# ELECTRONIC INTERACTIONS DISPLAYED IN THE SPECTRA OF SUBSTITUTED ALKOXYTRIMETHYLSILANES*

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Relative basicity of the oxygen, valence vibration ν(Si—O—C), and coupling constants $^1J(^{13}C—^1H)$ of $(CH_3)_3Si$-group were measured in the compounds of the type $(CH_3)_3SiOR$. These quantities and $^{13}C$ and $^{29}Si$ chemical shifts of the $(CH_3)_3Si$ group are discussed in the terms of electron-acceptor character of the $(CH_3)_3Si$ group, α-effect in the case of $R = (CH_3)_3SiCH_2$, and large electron-accepting ability of $ClCH_2$— and $(CH_3)_3Si$ groups in the case of $R = ClCH_2$. It was found that the electron-acceptor character of the $(CH_3)_3Si$-group in the compounds of the type $(CH_3)_3SiOR$ depends on the nature of the group R and an equation is derived which describes this dependence. When $(CH_3)_3SiOR$ compounds with $R = ClCH_2$ and $(CH_3)_3SiCH_2$ interact with phenol, the electron-accepting effect of the groups R is changed into electron-donating effect.

So far, only such systems of $R_nSi(OR')_{4-n}$ compounds have been chosen for IR and NMR spectroscopic studies of alkoxysilanes which could solve the question of the effects of substituents on the silicon atom on the nature of OR′ group (ref.[1,2] and the references therein). The effects of substitution in the OR′ fragment on the properties of alkoxysilanes have not yet been studied in detail. This effect is studied by the use of NMR and IR spectroscopy in the present paper with a series of the compounds of the type $(CH_3)_3SiOR$. The substituents R were chosen so that their inductive constants covered sufficiently broad interval of values.

## EXPERIMENTAL

All the compounds of the type $(CH_3)_3SiOR$ were prepared by the reaction of the corresponding alcohols with hexamethyldisilazane or chlorotrimethylsilane. The reaction was carried out in the presence of stoichiometric amount of dry pyridine in diethyl ether; the yields were 80—95%. The purity of the products was checked by gas chromatography and the identity of the compounds proved by $^1H$-NMR. Physical constants are given here only for compounds not characterized previously[3]. All of them agree with the literature values[4]. $ROSi(CH_3)_3$ (R, b.p. (°C/Torr), $n_D^{20}$): $CH_3$, 58, 1·3680; $Br(CH_2)_2$, 152, 1·4355; $C_6H_5$, 107/52, 1·4775; $HCl_2CCH_2$, 80/83, 1·4302;

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$Cl_3CCH_2$, 88/95, 1·4423; $(CH_3)_3SiO(CH_2)_2$, 170, 1·4010. The following compounds are described for the first time here: $Br(CH_2)_2OSi(CH_3)_3$, for $SiC_5H_{13}OBr$ (197·2) calculated: 30·46% C, 6·65% H; found: 30·36% C, 6·42% H; $HCl_2CCH_2OSi(CH_3)_3$, for $SiC_5H_{12}OCl_2$ (187·2) cal.: 32·09% C, 6·46% H; found: 32·13% C, 6·27% H; $Cl_3CCH_2O(Si(CH_3)_3$, for $SiC_5H_{11}OCl_3$ (22·16) calculated: 27·10% C, 5·00% H; found: 27·24% C, 4·96% H.

IR *spectra* (1 000—1 200 $cm^{-1}$ region) of approximately 5% solutions of the compounds $(CH_3)_3$ . . SiOR in $CCl_4$ were measured on a double-beam spectrometer Zeiss, model UR 20, equipped with a NaCl prism. The frequency scale was calibrated as usual[5]. The relative basicities of oxygen and chlorine atoms were determined from hydrogen bond spectra in the region 3 100—3 700 $cm^{-1}$ (LiF prism) measured in NaCl cells of 0·1 cm thickness. (The possibility of determination of the relative basicities of Cl and O atoms in organosilicon compounds containing simultaneously both atoms was studied recently[6].) The difference $\Delta\nu(OH)$ between the wavenumbers of phenol absorption band maxima $\nu(OH)_{assoc.}$ and $\nu(OH)_{nonassoc.}$ was taken for the measure of the relatively basicity. The values were obtained as the average of three measurements. The concentration of alkoxysilanes in $CCl_4$ was 0·5 M. In the case of the compounds $(CH_3)_3SiOC(CH_3)_3$ (1·0M) and $(CH_3)_3SiOCH_2Cl$ (in subst.) the concentration had to be raised as a consequence of low intensity of $\nu(OH)_{assoc.}$ absorption band. The coupling constants $^1J(^{13}C—^1H)$ were measured on Varian XL-100 spectrometer at the frequency of 100·1 MHz. The samples were measured in $CDCl_3$ solutions.

## RESULTS AND DISCUSSION

According to the generally accepted view, the shielding of nuclei other than $^1H$ is dominated by the paramagnetic term[16,17]. Recent studies of $^{29}Si$ chemical shifts in series of compounds of the type $(CH_3)_3SiA$ (A is an anion of organic or inorganic acid)[18] and $(CH_3)_nSi[OC(O)R]_{4-n}$ (with the same $n$)[19] are in keeping with this view. It can be deduced from these studies that the magnitude of $\delta^{29}$ Si correlates with the electronic density on the silicon atom.

Similar dependence holds also for the chemical shift $\delta^{29}Si$ of the compounds of the type $(CH_3)_3SiOR$ (Table I) which, with the exception of the compounds having R = $ClCH_2$ and $(CH_3)_3SiCH_2$, correlate with $\sigma^*$ constants[6–8] (Fig. 1). The better fit, which is obtained if $\delta(Si)$ of methoxytrimethylsilane is not included, is described by Eq. (*1*), where $r$ is a correlation coefficient. It follows from

$$\delta(Si) = 14{\cdot}88 + 8{\cdot}11\sigma^* ; \quad r = 0{\cdot}978 \qquad (1)$$

a comparison of the gradients in the $\delta(Si)$ *vs* $\sigma^*$ dependence in the series of $(CH_3)_3SiOC(O)R$ (data $\delta(Si)$ of ref.[17]; 3·86) and $(CH_3)_3SiOR$ (8·11) compounds that the introduction of C=O group between the group R and the oxygen atom in compounds $(CH_3)_3SiOR$ lowers the sensitivity of $\delta(Si)$ to the polar effect of the group R 2·10 times. This value is in relatively good agreement with the value of polar effect transmission over C(O) group found by Bowden[20]. Information about the electron density on the carbon atom of $(CH_3)_3Si$ group in $(CH_3)_3SiOR$ compounds can be obtained from carbon chemical shift $\delta(^{13}C)$ and coupling constant

$^1J(^{13}C—^1H)$. The magnitudes of these two quantities (Table I) do not vary regularly with varying polar effect of the group R; the carbon chemical shift is positive in the compounds $(CH_3)_3SiOR$ having R = alkyl (but also for R = $ClCH_2$ and $C_6H_5$) but it is negative when R = electronegative substituent ($\sigma^*(R) > 0$). In both cases the magnitude of either positive or negative shift is almost constant. With the exception of the compound with R = $(CH_3)_3SiCH_2$ the coupling constant $^1J(^{13}C—^1H)$ is also almost constant in the whole series of $(CH_3)_3SiOR$ compounds. Low sensitivity of $\delta(C)$ and especially of $^1J(^{13}C—^1H)$ to polar effects is apparently due to the

TABLE I

NMR[a] and IR[b] Data for $(CH_3)_3SiOR$ Compounds

| Compound | R | $\sigma^{*c}$ | $\delta$(Si) | $\delta$(C) | $J(^{13}C—H)$ | $\Delta\nu$(OH) | $\nu$(Si—O—C) |
|---|---|---|---|---|---|---|---|
| *1* | $(CH_3)_3C^d$ | −0·30 | — | 2·58 | — | 265 | 1 060[e]; 1 022[f] |
| *2* | $(CH_3)_3SiCH_2{}^g$ | −0·26 | 16·1 | 2·1(2·5) | 119·5 | 293 | 1 063 |
| *3* | $(CH_3)_3Si(CH_2)_2{}^g$ | −0·25 | 13·1 | 1·9(2·4) | 117·9 | 289 | 1 083 |
| *4* | $(CH_3)_2CH^d$ | −0·19 | 12·12 | 0·15 | 118·1 | 277 | 1 037[e]; 1 027[f] |
| *5* | $(CH_3)_3CCH_2{}^g$ | −0·165 | 14·1 | 1·4 | 118·0 | 255 | 1 094; 1 091[e] |
| *6* | $(CH_3)_3C(CH_2)_2{}^g$ | | 14·69 | 0·48 | — | 279 | 1 102 |
| *7* | $CH_3(CH_2)_2{}^g$ | −0·115 | 13·8 | 1·5 | 117·5 | 276 | 1 088, 1 107; 1 098[e]; 1 094[f] |
| *8* | $CH_3CH_2{}^g$ | −0·10 | 13·5 | 1·8 | — | 280 | 1 086[e]; 1 076, 1 107[f] |
| *9* | $CH_3$ | 0 | 17·0[h] | — | 117·8 | 274 | 1 055, 1 092; 1 104[e]; 1 090[f] |
| *10* | $CH_3O(CH_2)_3{}^d$ | 0·07 | 15·53 | −0·57 | 117·9 | — | — |
| *11* | $Cl(CH_2)_3{}^g$ | 0·137 | 16·7 | −0·5 | 118·3 | 264 | 1 101 |
| *12* | $CH_3O(CH_2)_2{}^d$ | 0·186 | 16·25 | −0·39 | 118·1 | — | — |
| *13* | $C_6H_5CH_2{}^d$ | 0·215 | 17·40 | −0·46 | 118·0 | 238 | 1 070, 1 096, 1 107 |
| *14* | $CH_2{=}CHCH_2{}^d$ | 0·23 | 16·59 | −0·41 | 117·7 | 256 | 1 085, 1 138 |
| *15* | $Br(CH_2)_2{}^d$ | 0·357 | 18·29 | −0·45 | 118·3 | — | — |
| *16* | $Cl(CH_2)_2{}^d$ | 0·385 | 18·36 | −0·51 | 118·1 | 233 | 1 096, 1 126 |
| *17* | $C_6H_5{}^d$ | 0·60 | 19·62 | 0·16 | — | 177[i] | — |
| *18* | $HCl_2CCH_2{}^d$ | 0·69 | 20·65 | −0·48 | 118·1 | 193 | 1 126 |
| *19* | $Cl_3CCH_2{}^d$ | 0·95 | 21·75 | −0·36 | 117·8 | 135 | 1 151 |
| *20* | $ClCH_2{}^d$ | 1·05 | 6·81 | 1·91 | 117·5 | 176 | 1 054, 1 102 |
| *21* | $(CH_3)_3SiO(CH_2)_2{}^g$ | — | 16·0 | −0·3 | 118·3 | 253 | — |

[a] NMR data pertinent to $(CH_3)_3Si$ group; all the chemical shifts are in $\delta$ scale relative to TMS signal, in p.p.m. units, the shifts to lower field (less shielded) are positive; coupling constants are in Hz units. [b] Quantities $\nu$ are in $cm^{-1}$. [c] Ref.[7]. Ref.[8] ($\sigma^*$ constants obtained as $6{\cdot}23 \,.\, \sigma_I$); ref.[9]; some $\sigma^*$ constants of $R(CH_2)_n$ groups were calculated as $\sigma^*R(CH_2)_{n-1/2.8}$. [d] $\delta$(Si) and $\delta$(C) taken from ref.[10]. [e] Ref.[11]. [f] Ref.[12]. [g] $\delta$(Si) and $\delta$(C) taken from ref.[13]. [h] Ref.[14]. [i] Ref.[15].

large distance of $CH_3$ group from the substituent R. Owing to this low sensitivity, it would be difficult to discuss the increase of the $J(^{13}C—^{1}H)$ value in $(CH_3)_3Si$ . . $CH_2OSi(CH_3)_3$ compound in the terms of polar effects.

Electron-accepting character of the silicon atom in $Y_3Si - X$ bonds (X is an atom with a $p$ orbital) was explained by the $(p - d)_\pi$ interaction. Recently an alternative explanation by $p - \sigma^*_{Si-Y}$ interaction was offered[21,22]. Of the two types of interactions the latter should affect the quantity $J(^{13}C—^{1}H)$ stronger as it leads to valence structure $CH_3^-$ $[Si(CH_3)_2OR]^+$. In $CH_3^-$ fragment of such a structure the $s$-character of originally $sp^3$ hybridized carbon atom is increased. The $p-d$ interaction should affect the coupling constant to a lesser extent. Varying electron-accepting character of Si atom in the series of $(CH_3)_3SiOR$ compounds and hence varying extent of one of the two interactions combined with practically constant value of $J(^{13}C—^{1}H)$ coupling for all R could suggest that the interpretation of electron-accepting character of Si atom in $(CH_3)_3SiOR$ compounds should rather include the $p-d$ interaction.

The relative basicity of oxygen atom in compounds $(CH_3)_3SiOR$ defined as $\Delta\nu(OH)$ of phenol interacting with the oxygen of Si—O—C grouping (Table I) is not linearly dependent on the $\sigma^*$ constants of groups R (Fig. 2). The sensitivity of $\Delta\nu(OH)$ to the substituent effect decreases when going from the negative to the positive values of the $\sigma^*$ constants. The dependence of $\Delta\nu(OH)$ on the $\sigma^*$ constants can be described by Eq. (2). The deviations of some points, which correspond

$$\Delta\nu(OH) = -75{\cdot}0(\sigma^*)^2 - 73{\cdot}2\sigma^* + 274{\cdot}6 \qquad (2)$$

to R = $(CH_3)_3C$, $(CH_3)_2CH$, and $(CH_3)_3CCH_2$ from this dependence (Fig. 2) can be explained by steric effects of the group R (compare[23]). In the case of R = $C_6H_5$ and $C_6H_5CH_2$ it is possible that due to its own interaction with phenol the phenyl

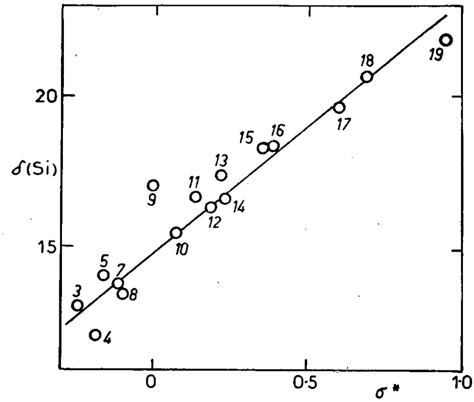


Fig. 1

The Dependence of the Chemical Shift δ(Si) on $\sigma^*$ Constant of the Group R in Compounds of the Type $(CH_3)_3SiOR$

group exercises stronger electron acceptive effect on the oxygen atom. The anomalous value of the relative basicity of oxygen in chloromethoxytrimethylsilane (Fig. 2, point *20*) will be discussed later. The shape of the dependence $\Delta\nu(OH)$ *vs* $\sigma^*$ for the compounds of the type $(CH_3)_3SiOR$ indicates that the behaviour of $(CH_3)_3Si$ group bonded to oxygen atom cannot be described by a constant, the role of electron-accepting character of the $(CH_3)_3Si$ group increases with increasing electron-donating effect of the group R.

The role of electron-acceptive character of $(CH_3)_3Si$ group in $(CH_3)_3SiOR$ compounds ($R = C_2H_5$ and $(CH_3)_3C$) was recently estimated[24] from the difference between the relative basicity (also $\Delta\nu(OH)$ of phenol) obtained experimentally and calculated from a correlation of the basicity with hyperconjugation and inductive effects of group R in saturated ethers $R_2O$. The same values of $\Delta\nu(OH)$ of $(CH_3)_3SiOR$ compounds ($R = C_2H_5$ and $(CH_3)_3C$) are obtained if they are calculated[24] according to the correlation equation assuming $\sigma^*[(CH_3)_3Si] = -0{\cdot}72$ as if they are obtained from a linear extrapolation of our dependence $\Delta\nu(OH)$ *vs* $\sigma^*$ to the region of $\sigma^* < 0$. (The dependence is valid in the interval $\sigma^* \sim 0{\cdot}5 - 1{\cdot}0$, in this interval the $(CH_3)_3Si$ group does not exhibit electron-accepting character, Fig. 2). As follows from Fig. 2 the use of the difference $\Delta\nu(OH)_{calcd.} - \Delta\nu(OH)_{exptl.}$ for estimation of the relative importance of electron accepting character of $(CH_3)_3Si$ group in $(CH_3)_3SiOR$ compounds is limited to such groups R which have steric effect so small that it does not lead to deviations from $\Delta\nu(OH)$ *vs* $\sigma^*$ plot. More accurate measure of the electron-accepting character of $(CH_3)_3Si$ group is provided by the difference between the values of $\Delta\nu(OH)$ obtained for the corresponding group R from the curve and the extrapolation line. This quantity $\Delta\Delta\nu(OH)$ can be expressed by Eq. (*4*) which is derived as a difference between the Eq. (*2*) for the curve and the equation of the extrapolation line, Eq. (*3*).

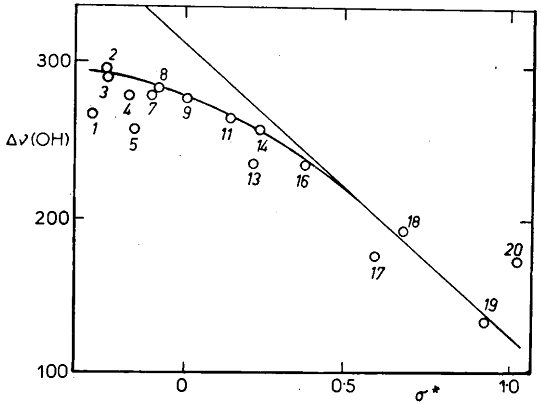


FIG. 2

The Dependence of the Quantity $\Delta\nu(OH)$ on $\sigma^*$ Constant of the Group R in the System $(CH_3)_3SiOR$–Phenol–$CCl_4$

$$\Delta\nu(\mathrm{OH}) = -178{\cdot}4\sigma^* + 310{\cdot}0\,, \tag{3}$$

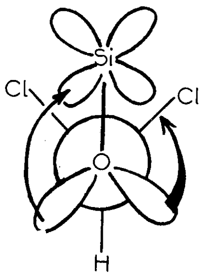
$$\Delta\Delta\nu(\mathrm{OH}) = 75{\cdot}0(\sigma)^2 - 105{\cdot}2\sigma^* + 36{\cdot}0\,. \tag{4}$$

Interpretation of the hypothetical assignment of (Si—O—C) wavenumber in terms of electronic effects of groups R in $(CH_3)_3SiOR$ compounds encounters with difficulties stemming from the fact that this vibration is not sufficiently characteristic. Wavenumber $\nu$ (Si—O—C) varies not monotonously in the series of compounds of the type $(CH_3)_3SiOR$ and the occurrence of two or more bands might be indicative of a conformation population.

Substituent constants $\sigma^*$ can be determined from the obtained dependences of $\delta(Si)$ and $\Delta\nu(OH)$ on this constant. Thus the values of 0·14 ± 0·05 and 0·24 ± 0·06 are obtained for $(CH_3)_3SiOCH_2$ group from the measured values of $\delta(Si)$ and $\Delta\nu(OH)$, resp. in $[(CH_3)_3SiOCH_2]_2$. In the same manner derived values of $\sigma^*$ constant of $(CH_3)_3C(CH_2)_2$ group are −0·22 ± 0·05 and −0·02 ± 0·06, resp.

It is interesting to note the behaviour of groups R = $(CH_3)_3SiCH_2$ and $ClCH_2$. In the ground state of $(CH_3)_3SiCH_2OSi(CH_3)_3$ molecule trimethylsilylmethyl group exhibits a weak electron-accepting effect (it follows from the $\delta(Si)$ *vs* $\sigma^*$ dependence that the constant of $(CH_3)_3SiCH_2$ group is +0·15 ± 0·05). The relative basicity of oxygen in the molecule of $(CH_3)_3SiCH_2OSi(CH_3)_3$ corresponds, however, to electron-donating effect of this group ($\sigma^* = -0{\cdot}26$) as it is experienced in other compounds containing oxygen atom, $(CH_3)_3SiCH_2CO_2X$ (X = R[7]; H (refs[25,26]). The fact that $(CH_3)_3SiCH_2$ group influences functional group Y in compounds of the type $(CH_3)_3SiCH_2Y$ in two different ways, *i.e.* in compounds with Y = $OSi(CH_3)_3$ by an electron-accepting effect and in compounds with Y = OC(O)X by an electron-donating effect, is also consistent with the values of $\delta(Si)$ of $Si(CH_3)_3$ group in compounds of the type $(CH_3)_3MCH_2C(O)O\,.\,Si(CH_3)_3$ [M, $\delta(Si)$ in p.p.m. units relative to TMS, measured in acetone-$d_6$ solutions at 19·87 MHz (ref.[27])] M = Si $\delta(Si)$ = 34·75 and M = C $\delta(Si)$ = 36·91. According to these values $(CH_3)_3SiO$ group is shielded more in $(CH_3)_3SiCH_2\,.\,COOSi(CH_3)_3$ compound. Electron-donating effect of $(CH_3)_3SiCH_2$ group in $(CH_3)_3MCH_2C(O)OSi(CH_3)_3$ must be larger than the same effect of $(CH_3)_3CCH_2$ group. Lower electron density on the silicon atom of $(CH_3)_3SiO$ group than it corresponds to electronic effects of $(CH_3)_3SiCH_2$ group with $\sigma^* = -0{\cdot}26$ was reported by us earlier[3] for the ground state of $(CH_3)_3SiCH_2OSi(CH_3)_3$ molecule. The decreased density was ascribed to the so-called α-effect, *i.e.* to the shift of electrons from oxygen to the silicon of $(CH_3)_3SiCH_2$ group. Mechanism of this interaction was explained by participation of *d* orbitals[28] and by antibonding $\sigma^*_{Si-C}$ orbital[29]. Electron-donating effect if $(CH_3)_3SiCH_2$ group which follows from the results of basicity measurements, can be explained, in accord with the validity of Badger–Bauer relationship[30] for low concentrations of structurally similar bases in inert solvent, by considering shift of electrons to an electron-deficient center resulting in a cancellation of the α-effect. The electron deficient center in the interaction of $(CH_3)_3SiCH_2O$ . . $Si(CH_3)_3$ with phenol is provided by the electron-deficient hydrogen of the phenol.

NQR frequencies of $^{35}Cl$ in the compounds of the type $(CH_3)_3SiO(CH_2)_nCl$ can be used in interpreting the spectral data of $(CH_3)_3$ $SiOCH_2Cl$ compound (Table I). These frequencies are ($n$, $\nu^{77}$ in MHz) 3,32·734; 2,33·655, and 1,32·379[31]. The increase in $\nu^{77}$ when going from $n = 3$ to $n = 2$ is in keeping with the values of $\Delta\nu(OH)$ and $\delta(Si)$ in both compounds. It indicates that the interaction of $(CH_3)_3SiO$ group and Cl atom over $CH_2CH_2$ fragment is determined by their electronegative character. (The generally known increased *s*-character of the orbitals of both C atoms of —$(CH_2)$— group in compounds of the type X—$(CH_2)_2$—Y (where X, Y = electronegative substituent) facilitates the interaction between the groups X and Y. This was also demonstrated in systems $(CH_3)_3SiO(CH_2)_2NR_2$ (ref.[32]). In contrast the decrease in $\nu^{77}$ when going from $n = 2$ to $n = 1$ indicates an increase in electron density on Cl atom which is undoubtedly due to electron donation of electrons from oxygen atom.* The shift of electrons from oxygen to chlorine atom should decrease the shielding of the silicon. According to the chemical shift $\delta(Si)$ in $(CH_3)_3SiOCH_2Cl$ silicon is in this compound shielded considerably more than in compounds of the type $(CH_3)_3SiOR$ where R = alkyl. This is in agreement with the finding that the hydrolysis of chloromethoxytrimethylsilane (rate determining step is the nucleophilic attack



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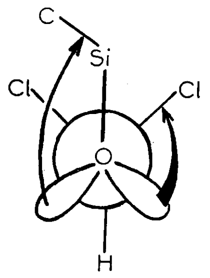

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* Anomalous decrease in NQR frequency of $^{35}Cl$ was observed for compounds similar to chloromethoxytrimethylsilane. Deviations from a correlation between NQR $^{35}Cl$ frequencies and $\sigma^*$ constants of groups R in the compounds of the type X—$CH_2Cl$ (X is a substituent with non-bonding electron pair) were interpreted by $n$-$\sigma$ conjugation[33]. This interpretation was supported by the finding[34] that the magnitude of the mentioned deviations depends linearly on the resonance parameter[35] $\sigma_R^0$ of the group X. The alternative explanation of anomalously low values of NQR $^{35}Cl$ frequencies in the series of $CH_3O(CH_2)_nCl$ compounds is based on very small amplitudes of oscillation of the $\nu^{77}$ frequency with n and it incorporates an intramolecular three-center bond ($n_O \rightarrow \sigma^*_{C-Cl}$ overlap)[36].

of a water molecule on the silicon atom) proceeds slowler than in the other alkoxysilanes[37]. The increased electron density on Si and Cl atoms in $(CH_3)_3SiOCH_2Cl$ could be interpreted by the involvement of both non-bonding electron orbitals of oxygen in the interactions $n_1 \rightarrow \sigma^*_{C-Cl}$ and $n_2 \rightarrow d$ or $n_2 \rightarrow \sigma^*_{Si-C}$ (structures *A* and *B*). This is in disagreement with the relative basicity of chlorine and oxygen atoms in this compounds ($\Delta\nu(OH) = 46\,cm^{-1}$ and $\Delta\nu(OH) = 176\,cm^{-1}$, resp.) The former value does not correspond to the electron density on Cl atom increased in the consequence of $n \rightarrow \sigma^*_{C-Cl}$ interaction (for alkyl chlorides $\Delta\nu(OH)$ of phenol is $60\,cm^{-1}$ [38]), the latter value is even larger than it would correspond to the $-I$ effect of $ClCH_2$ group (point *20*, Fig. 2). These data could be interpreted by the electron-accepting effect of $ClCH_2$ group in the ground state of $(CH_3)_3SiOCH_2Cl$ molecule being suppressed when this molecule interacts with phenol. Then, the $ClCH_2$ group is acting as an electron donor. Hence a detailed interpretation of this observation might include ceasing of $n \rightarrow \sigma^*_{C-Cl}$ interaction and increased role of $\sigma_{C-Cl} \rightarrow n$ or $n_{Cl} \rightarrow \sigma_{O-C}$ interaction in the complex of chloromethoxytrimethylsilane with phenol as results of forced electron transfer from oxygen atom of Si—O—C to electron-deficient hydrogen of phenol.

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