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STERIC EFFECTS IN THE IR-SPECTRA OF SILICON AND GERMANIUM MESITYL DERIVATIVES

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Summary

Frequencies (ν) and integrated intensities (A) of M—H (M = Si, Ge) stretching modes in IR spectra of organosilicon and organogermanium compounds, containing phenyl, xylyl and mesityl substituents, have been measured. In contrast to phenyl and xylyl derivatives, the influence of mesityl substituents on ν(M—H) and A(M—H) is shown to be determined not only by the inductive effect and d_π—p_π interaction, but also by the pronounced steric effects of mesityl groups.

Introduction

Silane and germane derivatives are considered to be the most convenient for spectroscopic investigation of the chemical bond in organosilicon and organogermanium compounds. This is explained by the fact that the modes of Si—H and Ge—H vibrations are highly characteristic [1—3]. Therefore, the frequency and integrated intensity of ν(M—H) (M = Si, Ge) bands are determined almost exclusively by electronic effects of the substituents bound to the M atom, indeed the frequency and intensity of the ν(M—H) bands appear to be the sole sources of data on electronic effects of the substituents in organosilicon and organogermanium compounds.

The dependence of ν(M—H) or A(M—H) on inductive and various conjugation effects, was systematically studied for a large number of silane and germane derivatives [4—7]. Primarily, only compounds with the substituents which do not exhibit large steric effects were investigated. This is why the bond angles of central Si or Ge atoms remain almost tetrahedral and the values of ν(M—H) and A(M—H) are independent of the substituent steric effects. Also, there is reason to believe that the presence of bulky substituents at the M atom results in a significant deviation of its bond angles from ~109.5°. This can (a) change the modes of the ν(M—H) vibrations and (b) change the values of M—X overlap integrals (X = is an atom with lone electron pairs or α,β-unsaturated hydrocarbon radical), i.e. can change the conjugation of the M atom with the X substituent. We were not acquainted with any theoretical or experimental work directly concerned with steric effects of substituents on ν(M—H) and A(M—H) for organosilicon and organogermanium compounds. Therefore, we made a comparative study on organosilicon and organogermanium compounds with substituents of significant steric effects and compounds with xylyl or phenyl substituents, the steric effects of which are small and do not affect the parameters of IR spectra.

Results and discussion

It was found [4,5] that ν(M—H) in organosilicon compounds R_3SiH and organogermanium compounds R_3GeH, (R = substituents which exert only an inductive influence on ν(M—H)) is connected with the sum of the Taft inductive constants of the R substituents by the linear equations:

$$\nu_{ind} = 23.1\Sigma\sigma^* + 2112 \qquad (R_3SiH) \qquad (1)$$

$$\nu_{ind} = 23.6\Sigma\sigma^* + 2021 \qquad (R_3GeH) \qquad (2)$$

It has been reported [6,7] that the corresponding equations for mono- and disubstituted germane derivatives are as follows:

$$\nu_{ind} = 23.6\Sigma\sigma^* + 2035 \qquad (R_2GeH_2) \qquad (3)$$

$$\nu_{ind} = 23.6\Sigma\sigma^* + 2049 \qquad (RGeH_3) \qquad (4)$$

From eq. 1—4, it might be expected that the experimental frequencies of ν(M—H) would decrease in the order: Ph > Xyl > Mes, due to the decrease in the electron-acceptor properties of the substituents at the M atom. (It is obvious from Table 1 that the sum of the Taft inductive constants of three substituents in this series decreases significantly). However, according to the data obtained the experimental values of ν(M—H) decrease when passing from phenyl to xylyl derivatives of silicon and germanium, while for mesityl derivatives this value increases sharply. Compound X is the only exception.

Let us consider the possible reasons for ν(M—H) changing. From eq. 1—4, the frequencies ν_{ind} and differences $\Delta\nu = \nu_{ind} - \nu_{exp}$ were calculated for the compounds studied. Analysis of $\Delta\nu$ indicates that there are several factors affecting this value.

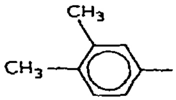
It has been found [4,7,9,10] that $\Delta\nu$ for Ph_3SiH, Ph_3GeH, Ph_2GeH_2, $PhGeH_3$ is determined by d_π—p_π interaction. This effect is opposite to the —I effect of the phenyl groups. Formally, this is equivalent to decreasing the —I effect of the substituents. As a result, the force constant of the M—H bond decreases, causing the decrease of ν_{exp} in comparison with ν_{ind}. The same effect is responsible for $\Delta\nu$ appearing for xylyl derivatives of silicon and germanium. The comparison of $\Delta\nu$ values for I and II, IV and V indicates, that the effect of d_π—p_π interaction in M—Xyl fragments is less than that in M—Ph fragments. It has been shown [11] that this is due to the smaller inductive effect of xylyl substituents compared to phenyl ones.

TABLE 1

VALUES OF ν(M—H), $\Delta\nu$, $A^{1/2}$ AND $\Delta A^{1/2}$ IN THE IR SPECTRA OF THE COMPOUNDS STUDIED

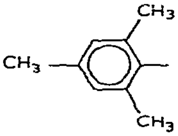
	Compound	ν_{exp} (cm^{-1})	ν_{ind} (cm^{-1})	$\Delta\nu_{I}$ (cm^{-1})	$A^{1/2}_{exp}$		$A^{1/2}_{ind}$	$\Delta A^{1/2}$	$\Sigma\sigma^*$
					heptane	CCl_4			
I	Ph_3SiH	2132	2153	+21	1.12	1.20	0.82	0.30	1.80
II	Xyl_3SiH [a]	2125	2138	+13	1.17	1.24	0.96	0.21	1.14
III	Mes_3SiH [a]	2159	2117	—42	1.19	—	1.16	0.03	0.21
IV	Ph_3GeH	2046	2063	+17	1.19	1.27	0.94	0.25	1.80
V	Xyl_3GeH	2042	2048	+6	1.24	1.33	1.07	0.17	1.14
VI	Mes_3GeH	2052	2026	—26	1.39	1.49	1.26	0.13	0.21
VII	Ph_2GeH_2	2062	2074	+12	1.60	1.68	1.45	0.15	1.69
VIII	Mes_2GeH_2	2074	2050	—24	1.77	1.86	1.66	0.11	0.63
IX	$PhGeH_3$	2082	2086	+4	1.69	1.78	—	—	1.58
X	$MesGeH_3$	2077	2074	—3	1.84	1.92	—	—	1.05

[a] Xyl =



,

Mes =



Values of σ^* xylyl and mesityl substituents were calculated according to the equation $\sigma^*(R_nC_6H_{5-n})$ $n(\sigma^0_R)$ + 0.600; σ^0_R values were used from ref. 8.

An anomalous increase is observed in the experimental values of ν(M—H) for mesityl derivatives. The values of ν_{exp} here exceed ν_{ind} values obtained by eq. 1—4. No such situation was observed for the silane or germane derivatives with phenyl or xylyl substituents. Therefore, we attributed the anomalous values of ν_{exp} to large steric effects of mesityl substituents in compounds III, VI and VIII.

From data reported [12], the angles between Mes—M—Mes bonds in compounds of Mes_3MH type (M = C, Si, Ge) are 118.3; 116.0 and 115.5°, respectively; i.e. the angle increases with decrease of the atomic radius of M. The distortion of the tetrahedral structure of Si and Ge atoms in the Mes_3MH type compounds and also, probably, in Mes_2GeH_2 leads to a change of the ν(M—H) mode in these compounds. NMR data indicate a "propeller" arrangement of three mesityl substituents at Si and Ge atoms [13,14]. This together with the distortion of the tetrahedral structure of central Si and Ge atoms in the compounds with three and, probably, two mesityl substituents change the d_π—p_π interaction between vacant d-orbitals of M atoms (M = Si, Ge) and π-electrons of aromatic rings. (It is known [15] that the degree of d_π—p_π interaction is strongly dependent on the overlap integrals of the interacting orbitals, i.e. on the molecular geometry).

Significant negative values of $\Delta\nu$ for compounds III, VI and VIII suggest that both the factors (the change of the vibration mode and of the d_π—p_π interaction) bring about a sharp decrease in electron density donation from the aromatic ring to M atoms by the conjugation mechanism in mesityl derivatives compared to phenyl and xylyl ones. Not only complete distortion of d_π—p_π interaction in M—Mes bonds takes place here, but there is also a sharp increase in ν_{exp} values due to the change of the M—H vibration mode in compounds III, VI and VIII. These two effects result in large negative $\Delta\nu$ values. Thus, although $\Delta\nu$ is a formal indication of the anomalously high electron-acceptor properties of the mesityl substituents in compounds III, VI and VIII the distortion of the molecular configuration is the real cause of the anomalous values of $\Delta\nu$.

The barriers to internal rotation around the M—$C_{arom.}$ bond in Mes_3SiH and Mes_3GeH are found to be 8.3 and 6.3 kcal mol^{-1}, respectively [13].

These data together with the values of the bond angles, given above, testify to the fact that steric hindrance is more dominant in organosilicon compounds than in organogermanium ones. This view is confirmed by IR data. The deviation from the correlation straight line (1) is found to be 42 cm^{-1} for Mes_3SiH, while for Mes_3GeH the deviation from the line (2) is 26 cm^{-1}. The large deviation from the correlation straight line for Mes_3SiH is indicative for the profound steric effects in organosilicon compounds. The values of $\Delta\nu$ in compounds IX and X, containing one phenyl and one mesityl substituent bound to the Ge atom, give conclusive evidence of the spectroscopic parameters being dependent on steric effects. In contrast to compounds I—III, IV—VI, VII—VIII, a decrease in ν_{exp}(Ge—H) is observed when passing from $PhGeH_3$ to $MesGeH_3$. Due to the fact that there is one aromatic substituent and three hydrogen atoms bonded to the Ge atom in compound X, the barrier of rotation around the M—$C_{arom.}$ bond is sharply decreased and practically no steric hindrance akin to that is observed in compounds with three and two mesityl groups. The decrease in $\Delta\nu$ for compound X, in comparison with $\Delta\nu$ for its phenyl analog IX, results from the smaller negative inductive effect of the mesityl group compared to that of the phenyl group. Thus, pronounced steric effects are absent in compounds with one mesityl substituent. This observation provides support for the conclusion [13,14], that the steric effects are determined by interaction of the *ortho*-methyl groups and the hydrogen atoms of neighbouring rings.

We now consider the data on the integrated intensity A(M—H).

As shown earlier [16—18], an increase in electron-acceptor properties of the substituents bound to the M atom, results in the decrease of the dipole moment of the M—H bond and, consequently, in the decrease of the integrated intensity A(M—H). The equations, relating to $A^{1/2}$ with the sum of the inductive Taft constants of three substituents R (for heptane solutions) have been derived for silane and germane derivatives, containing substituents exerting a solely inductive effect:

$$A^{1/2}_{ind} = 1.20 - 0.21\Sigma\sigma^* \qquad (R_3SiH)\ [19] \qquad (5)$$

$$A^{1/2}_{ind} = 1.30 - 0.20\Sigma\sigma^* \qquad (R_3GeH)\ [5] \qquad (6)$$

$$A^{1/2}_{ind} = 1.79 - 0.20\Sigma\sigma^* \qquad (R_2GeH_2)\ [20] \qquad (7)$$

As can be seen from Table 1, the intensity A(M—H) increases from phenyl to xylyl and mesityl derivatives. At first sight, the integrated intensity A(M—H) appears to be unaffected by steric effects, because $A^{1/2}$ increases as $\Sigma\sigma^*$ decreases. By equations 5—7, $A^{1/2}_{ind}$ for the compounds studied (I—VIII) has been calculated under the assumption of a purely inductive influence of three substituents (bound to the M atom) on the intensity A(M—H).

However, the substituents in compounds I—VIII exert an inductive influence as well as a mesomeric effect through the d_π—p_π interaction mechanism. For example [5,17,18,20] for compounds with X-substituents of similar type, the experimental values of intensity $A^{1/2}_{\text{exp}}$ differ from $A^{1/2}_{\text{ind}}$ due to the d_π—p_π interaction. The d_π—p_π interaction effect accompanied by transfer of electron density from the X-substituent to the M atom, leads to a decrease in the acceptor properties of X and, consequently, to an increase in the experimental intensity $A^{1/2}_{\text{exp}}$ in comparison with $A^{1/2}_{\text{ind}}$, which could have been expected under the assumption of the intensity depending exclusively on the inductive effect of the substituents. The difference $\Delta A^{1/2} = A^{1/2}_{\text{exp}} - A^{1/2}_{\text{ind}}$ is a quantitative measure of the d_π—p_π interaction effect. It can be seen from Table 1 (compounds I—VI), that $\Delta A^{1/2}$ values for mesityl derivatives of silicon and germanium are much smaller than those for the corresponding phenyl and xylyl derivatives. This is in agreement with anomalous values of intensity A(M—H), having been found earlier for the compounds bearing substituents with large steric effects. Thus, on studying silanes $(R_i)_3SiH$, the experimental values $A^{1/2}_{\text{exp}}$ are found to be smaller for the compounds with branched alkyl radicals R_i than the values $A^{1/2}_{\text{ind}}$, calculated by eq. 5 [16]. The decrease in intensity A(Si—H) for these derivatives of silane, as well as the increase in the frequency ν(Si—H), mentioned above for mesityl derivatives of silicon and germanium, is likely to be due to distortion of the tetrahedral structure of the bond angles of the central atom by branched alkyl radicals. Similarly, the distorted tetrahedral structure of the Si atom in Mes_3SiH brings about a sharp decrease in $A^{1/2}_{\text{exp}}$. The same phenomena cause the d_π—p_π interaction to weaken in the Si—Mes bond. Therefore, $A^{1/2}_{\text{ind}}$ and $A^{1/2}_{\text{exp}}$ for Mes_3SiH are very nearly the same.

In contrast to organosilicon compounds I and III, the decrease in $\Delta A^{1/2}$(Ge—H) is not so sharp when passing from phenyl to mesityl derivatives as it was in $\Delta A^{1/2}$(Si—H).

Steric hindrance is noted above to be of less significance in Mes_3GeH than in Mes_3SiH. Consequently, under the steric effects there is a less pronounced decrease in $A^{1/2}_{\text{exp}}$ Mes_3GeH than for organosilicon analog III. For compound VI, d_π—p_π interaction effecting $A^{1/2}_{\text{exp}}$ is not likely to be completely excluded. Both factors cause the increase in $A^{1/2}_{\text{exp}}$ for Mes_3GeH. Due to this, $\Delta A^{1/2}$ for Mes_3GeH (0.13) becomes much greater than for Mes_3SiH (0.03). In accordance with this, $\Delta A^{1/2}$ for compound VIII (which has two mesityl groups, bound to Ge atom) is close to $\Delta A^{1/2}$ for trimesitylgermane (VI).

The comparison of $\Delta\nu$ and $\Delta A^{1/2}$ for the compounds studied points to the fact that steric effects of substituents exert greater influence on frequency than on intensity. Based on experimental data only, it is impossible to ascertain the extent to which frequency and intensity change, when the mode of vibration is changed by steric effects. However, as stated above, steric effects in di- and trimesityl derivatives can bring about a decrease in overlapping of d_π and p_π orbitals during d_π—p_π interaction in M—Mes fragments. It follows [5,21,22], that ν(M—H) (which characterizes the force constant and energy of the M—H bond) depends on the overlap integrals in $M(Mes)_n$ groups to a much greater extent than A(M—H) (which characterizes the polarity of M—H bond). Thus, the decrease in $\Delta A^{1/2}$ for mesityl derivatives III, VI, VIII is suggested to be mainly determined by the change of the M—H vibration mode. The sharp decrease in $\Delta\nu$ for the same compounds is due to the vibration mode change and decrease of the group overlap integrals in $MMes_3$ and $GeMes_2$ fragments.

Research into the manner in which steric factors of mesityl substituents affect the ability of organometallic compounds to form complexes with electron-donor solvents are of great interest.

Previously [19,23], the measurement of A(M—H) was found to be a highly sensitive method for the investigation of complex formation, when the Group IV central element acts as an acceptor. This element forms weak additional σ-bonds [of $(p-d)\sigma$-type] using its vacant *nd* orbitals.

We have measured A(M—H) using inert (heptane) and electron-donor (CCl_4) solvents. It can be seen from Table 1 that $A_{\text{exp}}^{1/2}$ values for CCl_4 solutions are higher in the average by 0.09×10^2 $\text{mol}^{-1/2}$ $\text{l}^{1/2}$ cm^{-1} than those for heptane solutions. As regards the increase in the intensity in CCl_4 solutions, the compounds with mesityl substituents do not differ markedly from their phenyl and xylyl analogs. Detailed studies [19] show that the intensity increase (when passing from an inert solvent to CCl_4) is due to an increase in M—H bond polarity. The increase in polarity is a result of $Cl_3C\overline{\underline{Cl}}| \rightarrow M(H)(R_i)_3$ labile complex formation, which is accompanied by electron density transfer from CCl_4 to the M atom of the organometallic compound and then to the H atom of the M—H bond, the electronegativity of which is higher than that of the M atom. As this takes place, the polarity of the M—H bond as well as the integral intensity A(M—H) increase. Thus, the data obtained indicate that steric effects of mesityl substituents do not have a pronounced influence on the ability of organometallic compounds with these substituents to form complexes with CCl_4.

Experimental

The IR spectra were measured on a UR-20 "Zeiss" spectrometer. Heptane and carbon tetrachloride solutions (0.01—0.07 mol l^{-1}) were used to obtain spectra. The integrated intensity of ν(M—H) stretching modes A (mol^{-1} l $\text{cm}^{-2} \times 10^4$) was measured by Iogansen's method [24].

Gas—liquid chromatography was used to control the purity of the compounds.

The synthesis of the studied compounds followed the methods given in ref. 25 for silicon compound, ref. 26 for Xyl_3GeH and Mes_3GeH, ref. 27 for Ph_2GeH_2 and $PhGeH_3$. Mes_2GeH_2 and $MesGeH_3$ are obtained as coproducts in the syntensis of Mes_3GeH [27].

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