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INTEGRATED INTENSITY OF Ge—H STRETCHING MODES AND d_π—p_π INTERACTION IN TRISUBSTITUTED GERMANES $(R_i)_3GeH$

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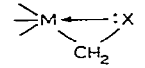
Summary

The integrated intensity (A) of Ge—H stretching modes in IR spectra of 30 trisubstituted germanes $(R_i)_3GeH$, has been studied. For R_3GeH compounds in which the R substituents do not form d_π—p_π bonds with the germanium atom, the correlation between $A^{1/2}$ and the sum of inductive Taft $\Sigma\sigma^*$ constants of the R_i substituents has been established. The contributions made by conjugation effects of a germanium atom with the R_i substituents to the integrated intensity of ν(Ge—H) bands are estimated. The formation of weak labile complexes of $(p \rightarrow d)\sigma$ triorganogermanes with carbon tetrachloride has been studied. The values of ν(Ge—H) intensity are compared with the data on disubstituted germanes $(R_i)_2GeH_2$ and silane derivatives $(R_i)_3SiH$.

Introduction

The analysis of a great deal of literature on reactivity (for example [1—3]) and physical and chemical properties [1—4] of organometallic compounds of silicon subgroup elements (M) shows that the substituents bound to these elements are capable (together with inductive effect) of resonance interaction with the M atoms. This capability is only characteristic of these substituents which contain atoms with lone pairs of electrons and α,β-unsaturated hydrocarbon radicals bound to the M atom. The possibility of resonance effects is in general accounted for by the existence of vacant *nd*-orbitals in M atoms [4—11]. The alternative treatment of the properties of organometallic compounds of non-transition elements has recently arisen [12]. However, the hypothesis connecting the resonance effects with *nd*-orbitals in M atoms seems at the present time to be more valid.

The vacant *nd*-orbitals participate both in intra- and inter-molecular processes.

In the ground electronic state three of them are thought to be most significant: (a) intramolecular $(p \rightarrow d)\pi$ or $d_\pi - p_\pi$ interaction in fragments M—X where X is the atom having the lone pairs of electrons or an α,β-unsaturated hydrocarbon radical [4—11], (b) intramolecular $(p \rightarrow d)\sigma$ interaction or the α-effect between M and X atoms in compounds having the fragment  $\underset{CH_2}{>M \leftarrow :X}$ [4,13—19], (c) intermolecular $(p \rightarrow d)\sigma$ interaction between M and X atoms of two different molecules or between the M atom and the electron-donor centre of the solvent [19—23].

At the present time using spectroscopic methods for organometallic compounds of the silicon subgroup elements the process a has received the most study and the process c is still not clearly understood. It is essential that firstly the relative ability of the M atom to participate in the processes a—c depends greatly on its nature. Secondly, various spectroscopic methods have different sensitivities to study the processes a—c. Thirdly, in a number of spectroscopic investigations the contributions to spectroscopic parameters under the influence of factors a—c (especially b and c) were groundlessly ignored or not taken into account at all.

It is clear from the above that a correct study of the processes a—c requires, on one hand, a careful choice of the compounds to be investigated which would permit a separate study of the contributions made by a—c processes and, on the other hand, a sensitive method for their investigation.

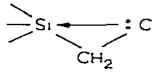
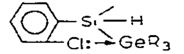
This brief analysis of the problem shows that some work where due attention was not paid to the role of some contributions of a—c need to be critically reviewed.

As is seen from the literature [11,19, 24—28], the integrated intensity of stretching modes in IR spectra is a highly sensitive method to investigate intramolecular interactions. Therefore, the purpose of this paper is a study of the integrated intensity of Ge—H stretching modes in IR spectra of trisubstituted germanes, $(R_i)_3GeH$. Special consideration is given to the purely inductive influence on the intensity, as well as the above-considered processes a—c. We have compared the intensity values of Ge—H stretching modes A(Ge—H) with those of the disubstituted germanes, $(R_i)_2GeH_2$ [27] and silane derivatives $(R_i)_3SiH$ [11,19]. The purpose of this comparison was to obtain the initial relationship for systematic studies of the relative role of factors a—c in organo-silicon and -germanium compounds in subsequent works.

Results and discussion

The integrated intensity of Ge—H stretching modes in IR spectra of organogermanium compounds have been studied insufficiently [27,28]. First of all, this refers to the compounds R_3GeH in which the R substituents are incapable of $(p \rightarrow d)\pi$ or $(p \rightarrow d)\sigma$ bonding to germanium atoms and therefore exert only inductive influence upon frequency and intensity of the ν(Ge—H) band. Although the theoretical calculations for ν(Ge—H) are not available, ν(Ge—H) vibrations are considered [29—32] to be as characteristic as ν(Si—H). According to the experimental data on ν(Ge—H) vibration may be considered to take place almost by changing the Ge—H coordinate. The mass of the R_i substituent exerts no influence on Ge—H vibration. Mechanical interaction between Ge—H modes and the R_i substituents are absent. Therefore, the electronic effects of R_i substituents are responsible for the change in ν(Ge—H) and A(Ge—H). It is simply the main correlation between $\nu = f(\Sigma\sigma)$ and $A^{1/2} = f(\Sigma\sigma)$ (the Hammett—Taft σ-constant of the R_i substituents). In an earlier communication it was noted that the correlation equation connecting ν(Ge—H) bands with the sum of the inductive Taft $\Sigma\sigma^*$ constant of three substituents for R_3GeH does not contain the contributions of the α-effect [28]. Moreover, to write the eq. 1 for compounds

$$A_{ind}^{1/2} = 1.32 - .0.12\ \Sigma\sigma^* \qquad (1)$$

R_3GeH [28], the values of $A^{1/2}$ of only four compounds were used, two of them containing chloro- and dichloro-methyl groups. The investigations carried out on studying the frequency and intensity of ν(Si—H) [18—19] showed that a chlorine atom in a chloromethyl group participates in intramolecular coordination (α-effect)  . The ν(Si—H) intensity of the coordinated molecules is greater than that in the same compounds which do not participate in intramolecular coordination. For  it was shown [18] that the germanium atom, as well as silicon can form intramolecular complexes. In this connection the eq. 1 describes the influence of two factors: inductive effect and α-effect. Due to the α-effect, the integrated intensity values of ν(Ge—H) for compounds containing chloro- and dichloro-methyl groups appear to be overestimated. This was confirmed by a small slope of the correlated straight line (Fig. 1).

To refine eq. 1, we have obtained more experimental data on A(Ge—H) in compounds R_3GeH in which the R substituents exert exclusively an inductive influence. For this purpose the compounds 1—8 (Table 1) fulfilling this condition were specially synthesized. The $A^{1/2}$ values obtained for the solutions of the above compounds in heptane are connected with the sum of inductive constants of the R substituents by the linear relation (eq. 2).

$$A_{ind}^{1/2} = 1.30 - 0.20\ \Sigma\sigma^*\ (r = 0.991;\ s = 0.01) \qquad (2)$$

Let us compare eq. 2 with the similar ones for the compounds R_3SiH [19] (ν(Si—H) vibrations are proved theoretically [33,34] and experimentally [5,7—9,29,30] to be highly characteristic) and R_2GeH_2 obtained for heptane solutions (eq. 3, 4).

$$A_{ind}^{1/2} = 1.20 - 0.21\ \Sigma\sigma^*\ (R_3SiH) \qquad (3)$$

$$A_{ind}^{1/2} = 1.79 - 0.20\ \Sigma\sigma^*\ (R_2GeH_2) \qquad (4)$$

By comparing eq. 2 and 3 it follows that the correlated straight lines have practically identical slopes. This indicates that the atoms of silicon and germanium transmit the inductive influence of the substituents (or possess the same conduction of the inductive effect) in the case when these atoms do not participate in conjugation. The intensity values of ν(M—H) stretching modes agree well with the results obtained earlier in a study of organo-silicon and -germanium com-

TABLE 1

INTEGRATED INTENSITY OF Ge—H STRETCHING MODES IN THE IR SPECTRA OF TRISUBSTITUTED GERMANES

No.	Compound	ν(Ge—H) (cm^{-1})	$A_{exp}^{1/2}$ (heptane)	$A_{exp}^{1/2}$ (CCl_4)	$\Sigma\sigma^*$
1	$(n\text{-}C_4H_9)_3GeH$	2013	1.37	1.46	—0.39
2	$(C_2H_5)_3GeH$	2015	1.35	1.44	—0.3
3	$(C_2H_5)_2(ClCH_2CH_2CH_2)GeH$	2019	1.30	1.40	—0.06
4	$(C_2H_5)_2(C_6H_5CH_2)GeH$	2020	1.30	1.39	0.015
5	$(C_2H_5)CH_3(ClCH_2CH_2CH_2)GeH$	2021	1.30	1.38	0.04
6	$(C_2H_5)(ClCH_2CH_2CH_2)_2GeH$	2023	1.26	1.37	0.18
7	$(C_2H_5)(C_6H_5CH_2)_2GeH$	2029	1.24	1.32	0.33
8	$(C_6H_5CH_2)_3GeH$	2038	1.15	1.21	0.645

pounds by other methods. So, the data on ν(M—H) [7,31,32] and ν(M—C) [35] frequencies in IR spectra and on chemical shifts in PMR spectra [36] enable us to conclude that when the substituents capable of d_π—p_π interaction are absent in the molecule, the silicon and germanium atoms have practically the same capability to transfer the inductive influence of the substituents.

Comparison of the eq. 2 and 3 also shows that the intensities of ν(M—H) stretching modes in compounds R_3GeH are greater than those in R_3SiH. According to the values of electronegativities of silicon, germanium and hydrogen atoms [37] one may presume a greater polarity of the Si—H bond, unlike Ge—H, and, consequently, a greater intensity of ν(Si—H) stretching modes. As has already been stated [27], one of the possible reasons for the disagreement mentioned may be a more prominent role of σ,σ-conjugation in organogermanium compounds when compared with those in organosilicon ones. The more prominent role of σ,σ-conjugation may be due to the large polarizability of bonds in germanium compounds than those in silicon.

It follows from the comparison of the eq. 2 and 4 that the correlated straight lines have practically identical slopes. This is not unexpected. Parallel alignment of correlated straight lines were observed in studying ν(M—H) frequencies in mono-, di- and tri-organosilanes [7], and in di- and tri-organogermanes [32]. When investigating the acid hydrolysis of silicon hydrides with differing extents of substitution, a plot was made in log K, $\Sigma\sigma^*$ (K is the rate constant of the hydrolysis) coordinates which illustrates three parallel straight lines [38]. The dependence of spin—spin coupling constants, $J(^{119}Sn—^{1}H)$ on $\Sigma\sigma^*$ substituents for stannanes is represented by three approximately parallel straight lines for mono-, di- and tri-alkylstannanes [39]. The parallel alignment of correlated straight lines 2 and 4 indicate, in our opinion, that the germanium atom does not change its conduction of the inductive effect when passing from triorganogermanes to diorganogermanes. The greater values of $A^{1/2}$ for R_2GeH_2 are due to the fact that ν(Ge—H) consist of two absorption bands with practically equal frequencies of ν_s(Ge—H) and ν_{as}(Ge—H). Really, the literature data show that in most cases symmetric and asymmetric M—H stretching modes of MH_2 and MH_3 groups in hydrides of silicon, germanium and tin are observed as a single band [7,29,32].

The tetrahalide derivatives of silicon subgroup elements are known to form complexes with electron-donating solvents. In this case the Group IVB element forms additional bonds of σ-type and changes hybridization from sp^3 to sp^3d or sp^3d^2 [1]. The labile complexes even form organosilanes [20]. It was shown [19] that IR spectroscopy makes it possible to study the formation of weak labile complexes of triorganosilanes with carbon tetrachloride. Therefore it is of interest to compare the integrated intensity values of ν(Ge—H) stretching modes measured in heptane (inert solvent) and in CCl_4 which can show weak electron-donating properties towards organogermanes.

The root square intensity values of Ge—H stretching modes in IR spectra of triorganogermanes, measured in heptane and CCl_4 solutions, are presented in Table 1. Taking into account the conclusions drawn in the literature [21—23], the compounds 1—8 may be regarded as models for the following reasons: (1) the influence of universal interaction upon A(Ge—H) remains practically constants; (2) the $\equiv$Ge—H···L hydrogen bond is absent since the $+I$-effect (or small $-I$-effect) of substituents bound to a germanium atom, and the great electronegativity of the hydrogen atom when compared with the germanium atom, results in the polarity of $Alk_3Ge^{\delta+}—H^{\delta-}$—H of Ge—H bond, i.e., there is a partial negative charge on the hydrogen atom; (3) the main contribution to ν(Ge—H) bands intensities is made by the action of the solvent.

It is seen from Table 1 that the intensities of IR bands of ν(Ge—H) in CCl_4 and heptane solutions vary symbathically. The relationship between the values of $A^{1/2}$ measured in CCl_4 solutions and $\Sigma\sigma^*$ is given by the straight line eq. 5.

$$A^{1/2}_{\text{ind}} = 1.39 - 0.19\ \Sigma\sigma^*\ (r = 0.99;\ s = \pm 0.01) \qquad (5)$$

Identical slopes of the correlation straight lines 2 and 5 indicate that the inductive influence of the R substituents in compounds R_3GeH upon the Ge—H bond polarity is constant and does not change when passing from heptane to CCl_4 solutions. The increase in the intensities of ν(Ge—H) stretching modes in CCl_4 solutions is due to the large dipole moment of the Ge—H bond, i.e. its great polarity. The increase in the dipole moment of Ge—H bond and the intensity of ν(Ge—H) band, in our opinion, is caused by formation of the solvate complex $Cl_3C—\underline{Cl}| \rightarrow Ge(H)R_3$. The complex formation is accompanied by the electron density transfer on the hydrogen atom of the Ge—H bond.

It should be noted that the point No. VIII in Fig. 1 corresponding to tribenzylgermane, is derived from equation 2 but deviated inconsiderably from the correlation straight line 5 towards smaller values of $A^{1/2}$. This may be caused by the influence of some factors the main of which are, in our opinion, the following. Firstly, the steric factors. Data [40] are available that indicate that the formation of intermolecular complexes by compounds which contain bulky substituents (tribenzylgermane included) is hindered because of overlapping Van der Waals radii of substituting groups. Secondly, the increase in acceptor properties of benzyl radicals. It is established [41] that formation of the complex $MX_4 \cdot L$ is accompanied by an increase in the electron density on the X atom (i.e., increasing their acceptor character), whilst the electron density on the central atom M does not vary considerably. Therefore, even a partial electron density distribution arising from solvation for $Ge—CH_2—C_6H_5$ must lead to an increase in the acceptor properties of benzyl radicals and, consequently, to a

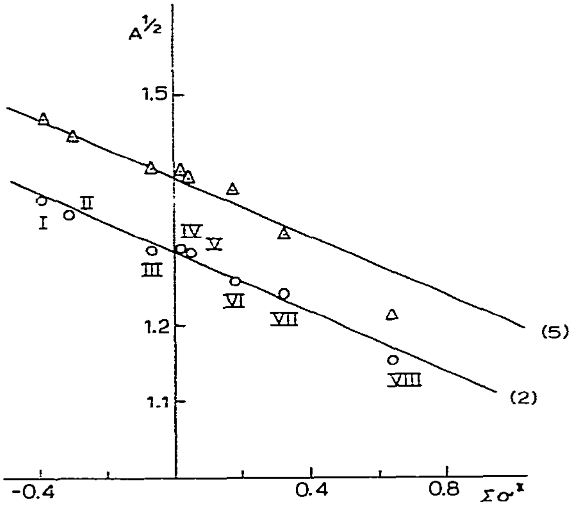


Fig. 1. The relationship between $A^{1/2}$ and $\Sigma\sigma^*$ of the substituents in triorganogermanes: (2) heptane solutions, (5) CCl_4 solutions.

decrease in ν(Ge—H) stretching mode intensities. Thus, the analysis of ν(Ge—H) band intensity values indicates the electron-donating properties of CCl_4 towards triorganogermanes. The solvation action of carbon tetrachloride, in respect to triorganogermanes and triorganosilanes, [19] is practically the same.

Now the dependence of the intensity values of ν(Ge—H) stretching modes in IR spectra on the inductive influence of the substituents has been clarified, the possibilities are open to study the conjugation effects with participation of the germanium atom. For compounds I—XXII (Table 2) the values of $A_{ind}^{1/2}$ calculated from equation 2 are much less that those of $A_{exp}^{1/2}$ found in the experiment. In our opinion, the reason for this is d_π—p_π interaction effect in Ge—X bonds. The values of $\Delta A^{1/2} = A_{exp}^{1/2} - A_{ind}^{1/2}$ quantitatively characterize this interaction. The values of $\Delta A^{1/2}$ show the increase in the Ge—H bond polarity under the influence of d_π—p_π interaction between the X substituents and the germanium atom.

From theoretical works [11,42—46], the extent of d_π—p_π interaction in the molecule is enhanced with the increase of the effective positive charge on the central atom. In addition, it is shown in some papers that the Hammett constants σ_p are the values proportional to the effective charge [11,28]. In this connection one may expect that the $\Delta A^{1/2}$ values correlate with $\Sigma\sigma_p$ constants of three substituents bonded to the germanium atom. The relationship between these values for compounds R_3GeH is given by the striaght line equation 6 (Fig. 2).

$$\Delta A^{1/2} = 1.09\ \Sigma\sigma_p + 0.36\ (r = 0.996;\ s = \pm 0.04) \qquad (6)$$

A similar relationship for compounds R_2GeH_2 is shown (eq. 7).

$$\Delta A^{1/2} = 0.93\ \Sigma\sigma_p + 0.16\ [27] \qquad (7)$$

Comparing the equations 6 and 7 indicates that the increase in the positive

TABLE 2

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

No.	Compounds	ν(Ge—H) (cm^{-1})	$A_{\text{exp}}^{1/2}$	$A_{\text{ind}}^{1/2}$	$\Delta A^{1/2}$	$\Sigma\sigma_p$	$\Delta\nu$ (cm^{-1})
I	$(C_6H_5)(CH_3)_2GeH$	2044	1.16	1.18	—0.02	—0.35	—9
II	$(C_6H_5)CH_3(C_2H_5)GeH$	2038	1.27	1.20	0.07	—0.33	—3
III	$(C_6H_5)_2(CH_3)GeH$	2047	1.19	1.06	0.13	—0.19	2
IV	$(C_6H_5)_2(C_6H_{13})GeH$	2039	1.27	1.09	0.18	—0.13	7
V	$(C_2H_5)_2IGeH$	2057	1.07	0.87	0.20	—0.12	15
VI	$(CH_3)_2ClGeH$	2085	0.98	0.72	0.26	—0.11	5
VII	$(n\text{-}C_4H_9)_2BrGeH$	2062	1.05	0.79	0.26	—0.09	19
VIII	$(C_2H_5)_2ClGeH$	2065	1.05	0.76	0.29	—0.08	20
IX	$(C_2H_5)_2BrGeH$	2062	0.99	0.78	0.21	—0.07	20
X	$(C_6H_5)_3GeH$	2046	1.19	0.94	0.25	—0.03	18
XI	$(C_6H_5)_2FGeH$	2086	1.28	0.86	0.42	0.04	36
XII	$(C_6H_5)(CH_3)ClGeH$	2084	1.01	0.60	0.41	0.05	20
XIII	$(C_6H_5)Cl(C_6H_{13})GeH$	2074	1.12	0.63	0.49	0.11	26
XIV	$(C_6H_5)_2ClGeH$	2082	1.08	0.48	0.60	0.21	36
XV	$(CH_3)Cl_2GeH$	2125	0.82	0.14	0.68	0.29	33
XVI	$(C_2H_5)Cl_2GeH$	2113	0.87	0.16	0.71	0.31	42
XVII	$(C_2H_5)Br_2GeH$	2100	0.96	0.20	0.76	0.31	51
XVIII	$(n\text{-}C_3H_7)Cl_2GeH$	2112	0.90	0.16	0.74	0.33	43
XIX	$(C_6H_5)BrClGeH$	2109	0.89	0.04	0.35	0.45	61
XX	$(C_6H_5)Br_2GeH$	2106	0.89	0.02	0.87	0.45	66
XXI	Cl_3GeH	2157	0.64	—0.44	1.08	0.69	69
XXII	$(C_6F_5)_3GeH$	2150	0.58	—1.10	1.68	1.23	154

charge on the germanium atom (i.e., when the values of $\Sigma\sigma_p$ constants increase) the extent of d_π—p_π interaction in the molecule increases. The difference between the values ρ (1.09 and 0.93) is probably determined by the nonuni-

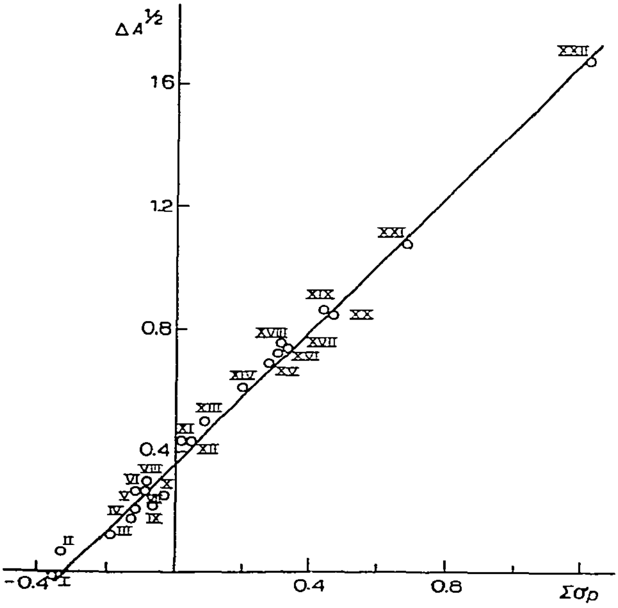


Fig. 2. The relationship between $\Delta A^{1/2}$ and $\Sigma\sigma_p$ of the substituents in triorganogermanes.

formity of the choice of objects, since not all types of substituents are equally represented in the correlation analysis of $\Delta A^{1/2}$ for R_3GeH and R_2GeH_2. For compounds R_3GeH there is available a great number of substituents for which the $\Sigma\sigma_p$ values vary within the range $-0.35 \div 1.23$.

$\Delta\nu$ is the independent value which characterized the conjugation effects in germanium derivatives. It is the difference between the frequency of Ge—H stretching mode, calculated on the assumption of purely inductive influence of substituents on the position of this frequency (ν_{ind}), and the experimental value of this frequency (ν_{exp}). The values of $\Delta\nu$ in the IR spectra of germanium derivatives were analysed earlier [32,47]. The values of $\Delta\nu$ show the influence of the conjugation effect with participation of the germanium atom on the force constant of Ge—H bond and, therefore, on the energy of this bond. Consequently, the values $\Delta\nu$, as well as $\Delta A^{1/2}$, quantitatively characterize the conjugation effects (d_π—p_π interaction effect in this case). These values characterize the properties of the Ge—H bond closely related to each other - its energy and polarity. It is therefore of interest to compare the values $\Delta A^{1/2}$ and $\Delta\nu$. For compounds I—VIII (Table 1) in which the R substituents exert exclusively the inductive influence, the dependence between the values ν_{ind} and the sum of inductive Taft constants of three substituents ($\Sigma\sigma^*$) is of the form shown in equation 8.

$$\nu_{ind} = 23.6\ \Sigma\sigma^* + 2021 \text{ (heptane)} \qquad (8)$$

The equation 8 is slightly different from the equation obtained earlier [31]. In this work ν(Ge—H) data taken from several references were used. The values ν(Ge—H) used to calculate equation 8 are measured under quite similar experimental conditions. The linear relationship between the values $A^{1/2}_{ind}$ and ν_{ind} and the value $\Sigma\sigma^*$ indicates that they are linearly related to each other. In accord with equations 2 and 8, the relationship between the values $A^{1/2}_{ind}$ and ν_{ind} is of the form shown in equation 9.

$$A^{1/2}_{ind} = 18.42 - 0.0085\ \nu_{ind} \qquad (9)$$

Therefore, in the IR spectra of the compounds in which the substituents are incapable of d_π—p_π interaction with the germanium atom, the values of $A^{1/2}_{ind}$ and ν_{ind} are connected by the linear equation 9.

Let us consider the correlation of values $\Delta A^{1/2}$ and $\Delta\nu$ presented in Table 2. Fig. 3 shows that these values are related to each other by linear dependence. It should be noted that the correlation between $\Delta A^{1/2}$ and $\Delta\nu$ given in Fig. 3 is highly limited in character. Indeed, when studying the frequencies and intensities of Si—H stretching modes we pointed out that the dependence between $\Delta A^{1/2}$ and $\Delta\nu$ for silane derivatives is represented as a curved line (eq. 10) [11].

$$\Delta\nu = 4\ \Delta A^{1/2} + 52(\Delta A^{1/2})^{1/2}\ [(R_i)_3SiH] \qquad (10)$$

Thus, the values ν_{ind} and $A^{1/2}_{ind}$ are related linearly and the values $\Delta\nu$ and $\Delta A^{1/2}$, as followed from [11], are related, in the general case, by a non-linear dependence. Therefore, the linear dependence observed between the values $\Delta A^{1/2}$ and $\Delta\nu$ for compounds $(R_i)_3GeH$ (Fig. 3) is of specific and, to some extent random,

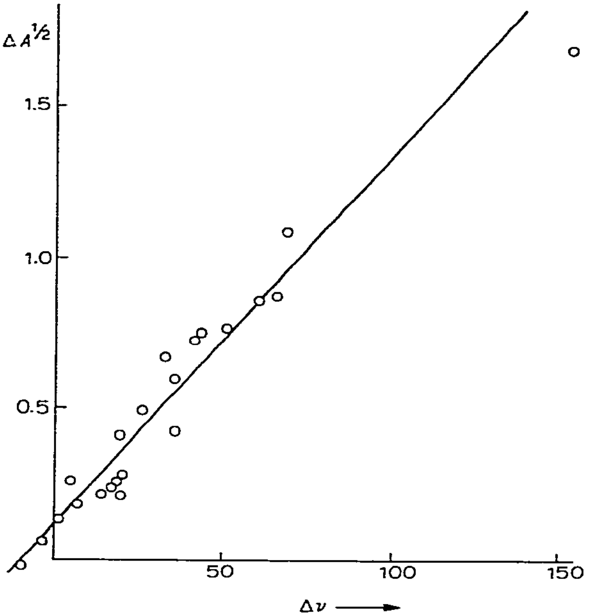


Fig. 3. The relationship between $\Delta A^{1/2}$ and $\Delta\nu$ in triorganogermanes.

character. The existence of this dependence is due to a limited number of compounds used for correlation. The substituents capable of d_π—p_π interaction with the germanium atom are only halogens and phenyl groups.

Experimental

IR measurements

The IR spectra were measured on a UR-20 "Zeiss" spectrometer. Heptane and carbon tetrachloride solution (0.04—0.09 mol l^{-1}) were used to obtain spectra. The integrated intensity of Ge—H stretching modes A (mol^{-1} l cm^{-2} × 10^4) was measured by Iogansen's method [48].

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

Synthesis of studied compounds

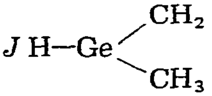
$(C_2H_5)_2(ClCH_2CH_2CH_2)GeH$. Diethylchlorogermane, Et_2GeHCl, (9.72 g, 0.0582 mol) and allyl chloride (4.46 g, 0.0582 mol) were heated 2 h at 100—110°C with 50 mg of azobis(isobutyronitrile) (AIBN). 6.84 g of $Et_2Ge(Cl)(CH_2)_3Cl$, b.p. 118—120°C/13 mmHg was isolated (48%). The reduction of this compound by $LiAlH_4$ in Et_2O gave 5.15 g of $Et_2Ge(H)(CH_2)_3Cl$ (88%). B.p. 96°C/30 mmHg; NMR (C_6H_6): δ(GeH), 3.78(m); $\delta(CH_2Cl)$, 3.18(t) ppm.

$(C_2H_5)(CH_3)(ClCH_2CH_2CH_2)GeH$. Methylethylchlorogermane (MeEtGeHCl) (11.11 g, 0.0725 mol) and allyl chloride (5.55 g, 0.0725 mol) were heated for 8 h at 100—110°C with 50 mg of AIBN. Distillation gave 6.95 g of MeEtGe(Cl)-$(CH_2)_3Cl$, b.p. 102°C/12 mmHg (42%). The reduction of this compound by $LiAlH_4$ in Et_2O gave 4.70 g of MeEtGe(H)$(CH_3)_3Cl$. B.p. 62°C/12 mmHg (85%);

NMR (C_6H_6): δ(GeH) 3.82(m); $\delta(CH_2Cl)$, 3.13(t); $\delta(CH_3)$, 0.01(d); $\delta(C_2H_5)$, 0.40—0.75(m) ppm.

$(C_2H_5)(ClCH_2CH_2CH_2)_2GeH$. Ethylchlorogermane ($EtGeH_2Cl$) (10.00 g, 0.072 mol) and allyl chloride (11.16 g, 0.144 mol) were heated 2 h at 130°C with 50 mg of AIBN. Distillation gave 6.20 g of $EtGe(Cl)[(CH_2)_3Cl]_2$, b.p. 136—140°C/4 × 10^{-2} mmHg (30%). The reduction of this compound by $LiAlH_4$ in Et_2O gave 5.27 g of $EtGe(H)[(CH_2)_3Cl]_2$ (87% undistillated); NMR (CCl_4): δ(GeH), 3.80(m); $\delta(CH_2Cl)$, 3.47(t); $\delta(C_2H_5)$, 0.78—2.08(m) ppm.

$(C_2H_5)(C_6H_5CH_2)_2GeH$. Dibenzylchlorogermane ($(C_6H_5CH_2)_2GeHCl$) (12.00 g, 0.041 mol) was added to a 15% excess of a solution of EtMgBr in Et_2O. The mixture was heated for 2 h at 35°C. After hydrolysis and extraction by Et_2O/C_6H_6, distillation gave 8.25 g of $Et(C_6H_5CH_2)_2GeH$ (70%), b.p. 138—142°C/5 × 10^{-2} mmHg. NMR (C_6D_6): δ(GeH), 4.18(m); $\delta(CH_2)$, 2.18(d); $\delta(C_2H_5)$, 0.60—1.00 (m) ppm.

$(CH_3)(C_2H_5)(C_6H_5)GeH$. $C_6H_5(CH_3)ClGeH$ (3.72 g, 0.019 mol) was alkylated by EtMgBr (0.027 mol, 50% excess) in Et_2O. 2.88 g of $C_6H_5(CH_3)(C_2H_5)GeH$ was obtained after hydrolysis and distillation (78%). B.p. 110°C/55; n_D^{20} = 1.5180; NMR (CCl_4): GeH, 4.47(sext) ppm,  $J\ \mathrm{H{-}Ge}\begin{matrix}\diagup CH_2\\ \diagdown CH_3\end{matrix}$ = 3.0 Hz.

$(C_6H_5)(CH_3)GeHCl$. Methylphenylgermane $C_6H_5(CH_3)GeH_2$ (5.6 g, 0.031 mol) was treated with $ClCH_2OCH_3$ (2.50 g, 0.031 mol) according to ref. 49. Distillation gave 4.67 g of $C_6H_5(CH_3)GeHCl$. B.p. 108—110°C/25 mmHg; n_D^{20} = 1.5544; NMR (CCl_4): δ(GeH), 6.0 (q); $\delta(CH_3)$, 0.87(d) ppm J (H—Ge—CH_3) 3 Hz.

$(C_6H_5)(Cl)(Br)GeH$. Phenylmethoxychlorogermane ($C_6H_5(Cl)(OCH_3)GeH$) (2.20 g, 0.011 mol) was treated with 1 cm^3 of 40% HBr and extracted by C_6H_6. The benzene solution, dried over Na_2SO_4, was distilled to give 1.92 g of C_6H_5-(Cl)(Br)GeH (72%). NMR (CCl_4): δ(GeH), 6.84(s) ppm.

The other compounds were prepared using methods previously described [49—60].

References

1 E.A.V. Ebsworth, Organometallic Compounds of the Group IV Elements, in A.G. McDiarmid (Ed.), The Bond to Carbon, Marcel Dekker, New York, N.Y., 1968.

2 C.I. Attridge, Organometal Chem., Rev., A, 5 (1970) 324.

3 M.G. Voronkov, V.P. Mileshkevich and Yu.A. Yezhelevsky, Siloksanovaya svyaz, Izd. "Nauka", Novosibirsk, 1976.

4 A.N. Egorochkin, N.S. Vyazankin and S.Ya. Khorshev, Usp. Khim., 41 (1972) 828.

5 G.A. Razuvaev, A.N. Egorochkin, N.S. Vyazankin, S.Ya. Khorshev and V.F. Mironov, Dokl. Akad. Nauk SSSR, 185 (1969) 100.

6 A.N. Egorochkin and N.S. Vyazankin, Dokl. Akad. Nauk,SSSR, 193 (1970) 590.

7 A.N. Egorochkin, N.S. Vyazankin, S.Ya. Khorshev, T.I. Chernysheva and O.V. Kuz'min, Izv. Akad. Nauk SSSR, Ser. Khim., (1970) 1651.

8 A.N. Egorochkin, S.Ya. Khorshev, N.S. Vyazankin, T.I. Chernysheva and O.V. Kuz'min, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 544.

9 A.N. Egorochkin, S.Ya. Khorshev, N.S. Vyazankin, T.I. Chernysheva and O.V. Kuz'min, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 776.

10 A.N. Egorochkin and N.S. Vyazankin, Dokl. Akad. Nauk SSSR, 196 (1971) 345.

11 A.N. Egorochkin, S.Ya. Khorshev, N.S. Ostasheva, M.G. Voronkov, N.S. Vyazankin, T.V. Kashik, O.V. Kuz'min, N.S. Nametkin and N.A. Pritula, J. Organometal. Chem., 99 (1975) 47.

12 J.I. Musher, Angew. Chem. Intern. Edit., 8 (1969) 54.
13 E.W. Abel, D.A. Armitage and S.P. Tyfield, J. Chem. Soc., A, (1967) 544.
14 J.M. Bellama and A.G. McDiarmid, J. Organometal. Chem., 24 (1970) 91.
15 M.G. Voronkov, V.P. Feshin, V.F. Mironov, S.A. Mikhaylyants and T.K. Gar, Zh. Obshch. Khim., 41 (1971) 2211.
16 V.P. Feshin and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 209 (1973) 400.
17 A.N. Egorochkin, S.E. Skobeleva, E.I. Sevast’yanova, I.G. Kosolapova, V,D. Sheludyakov, E.S. Rodionov and A.D. Kirilin, Zh. Obshch. Khim., 46 (1976) 1795.
18 S.Ya. Khorshev, A.N. Egorochkin, E.I. Sevast‘yanova, N.S. Ostasheva and O.V. Kuz’min, Zh. Obshch. Khim., 46 (1976) 1801.
19 S.Ya. Khorshev, A.N. Egorochkin, E.I. Sevast’yanova and O.V. Kuz’min, Zh. Obshch. Khim., 48 (1978) 1348.
20 N.M. Alpatova and Yu.M. Kessler, Zh. Strukt. Khim., 5 (1964) 332.
21 M.G. Voronkov and G.I. Lebedeva, Izv. Akad. Nauk SSSR, Ser. Khim., (1973) 2473.
22 G.I. Lebedeva and M.G. Voronkov, Izv. Akad. Nauk SSSR, Ser. Khim., (1973) 2597.
23 M.G. Voronkov and G.I. Lebedeva, Zh. Obshch. Khim., 47 (1977) 100.
24 L.A. Gribov, Teoriya intensivnostey v infrakrasnykh spektrakh mnogoatomnykh molekul, Izd. Akad. Nauk SSSR, Moskva, 1963.
25 A.N. Egorochkin, N.S. Vyazankin, N.S. Ostasheva, O.V. Kuz’min, I.F. Kovalev, N.S. Nametkin and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 210 (1973) 1094.
26 A.N. Egorochkin, N.S. Vyazankin, N.S. Ostasheva, O.V. Kuz’min, N.S. Nametkin, I.F. Kovalev and M.G. Voronkov, J. Organometal. Chem., 59 (1973) 117.
27 A.N. Egorochkin, S.Ya. Khorshev, E.I. Sevast’yanova, S.Kh. Ratushnaya, J. Satge, P. Riviere, J. Barrau and S. Richelme, J. Organometal. Chem., 155 (1978) 175.
28 A.N. Egorochkin, S.Ya. Khorshev, N.S. Ostasheva, E.I. Sevast’yanova, J. Satge, P. Riviere and J. Barrau, J. Organometal. Chem., 105 (1976) 311.
29 Yu.P. Egorov, V.P. Morozov and P.F. Kovalev, Ukr. Khim. Zh., 31 (1965) 123.
30 Yu.P. Egorov, Teor. Eksp. Khim., 1 (1965) 30.
31 A.N. Egorochkin, S.Ya. Khorshev, N.S. Ostasheva, J. Satge, P. Riviere, J. Barrau and M. Massol, Dokl. Akad. Nauk SSSR, 215 (1974) 858.
32 A.N. Egorochkin, S.Ya. Khorshev, J. Satge, P. Riviere and J. Barrau, J. Organometal. Chem., 99 (1975) 239.
33 I.F. Kovalev, Dokl. Akad. Nauk SSSR, 134 (1960) 559.
34 I.F. Kovalev, Optika i spektroskopiya, 10 (1961) 707.
35 A.N. Egorochkin, S.Ya. Khorshev and N.S. Vyazankin, Dokl. Akad. Nauk SSSR, 185 (1969) 353.
36 A.N. Egorochkin, N.S. Vyazankin, A.I. Burov and S.Ya. Khorshev, Izv. Akad. Nauk SSSR, Ser. Khim., (1970) 1279.
37 S.S. Batsanov, Usp. Khim., 37 (1968) 778.
38 O.W. Steward and O.R. Pierce, J. Amer. Chem. Soc., 83 (1961) 4932.
39 K. Kawakami, T. Saito and R. Okamara, J. Organometal. Chem., 8 (1967) 377.
40 N.S. Brown, J. Chem. Soc., (1956) 1248.
41 O.Kh. Poleshchuk and Yu.K. Maksyutin, Usp. Khim., 45 (1976) 2097.
42 H.H. Jaffe, J. Phys. Chem., 58 (1954) 185.
43 D.P. Craig, A. Maccoll, R.S. Nyholm, L.E. Orgel and L.E. Sutton, J. Chem. Soc., (1954) 332.
44 D.P. Craig and D.W. Magnusson, J. Chem. Soc., (1956) 4895.
45 D.P. Craig and C. Zauli, J. Chem. Phys., 37 (1962) 609.
46 D.P. Craig and K.A.R. Mitchell, J. Chem. Soc., (1965).4682.
47 A.N. Egorochkin, S.Ya. Khorshev, N.S. Ostasheva, J. Satge, P. Riviere and J. Barrau, M. Massol, J. Organometal. Chem., 76 (1974) 29.
48 A.V. Iogansen, Opt. Spektrosk., 26 (1964) 813.
49 J. Satgé and P. Rivière, Bull. Soc. Chim. Fr., (1966) 1773.
50 J. Satgé, Ann. Chim. (Paris), 6 (1961) 519.
51 P. Rivière, Thèse, Toulouse, 1971.
52 M. Lesbre and J. Satgé, C.R. Acad. Sci. Paris, 252 (1961) 1976.
53 E. Amberger and H. Boeters, Angew. Chem., 73 (1961) 114.
54 H.H. Anderson, J. Amer. Chem. Soc., 82 (1960) 3016.
55 O.H. Jonson and D.M. Harris, J. Amer. Chem. Soc., 72 (1950) 5566.
56 M. Massol and J. Satgé, Bull. Soc. Chim. Fr., (1966) 2737.
57 V.F. Mironov and A.I. Kravchenko, Zh. Obshch. Khim., 34 (1964) 1356.
58 M. Massol, Thèse Toulouse, 1967.
59 P. Rivière, G. Dousse and J. Satgé, Synth. React. Inorg. Met. Org. Chem., 4 (1974) 281.
60 R.J. Cross and F. Glockling, J. Chem. Soc., (1964) 4125.