the $\sigma_R{}^0$ values characterize the conjugation of substituents with the triple bond, then the σ_p parameters are a quantitative measure of two (inductive and resonance) effects.

It is likely that the σ_p values of substituents X listed in Table 1 characterize their electronic effects in self-associated XC≡CH molecules participating also in the formation of H-complexes with THF (see Eq. (4)) rather than in individual molecules. Considering the formation of such H-complexes, one must take into account, first, the self-association of XC≡CH molecules accompanied by the appearance of partial charge δ^+ on the triple bond considered above and, second, the appearance of partial negative charge δ^- on the atoms of the C≡C fragment due to transfer of the π-electron density from THF to acceptor XC≡CH molecules in intermolecular H-complexes. It is likely that the relatively low correlation coefficient (0.949) of Eq. (5) is a consequence of the dependence of the net charge on the triple bond on two factors acting in opposite directions. Therefore, one should be careful when analyzing the σ_p values of substituents X in XC≡CH molecules calculated using Eq. (5).

Taking into account these remarks, let us consider the σ_p values in Table 1. The σ_p values we calculated for organic substituents in compounds **2**, **4**, **6**, and **8** (-0.14 to -0.18) differ little from those commonly used for alkyl groups, for instance, Me (-0.17), Et (-0.15), and Bu^t (-0.20).[14] At the same time, the negative σ_p values for corresponding silicon-containing substituents are much smaller, as follows from comparison of pairs of compounds **1** and **2**, **3** and **4**, **5** and **6**, and **7** and **8**. Thus, the total electronic effect (the sum of the inductive effect and σ,π-conjugation) changes appreciably as the hydrogen atom in the OH group is replaced by the $SiMe_3$ fragment. Such a change is caused by distinctions between both inductive and resonance effects of organic and corresponding silicon-containing substituents. We consider it taking the Me_3SiOCH_2 and $HOCH_2$ substituents as an example.

According to the published data,[14] the average value of the inductive σ_I constant of the $HOCH_2$ substituent is +0.08. At the same time, the σ_I values of the $OSiMe_3$ substituent reported in two different studies[14,15] differ substantially. Taking σ_I as +0.31 [14] and using the relationship $\sigma(CH_2Y) = \sigma(Y)/2.8$, we get, for instance, $\sigma_I = +0.11$ [14] for the Me_3SiOCH_2 group. The use of the σ_p values from Table 1 and the relationship $\sigma_R = \sigma_p - \sigma_I$ leads to the values of resonance σ_R parameters equal to -0.22 and -0.17 for the $HOCH_2$ and Me_3SiOCH_2 substituents, respectively.

Thus, the same negative values of $\sigma_R{}^0$ parameters (-0.09) for both substituents in question increase to -0.17 and -0.22 for Me_3SiOCH_2 and $HOCH_2$, respectively, when passing to σ_R parameters. A similar effect is characteristic of resonance electron donor substituents of the $+M$ type. The $\sigma_R{}^0$ parameters describe the properties of such substituents in the absence of the effects of direct polar conjugation and, in particular, in the molecules of individual compounds. The σ_R parameters characterize the resonance properties of the substituents participating in the direct polar conjugation that occurs, for instance, in H-complexes due to the appearance of partial δ^+ and δ^- charges on the molecules of the hydrogen bond donor and acceptor, respectively (for more detail, see Refs. 11—13). Joining the direct polar conjugation as an additional channel of conjugation results in more pronounced resonance donor properties of substituents of the $+M$ type, *i.e.*, in increased negative values when passing from $\sigma_R{}^0$ to σ_R parameters.

At the same time, a detailed interpretation of σ_p parameters of the substituents in the molecules of compounds **1**—**8** can be hampered due to the reasons indicated above. More reliable information on the electronic effects of the Me_3SiOCH_2 substituent can be obtained from the IR spectra of H-complexes of trimethylsilyloxypropynes **9** and **10** with phenol (see Eqs. (6) and (7)). These compounds form no self-associates. If they form H-complexes with phenol acting as a hydrogen bond acceptor, then the small (~0.01 *e*) positive charge (δ^+)[12] appears on the carbon atoms of the C≡C bond. In this case the effect of substituents is described by the σ_p parameters (Eq. (7)). As can be seen from the data in Table 2, the average σ_p value of the Me_3SiOCH_2 substituent is −0.03. Taking $\sigma_I(Me_3SiOCH_2)$ as +0.11 and using the relationship $\sigma_R = \sigma_p - \sigma_I$, we get −0.14 as the most reliable σ_R value for the Me_3SiOCH_2 substituent at the triple bond.

It is of interest to compare σ-parameters of the Me_3SiOCH_2 and Me_3SiCH_2 substituents. The trimethylsilylmethyl group is a typical resonance $+M$-donor toward the triple bond. The negative values of σ_R^0 and σ_R parameters (−0.21 and −0.24, respectively) are due to σ,π-conjugation of the Si—C σ-bond with the π-system of the triple bond.[11] The Me_3SiCH_2 substituent is a stronger $+M$-donor than its complete carbon analog Me_3CCH_2, for which the σ_R^0 and σ_R values are equal to −0.09 [16,17] and −0.12,[17] respectively. As follows from consideration of σ,π-conjugation in organic and silicon-containing benzene derivatives,[18] the higher polarizability of the Si—C bond as compared to that of the C—C bond is one of the important factors determining the distinctions between the properties of substituents (in particular, of the Me_3SiCH_2 and Me_3CCH_2 groups). Thus, refraction (R_D) of the Si—C and C—C bonds (a quantitative measure of their polarizability) is equal to 2.9 and 1.3 cm^3, respectively.[18] Both the resonance donor properties of Me_3MCH_2 groups (M is an element of the silicon subgroup) and refraction of the M—C bonds increase as the atomic number M increases in the series Si < Ge < Sn < Pb.[18]

As to the capability for σ,π-conjugation, the Me_3SiOCH_2 substituent differs considerably from Me_3SiCH_2. One should take into account the higher polarizability of the Si—C bond (R_D = 2.5 cm^3) as compared to that of the C—O bond (R_D = 1.5 cm^3) when comparing the σ,π-conjugation in the $-C{\equiv}C-CH_2SiMe_3$ and $-C{\equiv}C-CH_2OSiMe_3$ fragments. Accordingly, the capability of the Me_3SiOCH_2 substituent for σ,π-conjugation with the triple bond in model compounds in question appears to be lower than that of the Me_3SiCH_2 group.

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