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THE INTENSITY OF Ge—H STRETCHING MODES IN THE IR SPECTRA OF ORGANOGermanium COMPOUNDS R'_2GeH_2

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Summary

The integrated intensity (A) of Ge—H stretching modes in the IR spectra of 20 compounds of the type R_2GeH_2 , $RXGeH_2$ and X_2GeH_2 containing substituents R which are incapable of $d_\pi-p_\pi$ -interaction with the germanium atom, and substituents X which do form $d_\pi-p_\pi$ -bonds with the germanium atom, has been studied. It has been shown that for R_2GeH_2 compounds the values of $A^{1/2}$ are related to the sum of the Taft constants σ^* of the three substituents R ($\Sigma\sigma^*$) by the equation $A^{1/2} = 1.79 - 0.2 \Sigma\sigma^*$.

For compounds $RXGeH_2$ and X_2GeH_2 the experimental values of intensity $A_{exp}^{1/2}$ differ from $A_{ind}^{1/2}$ as a result of the $d_\pi-p_\pi$ -character of Ge—X bonds. The differences $\Delta A^{1/2} = A_{exp}^{1/2} - A_{ind}^{1/2}$ describe the effect of $d_\pi-p_\pi$ -interaction which increases with increasing effective positive charge on the germanium atom.

Confirmation of the less pronounced ability of the germanium atom to undergo $d_\pi-p_\pi$ -interaction in comparison with the silicon atom has been obtained.

Introduction

Organogermanium compounds are of considerable interest in the development of the theory of chemical bonding in organometallic compounds of non-transition metals and in particular in compounds of the silicon subgroup. On passing from pure organic compounds, first to organosilicon and then to organogermanium compounds, the polarizability of chemical bonds increases. It may therefore be expected that organogermanium compounds will exhibit conjugation effects such as σ,σ or σ,π . In addition the germanium atom, like the silicon atom, under normal circumstances does not form $p_\pi-p_\pi$ -type multiple bonds but it can expand its electron shell at the expense of vacant 4d orbitals (a transition from sp^3 hybridization to sp^3d and sp^3d^2). This process is accompanied by formation

of additional σ - or π -type chemical bonds. A dative $d_{\pi}-p_{\pi}$ -bond is formed when the germanium atom is bonded to a radical X which has lone electron pairs.

Another type of bond is formed in the system $\text{>Ge} \begin{array}{l} \longleftarrow \\ \diagdown \text{CH}_2 \end{array} : \text{X}$ when substituents

X (Hal, OR, NR_2) having lone electron pairs are bonded to the carbon atom which is bonded directly to the germanium atom. In this case a $(p \rightarrow d)\sigma$ -bond is formed (α -effect). A $(p \rightarrow d)\sigma$ -bond may also occur in intermolecular interactions, for instance in the formation of labile complexes with electron-donating solvents [1] by organogermanium compounds. When π - or σ -type dative bonds are formed either by $(p \rightarrow d)\pi$ -interaction or by $(p \rightarrow d)\sigma$ -conjugation the germanium atom is the p - or π -electron acceptor. The difference between these two types of interaction is that in π -bonds formation, the predominant role is played by the d_{ϵ} -orbitals of the germanium atom but when σ -bonds are formed it is the d_{γ} -orbitals which are dominant.

Silane and germane derivatives were shown earlier [1-7] to be the most suitable compounds for spectroscopic studies of conjugation effects in organic compounds of silicon and germanium. The stretching vibration of the M-H (M = Si, Ge) bond in their IR spectra has a highly characteristic shape [7-11], therefore, spectroscopic parameters such as frequency $\nu(\text{M-H})$ and absorption band intensity $A(\text{M-H})$ change solely under the influence of the electronic effects of substituents. It must be noted that a study of absorption band intensity variations provides more information about the effects of intra- and intermolecular interaction than can be obtained from a study of the frequencies of the above vibrations [12]. Thus, when the values of $A(\text{M-H})$ were analyzed, information was obtained on the following intramolecular and intermolecular interactions in silicon and germanium derivatives: (a) the inductive effect of substituents R in compounds R_3SiH [13,14], R_2SiH_2 [15] and R_3GeH [16]; (b) σ, σ -, σ, p -, σ, π - and σ, d -type conjugation effects [17]; (c) the intramolecular coordination (α -effect) in silanes containing chloromethyl groups [18]; (d) the effect of $d_{\pi}-p_{\pi}$ -interactions in derivatives of silane and germane [13,16,17]; and (e) the formation of labile complexes of silane with an electron-donating solvent [18].

Thus, spectroscopic studies provide useful information on intramolecular interactions in organic compounds of elements of the silicon subgroup, which is important in understanding their reactivity.

At the same time, the intensity of Ge-H stretching modes in the IR spectra of organogermanium compounds has not yet been studied sufficiently. This is especially true for those compounds R_3GeH and R_2GeH_2 in which the substituents R do not form $(p \rightarrow d)\pi$ or $(p \rightarrow d)\sigma$ -type bonds with the germanium atom and therefore affect only inductively the frequency and the intensity of $\nu(\text{Ge-H})$ bands. Thus, the correlation equation which connects the intensity of the $\nu(\text{Ge-H})$ bands with the sum of the inductive constants $\Sigma\sigma^*$ for the substituents on germanium atom in the IR spectra of R_3GeH compounds apparently contains α -effect contributions that are unaccounted for [16].

Bearing in mind both the above and the lack of literature references concerning the spectroscopic analysis of diorganogermanium compounds, we make the purpose of the present paper that of studying the intensity of Ge-H stretching modes in the infrared spectra of R_2GeH_2 in order to obtain more information on intramolecular interactions in organogermanium compounds.

Results and discussion

According to data obtained earlier by us [16], and taken from the literature [19], the values of $A(\text{Ge-H})$ depend on the nature of other substituents bonded to the germanium atom: electron-donating substituents increase while electron-attractors decrease the value of $A(\text{Ge-H})$.

For the stretching vibration $\nu(\text{Ge-H})$, which is highly characteristic in shape, the relation $A \sim \mu^2$ [12,16] is valid, where μ is the dipole moment of Ge-H bond. Therefore the variation of intensity of $A(\text{Ge-H})$ with varying the radical R bonded to the germanium atom is caused by variation of the dipole moment of the Ge-H bond under the influence of substituents R.

It has already been noted above that the intensity of the $\nu(\text{M-H})$ absorption bands depends on a number of factors. However, correlation analysis provides a definite division between the influences of the inductive and mesomeric effects on $A(\text{Ge-H})$. In order to carry out the analysis it is necessary to have a series of compounds R_2GeH_2 in which the substituents R possess only an inductive effect and have no conjugative ability. To satisfy this requirement we have specially synthesized compounds I-VIII (Table 1).

As is seen from the data presented in Table 1, the intensity of the $\nu(\text{Ge-H})$ band does not maintain a constant value since the dipole moment of the Ge-H bond varies with varying the substituents. Highest values for intensities are observed in the case of diorganogermanes R_2GeH_2 where R are substituents exhibiting a +I-effect (e.g. C_2H_5 , $n\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$) or a small -I-effect (e.g. $\text{ClCH}_2\text{CH}_2\text{CH}_2$, $\text{C}_6\text{H}_5\text{CH}_2$). The maximum polarity of the type $\text{Ge}^{\delta+}-\text{H}^{\delta-}$ for a Ge-H bond is realized in alkyl derivatives. This is due to the electron-donating nature of alkyl groups and the greater electronegativity of the hydrogen atom than the germani-

TABLE 1
VALUES OF $\nu(\text{Ge-H})$, $A_{\text{exp}}^{1/2}$, $A_{\text{ind}}^{1/2}$, AND $\Delta A^{1/2}$ IN THE IR SPECTRA OF THE COMPOUNDS STUDIED

No.	Compound	$\nu(\text{Ge-H})$	$A_{\text{exp}}^{1/2}$	$\Sigma\sigma^*$	$A_{\text{ind}}^{1/2}$	$\Delta A^{1/2}$	$\Sigma\sigma_p$
I	$(n\text{-C}_4\text{H}_9)_2\text{GeH}_2$	2042	1.76	0.23			
II	$(n\text{-C}_3\text{H}_7)_2\text{GeH}_2$	2042	1.74	0.26			
III	$(\text{C}_2\text{H}_5)_2\text{GeH}_2$	2042	1.73	0.29			
IV	$\text{C}_2\text{H}_5(\text{ClCH}_2\text{CH}_2\text{CH}_2)\text{GeH}_2$	2049	1.69	0.53			
V	$\text{C}_2\text{H}_5(\text{HOCH}_2\text{CH}_2)\text{GeH}_2$	2054	1.65	0.59			
VI	$\text{C}_2\text{H}_5(\text{C}_6\text{H}_5\text{CH}_2)\text{GeH}_2$	2049	1.67	0.66			
VII	$(\text{ClCH}_2\text{CH}_2\text{CH}_2)_2\text{GeH}_2$	2055	1.65	0.77			
VIII	$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{GeH}_2$	2057	1.61	0.92			
IX	$\text{C}_6\text{H}_5(\text{C}_2\text{H}_5)\text{GeH}_2$	2056	1.59	0.99	1.59	0.00	-0.16
X	$\text{C}_6\text{H}_5(\text{CH}_3)\text{GeH}_2$	2061	1.58	1.09	1.57	0.01	-0.14
XI	$\text{C}_6\text{H}_5(\text{HOCH}_2\text{CH}_2\text{CH}_2)\text{GeH}_2$	2062	1.69	1.16	1.56	0.13	-0.09
XII	$\text{C}_6\text{H}_5[\text{i-C}_3\text{H}_7(\text{HO})\text{CH}]\text{GeH}_2$	2066	1.59	1.52	1.48	0.11	-0.02
XIII	$\text{C}_6\text{H}_5[\text{CH}_3(\text{HO})\text{CHCH}_2]\text{GeH}_2$	2066	1.73	1.25	1.54	0.19	0.00
XIV	$(\text{C}_6\text{H}_5)_2\text{GeH}_2$	2062	1.60	1.69	1.45	0.15	0.02
XV	$\text{Cl}(n\text{-C}_4\text{H}_9)\text{GeH}_2$	2094	1.38	3.26	1.14	0.24	0.07
XVI	$\text{Br}(n\text{-C}_4\text{H}_9)\text{GeH}_2$	2092	1.35	3.16	1.16	0.19	0.08
XVII	$\text{Cl}(\text{C}_2\text{H}_5)\text{GeH}_2$	2093	1.38	3.29	1.13	0.25	0.08
XVIII	$\text{Cl}(\text{ClCH}_2\text{CH}_2\text{CH}_2)\text{GeH}_2$	2099	1.35	3.53	1.08	0.27	0.10
XIX	$\text{Cl}(\text{C}_6\text{H}_5)\text{GeH}_2$	2102	1.33	3.99	0.99	0.34	0.24
XX	$(\text{C}_6\text{F}_5)_2\text{GeH}_2$	2140	1.02	8.49	0.09	0.93	0.82

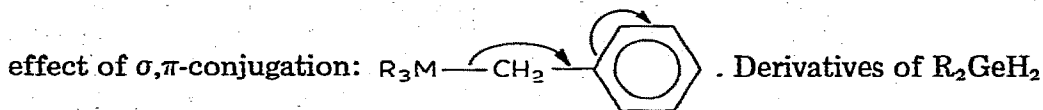
um atom. Because of the considerable value of the dipole moment of the Ge—H bond, the intensity of $\nu(\text{Ge—H})$ bands in the infrared spectra of these compounds is high. However an increase of the electron-attracting properties of substituents R (compounds IX—XX) is accompanied by a decrease in electron density on the hydrogen atom in the Ge—H bond. Thus the magnitude of the dipole moment of the Ge—H bond and the intensity of the $\nu(\text{Ge—H})$ band are decreased.

The donor—acceptor properties of the substituents can be described quantitatively with Taft—Hammett σ -constants. By virtue of this we obtained a linear equation for R_2GeH_2 compounds in which the substituents R possess only an inductive effect (compounds I—VII) (eq. 1).

$$A_{\text{ind}}^{1/2} = (1.79 \pm 0.01) - (0.20 \pm 0.02) \Sigma \sigma^* \quad (r = 0.975; s = \pm 0.01) \quad (1)$$

Equation 1 relates the magnitude of the square root of the intensity to $\Sigma \sigma^*$ ($= \sigma_{\text{R}}^* + \sigma_{\text{R}}^* + \sigma_{\text{H}}^*$) (the sum of the inductive constants of substituents). One of the hydrogen atoms was considered as a substituent.

We demonstrated earlier [20,21] in our study of organosilicon and organo-germanium derivatives of benzene and thiophene that the group R_3MCH_2 (M = Si, Ge) attached to a benzene or thiophene ring possesses enhanced electron-releasing properties during formation of a hydrogen bond of $\pi \cdots \text{H—O—R}$ type involving the π -electrons of the aromatic ring. This is a consequence of the



which have $\text{C}_6\text{H}_5\text{CH}_2$ groups bonded to the germanium atom (compounds VI, VIII) reveal no anomalies in the intensity of $\nu(\text{Ge—H})$ bands in comparison with compounds which contain no such substituents (Fig. 1). Therefore, in inert solvents the effect of σ, π -conjugation has no influence on the intensity of $\nu(\text{Ge—H})$ absorption bands in compounds whose other substituents show only an inductive effect. Besides this, the magnitude of the effect of σ, π -conjugation in the ground electron state is small and therefore has practically no influence on $A(\text{Ge—H})$. This effect however, does change the energy of the highest occupied molecular orbital of the aromatic ring. Therefore, σ, π -conjugation is revealed in experiments on hydrogen bonding when the orbital participates directly in H-bonding [20,21].

There are interesting peculiar features of the intensity of $A(\text{Ge—H})$ in alcohol substituted germanium compounds (compounds V, XI—XIII). The value of $A^{1/2}$ in $\text{C}_2\text{H}_5\text{Ge(H)}_2\text{CH}_2\text{CH}_2\text{OH}$ is also governed by equation 1 for low concentrations of solutions of this compound in heptane (0.01 mol/l). The substituent $\text{CH}_2\text{CH}_2\text{OH}$ in the molecule exerts only an inductive influence on the polarity of the Ge—H bond. However, the presence in the group of both an electron-donating oxygen atom and a mobile hydrogen atom can result in formation by this compound of various intermolecular complexes. The most important of these are the cyclic and linear associates which are produced at the expense of the hydrogen bond by $\text{CH}_2\text{CH}_2\text{OH}$ groups and the labile complexes H_2RGeCH_2 —

$\text{CH}_2\text{O} \cdots \text{H} \rightarrow \text{GeH}_2\text{R}_2$ where the germanium atom behaves as a p -electron-acceptor. In this case the germanium atom forms one or two additional ($p \rightarrow d$) σ -bonds.

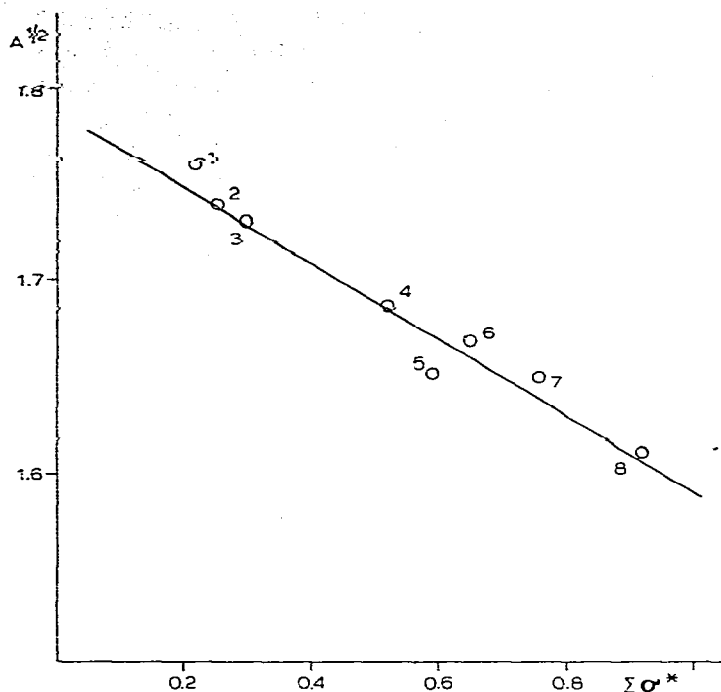


Fig. 1. The relationship between $A^{1/2}$ and $\Sigma\sigma^*$ of the substituents in diorganogermanes.

This should result in an increase of the intensity of the $\nu(\text{Ge-H})$ absorption band and, indeed, when the concentration of solution of $\text{C}_2\text{H}_5\text{Ge}(\text{H})_2\text{CH}_2\text{CH}_2\text{OH}$ in heptane is increased from ca. 0.01 to ca. 0.05 mol/l the value of $A^{1/2}$ increases from 1.65 to $1.74 \times 10^2 \text{ mol}^{-1/2} \text{ l}^{-1} \text{ cm}^{-1}$.

Thus, we may draw the conclusion that the compound $\text{C}_2\text{H}_5\text{Ge}(\text{H})_2\text{CH}_2\text{CH}_2\text{OH}$ both as a neat substance and in solutions at high concentrations forms self-associates both at the expense of the hydrogen bond and according to a $(p \rightarrow d)\sigma$ -type mechanism. These rules were seen to be obeyed in a study of triorganosilanes in an electron-donating solvent [18]. The formation of a labile silane-solvent complex is accompanied by transfer of the electron density from the solvent to silane and, therefore, by an increase of electron density on the hydrogen atom of the Si-H bond. The magnitude of the dipole moment of the Si-H bond and the intensity of $\nu(\text{Si-H})$ absorption band increase.

Values $A^{1/2}$ as a function of $\Sigma\sigma^*$ (which show a dependence similar to that expressed in eq. 1) for compounds R_3MH whose substituents R only show an inductive effect have been obtained previously.

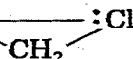
$$A_{\text{ind}}^{1/2} = 1.2 - 0.21 \Sigma\sigma^* (\text{R}_3\text{SiH, heptane}) [18] \quad (2)$$

$$A_{\text{ind}}^{1/2} = 1.32 - 0.12 \Sigma\sigma^* (\text{R}_3\text{GeH, heptane}) [16] \quad (3)$$

The identical angles of slope of the straight line correlations 1 and 2 indicate that the inductive influence of substituents R on the polarity of the M-H bond is practically the same for compounds R_3SiH and $\text{Ge}(\text{H})_2\text{R}_2$. Consequently,

silicon and germanium atoms must transfer the inductive influence of their substituents to an equal extent if these atoms are not participating in conjugation.

Unlike correlations 1 and 2, the angles of slope of the straight line correlations 1 and 3 differ significantly. We believe that this is caused by the following factors. In order to derive eq. 3 we used $A^{1/2}$ values for only four compounds [16] two of which contained chloro- and dichloro-methyl groups. According to recent studies of the frequency and the intensity of $\nu(\text{Si-H})$ bands [18,22], the chlorine atom of the group CH_2Cl participates in the intramolecular coordination:



(α -effect [23]). It has been established experimentally that this intramolecular coordination is accompanied by transfer of the electron density from the chlorine atom to the silicon atom [23]. The intensity of $\nu(\text{Si-H})$ bands of coordinated molecules is significantly greater than that of $\nu(\text{Si-H})$ bands in the same compounds which are not undergoing intramolecular coordination. This is connected with the fact that the CH_2Cl fragment exhibits, together with acceptor properties associated with the inductive mechanism, electron-releasing properties associated with the α -effect mechanism. The latter leads to an increase of the negative charge on the hydrogen atom in the Si-H bond and an increase of the intensity of the $\nu(\text{Si-H})$ absorption band.

The above explains the smaller angle of the slope of correlation 3 than correlations 1 and 2. This difference is due to the fact that relation 3, unlike the relations 1 and 2, describes an intensity influenced not just by the inductive effect but by a combination of two factors (both the inductive effect and the α -effect). Therefore, equation 3 must be made more accurate. This is done by increasing the amount of data on $A(\text{Ge-H})$ in R_3GeH compounds in which the R substituents show only an inductive effect. We plan to consider this question in a special publication.

Let us now consider the intensity of $\nu(\text{Ge-H})$ bands in compounds IX-XX in which the substituents are capable both of exhibiting an inductive effect and of forming $d_\pi-p_\pi$ bonds with the germanium atom. In compounds IX-XX such substituents include $\text{R}' = \text{Cl}, \text{Br}, \text{C}_6\text{H}_5$ and C_6F_5 . Equation 1 makes it possible to estimate the inductive influence of these substituents on the polarity of the Ge-H bond. The values $A_{\text{ind}}^{1/2}$ calculated from eq. 1 describe the influence of only the inductive effect of the substituents R' on the intensity of the absorption bands $\nu(\text{Ge-H})$. As follows from Table 1 the values $A_{\text{ind}}^{1/2}$ are smaller in all cases than the values $A_{\text{exp}}^{1/2}$. Therefore, the differences $\Delta A^{1/2} = A_{\text{exp}}^{1/2} - A_{\text{ind}}^{1/2}$ are a measure of the effect of conjugation (in our case $d_\pi-p_\pi$ -interactions in the $\text{Ge-R}'$ bond) on the intensity of $\nu(\text{Ge-H})$ absorption bands. The quantities $\Delta A^{1/2}$ characterize the increase of polarity of the Ge-H bond under the influence of conjugation of substituents R' with the germanium atom and depend essentially on the nature of the given substituents.

The values of $\Delta A^{1/2}$ for germanium-containing alcohols (compounds XI-XIII) have been calculated for low concentration solutions (ca. 0.01 mol/l) of these compounds in heptane. When the concentration is increased from ca. 0.01 to ca. 0.05 mol/l the values of $A^{1/2}$ and $\Delta A^{1/2}$ respectively for these compounds increase by ca. $0.1 \times 10^3 \text{ mol}^{-1/2} \text{ l}^{1/2} \text{ cm}^{-1}$. The reasons for this are those described above for $\text{C}_2\text{H}_5\text{Ge}(\text{H})_2\text{CH}_2\text{CH}_2\text{OH}$.

For calculating $A_{\text{ind}}^{1/2}$ for compounds containing substituents R' capable of

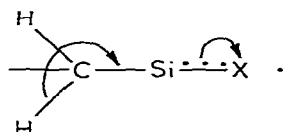
$d_{\pi}-p_{\pi}$ -interaction, it was assumed that eq. 1 is also valid. This approach has proved fruitful in a study of the intensity of $\nu(\text{Si-H})$ bands in the IR spectra of triorganosilanes [17]. The existence of linear correlations (4), (5) and (6) indi-

$$\Delta A^{1/2} = 1.47 \Sigma \sigma_p + 0.12 \quad (\text{X}_3\text{SiH}) \quad (4)$$

$$\Delta A^{1/2} = 1.47 \Sigma \sigma_p + 0.34 \quad (\text{X}_2\text{AlkSiH}) \quad (5)$$

$$\Delta A^{1/2} = 1.47 \Sigma \sigma_p + 0.50 \quad (\text{XAlk}_2\text{SiH}) \quad (6)$$

cates that the alkyl groups in silane derivatives reveal increased electron-donating ability only when the silicon atom participates in $d_{\pi}-p_{\pi}$ interaction; in other words, when the double bond character of Si-X bond is activated. We explain

this by the effect of σ, d -conjugation 

Let us consider the values $\Delta A^{1/2}$ for compounds $\text{R}'_2\text{GeH}_2$. As can be seen from Table 1 the values $\Delta A^{1/2}$ vary over a wide range from 0.01 to 1 depending on the nature of R' . From the correlation of values $\Delta A^{1/2}$ with the sum of Hammett σ_p -constants of substituents R bonded to the germanium atom ($\Sigma \sigma_p$) (which has been established earlier [16,17]) we may derive the linear dependence (eq. 7) (Fig. 2).

$$\Delta A^{1/2} = (0.93 \pm 0.04) \Sigma \sigma_p + (0.16 \pm 0.01) \quad (r = 0.992; s = \pm 0.04) \quad (7)$$

The values $\Sigma \sigma_p$ characterize quantitatively the relation between the donor and the acceptor properties of the substituents bound to the germanium atom. The

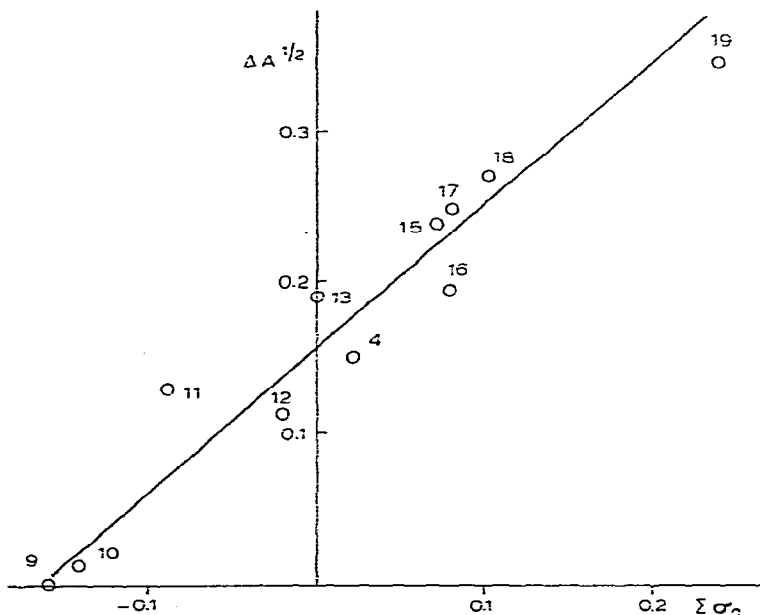
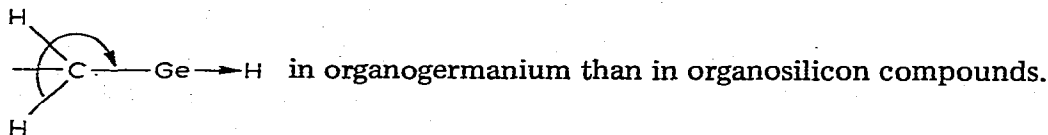


Fig. 2. The relationship between $A^{1/2}$ and $\Sigma \sigma_p$ of the substituents in diorganogermanes.

values are proportional to the effective charge induced by substituents on the germanium atom [16,17]. As follows from eq. 7, the increase of the effective charge on the germanium atom (characterized by the quantities $\Sigma\sigma_p$) is accompanied by increasing $d_\pi-p_\pi$ -interaction in the molecule (characterized by the quantities $\Delta A^{1/2}$).

A comparison of the straight line correlations 4 and 7 on the one hand is a testimony of the greater increase of $d_\pi-p_\pi$ -interaction in organosilicon compounds in comparison with organogermanium compounds (for the same increase in value of the effective charge on the central atom) and on the other hand confirms the greater ability of the silicon atom than the germanium atom to undergo $d_\pi-p_\pi$ -interaction.

Note that values for compounds containing an alkyl group bound to a germanium atom are also described by relation 7. It follows from a comparison of $A^{1/2}$ values for silanes and germanes containing identical substituents e.g. for $C_2H_5-(C_6H_5CH_2)_2MH$ and $ClCH_2CH_2CH_2(C_2H_5)MH_2$ the values of $A^{1/2}$ of absorption bands $\nu(Si-H)$ and $\nu(Ge-H)$ are 1.13; 1.23 and 1.56; 1.69 respectively, that the intensity of $\nu(M-H)$ bands is higher in organogermanium compounds. On the basis of electronegativity values for atoms Si (1.9), Ge (2.0) and H (2.1) [24], however, a greater value for the polarity of the Si-H bond than the Ge-H bond might be expected. The reasons for the discrepancy between experimental and inferred polarity values for Si-H and Ge-H bonds are not quite clear at present and require special consideration. One of the causes of this discrepancy may be the more important role of the effect of σ,σ -conjugation



The increased importance of σ,σ -conjugation is caused by the greater polarizability of organogermanium than organosilicon compounds. Therefore, the greater values of $A^{1/2}$ for organogermanes than organosilanes are apparently connected with the greater contribution of σ,σ -conjugation in germanium compounds. If this assumption is true, it may be concluded that relation 1 describes the influence of two effects on $A^{1/2}$, the inductive effect and σ,σ -conjugation. Therefore $A_{ind}^{1/2}$ values already contain a contribution from σ,σ -conjugation, whereas the differences $\Delta A^{1/2} = A_{exp}^{1/2} - A_{ind}^{1/2}$ characterize the effect of $d_\pi-p_\pi$ -interaction only. Because of this the values corresponding to compounds with an alkyl group are also described by eq. 7.

In conclusion it must again be emphasised that the assumption that the effect of σ,σ -conjugation is responsible for the greater polarity of Ge-H bonds than Si-H bonds has yet to be verified.

Experimental

The IR spectra of solutions in heptane (concentrations 0.01–0.06 mol/l) were measured on UR-20 Zeiss spectrometer. Calibration of the spectrometer was controlled by using the Ge-H bond-containing compounds studied earlier. The

integrated intensity of $\nu(\text{Ge-H})$ bands A ($\text{mol}^{-1} \text{ litre cm}^{-2} \times 10^4$) was measured by Iogansen's method [25].

The purity of the compounds studied was checked by gas-liquid chromatography.

The compounds studied were prepared using methods previously described [26-32].

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