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THE INTENSITY OF Ge—H STRETCHING MODES AND CONJUGATION EFFECTS IN ORGANOGERMANIUM COMPOUNDS

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Summary

It has been shown that the integrated intensity (A) of Ge—H stretching modes in the IR spectra of triorganogermanes, R_3GeH, containing no d_π—p_π bonds between the germanium atom and the substituents is related to the sum of the Taft constants σ^* of the substituents R ($\Sigma\sigma^*$) by the equation $A^{1/2} = 1.32 - 0.12\ \Sigma\sigma^*$. If a molecule contains substituents X capable of forming d_π—p_π bonds with the germanium atom, A depends not only on the $-I$ effect of the substituents X but also on the effect of the d_π—p_π interaction in the Ge—X bonds. The d_π—p_π interaction in the molecule increases with increasing positive effective charge on the germanium atom. The values of A in alkyl-substituted compounds are indicative of the σ,σ-conjugation effect.

Introduction

The chemical and physical properties of organic compounds of silicon subgroup elements are known to be different in many aspects from those of carbon, their nearest neighbour in Group IVB [1]. Thus silicon subgroup elements do not form multiple p_π—p_π bonds under ordinary conditions while such bonds are typical of carbon. However, unlike carbon the silicon subgroup elements form additional bonds involving vacant nd-orbitals [1—3]. These additional bonds may be either of σ- or of π-type. In the case of π-type bond formation the so-called d_π—p_π interaction occurs. This d_π—p_π interaction is observed in M—X bonds of the compounds MX_nR_{4-n} (M = Si, Ge, Sn and probably, Pb; R is an alkyl radical) when X is an atom having lone electron pairs or an α,β-unsaturated hydrocarbon radical. Upon d_π—p_π interaction a partial p electron delocalization of X occurs towards the vacant nd-orbitals in the M atom. The multiplicity of the M—X bond increases as delocalization takes place. In the ground electronic state the energy of the d_π—p_π interaction effects is much smaller then the energy of an ordinary bond. The magnitude of the d_π—p_π interaction effect in the M—X bond depends on the nature of M and X. Thus, the d_π—p_π interaction decreases with an increase of the atomic number of the element M in the silicon subgroup; no reliable data on the d_π—p_π interaction in lead derivatives are available. For organosilicon and organogermanium compounds the dependence of the d_π—p_π interaction on the nature and the number of substituents in a molceule has also been studied [4—11]. Nevertheless many aspects of the d_π—p_π interaction have not been sufficiently studied. This makes the application of new methods to the investigation of this effect an urgent problem. The purpose of this work was to study the intensity of Ge—H stretching modes in order to obtain further information on the d_π—p_π interaction in organogermanium compounds.

Chemical bonds formed by silicon subgroup elements are known to have greater polarizability as compared to those involving carbon. When the substituents X remain unchanged the polarizability of the M—X bond increases with increasing atomic number of an element M from the silicon subgroup. So the conjugation effects of σ,σ-, σ,p- etc. type may be expected to play an important role in these organometallic compounds. Thus, another object of this work was to use data on the intensity of Ge—H stretching modes to study the σ,σ-conjugation effect in organogermanium compounds.

Silane and germane derivatives were earlier shown [3—11] to be most suitable compounds for spectroscopic studies of the conjugation effects. Infrared studies of these compounds satisfy all the conditions necessary for accurate estimation of the role of the d_π—p_π interaction effect. As was shown in ref. 3 these conditions are (1) allowance for the changes in the chemical bond polarity (in our work M—H bonds, where M = Si, Ge) due to the inductive effect and other conjugation effects except the d_π—p_π interpretation, (2) availability of series of compounds whose spectroscopic parameters (a) depend on substituent electronic effects only and (b) are sufficiently sensitive to the action of these effects. When all these conditions are satisfied correlation analysis methods make it possible to separate the d_π—p_π interaction effect from all other electronic effects.

The stretching vibrations of Si—H [12] and Ge—H [11,13—15] bonds are highly characteristic in shape. When these vibrations take place only the M—H coordinate changes considerably. The mass of the three other substituents bonded to the metal atom has no influence on the ν(M—H) vibration. Besides, no mechanical interaction of ν(M—H) with other substituent vibrations exists in the molecule. However, experiments show that ν(Si—H) and ν(Ge—H) values [4—11,15] as well as the intensity of the Si—H stretching modes, A(Si—H) [16—18] do not remain constant when the substituents bonded to Si or Ge are changed. This is due to the substituent electronic effects which cause changes in the force constants of M—H bonds and in the polarity of Si—H bonds. Different aspects of the d_π—p_π interaction in organosilicon and organogermanium compounds [3—11,15—18] were considered when analyzing ν(M—H) and A(Si—H) values. Thus, a comparison of the dependence of ν(M—H) and ν(Ge—H) on the substituent electronic effects revealed that the main specific features of the d_π—p_π interaction in organogermanium and organosilicon compounds are similar [11,15], with the magnitude of the d_π—p_π interaction effect being smaller in organogermanium compounds.

An investigation of organosilicon compounds [18] has shown that studies of A(Si—H) greatly contribute to our knowledge of the conjugation effect in organosilicon compounds obtained from an analysis of ν(Si—H). This may be attributed to the fact that band intensities are more sensitive to conjugation effects than frequencies [19]. Hence, it seems to be urgent that information on A(Ge—H) be obtained in order to further study the d_π—p_π interaction, since in organogermanium compounds this effect is less pronounced.

Results and discussion

Available data [20] show that the values of A(Ge—H) as well as A(Si—H) are dependent on the nature of the three other substituents on a Group IVB element. The integrated intensity of Ge—H bands decreases with an increase of the electron-attracting properties of the substituents. It follows from what has been said above that A(Ge—H) changes under the influence of the inductive effect of the substituents and conjugation effects (including the d_π—p_π interaction). In order to distinguish the d_π—p_π interaction effect correctly one should determine the type of A(Ge—H) dependence on the inductive effect of the substituents.

Influence of the inductive effect of substituents on the integrated intensity of Ge—H bands

To estimate the influence of the inductive effect of substituents in $(R_i)_3$GeH compounds (R_i is a substituent) on A(Ge—H) it is necessary to have compounds in which the substituents, R_i, do not conjugate with the germanium atom. We prepared compounds in which the substituents do not form normal d_π—p_π bonds with germanium (Table 1) and measured the integrated intensity of the Ge—H bands in the IR spectra of these compounds.

As has been stated above, the stretching vibration of the Ge—H bond is highly characteristic in shape. The integrated intensity of the Ge—H stretching mode, A(Ge—H), is therefore proportional to the square of the first derivative of the dipole moment of this bond in the normal coordinate

$$A \sim \left[\frac{\delta\mu(\mathrm{Ge{-}H})}{\delta q(\mathrm{Ge{-}H})}\right]^2 \tag{1}$$

where μ is the dipole moment. Due to the highly characteristic nature of the vibration under discussion the Ge—H bond can, with good approximation, be regarded as a diatomic molecule. Then, as was shown in ref. 19:

$$\frac{\delta\mu}{\delta q} \approx \frac{\mu}{r_0} \tag{2}$$

where r_0 is the interatomic distance in Ge—H. Hence,

$$A \sim \left[\frac{\mu(\mathrm{Ge{-}H})}{r_0(\mathrm{Ge{-}H})}\right]^2 \tag{3}$$

i.e.

$$A^{1/2} \sim \frac{\mu(\text{Ge—H})}{r_0(\text{Ge—H})} \qquad (4)$$

From eq. 3 and 4 it can be seen that changes in the A(Ge—H) value are due to changes in the dipole moment of the Ge—H bond under the influence of the three substituents bonded to the germanium atom. In fact, the hydrogen atom in trialkylgermanes is more electronegative than the germanium atom (or the Alk_3Ge radical as a whole). Therefore the following order of Ge—H bond polarities can be written for trialkylgermanes: $Alk_3\overset{\delta^+}{Ge}—\overset{\delta^-}{H}$. According to eq. 4 a fairly high value of the dipole moment of the Ge—H bond gives high A(Ge—H) values for trialkylgermanes. An increase in the electron-attracting properties of the three substituents bonded to the germanium atom decreases the electron density on the hydrogen atom in the Ge—H bond. (This is evident in PMR spectra of germane derivatives; see for example ref. 21.) Such an increase also results in a decrease of the dipole moment of the Ge—H bond and, hence, of the A(Ge—H) value. This qualitative information on the effect of the substituents on the polarity of Ge—H can be expressed quantitatively. The donor—acceptor properties of substituents can be described with Taft—Hammett σ constants. Taking eq. 3 and 4 into account and considering the correlation between σ constants and $A^{1/2}$ value to be theoretically grounded [22] we obtain the following linear equation

$$A^{1/2} = 1.32 - 0.12\Sigma\sigma^{\star} \qquad (r = 0.99) \qquad (5)$$

This equation relates the $A^{1/2}$ values to the sums of the inductive constants of the substituents ($\Sigma\sigma^{\star}$) for the compounds shown in Table 1. Taft $\sigma^{\star}$ constants were used for correlation since we initially assumed that the inductive effect of the substituents causes a change in intensity for the given compounds.

Effect of d_π—p_π interaction

If it is assumed that eq. 5 does not only show the relation between $A^{1/2}$ and $\Sigma\sigma^{\star}$ for compounds without d_π—p_π bonds with the germanium atom, then also the influence of the I effect on A(Ge—H) in compounds with any substituents may be taken into account with the help of this equation. In Table 2 are given experimental values of the integrated intensity of Ge—H bands ($A_{\text{exp.}}^{1/2}$), measured by us for a series of compounds with substituents capable of d_π—p_π interaction with germanium. Table 2 also shows that $A_{\text{calc.}}^{1/2}$ values are smaller than $A_{\text{exp.}}^{1/2}$.

The difference $\Delta A^{1/2} = A_{\text{exp.}}^{1/2} - A_{\text{calc.}}^{1/2}$ arises from the fact that the substituents of the given compounds not only exert inductive $-I$ effects, but take part in conjugation with the germanium atoms as well. The d_π—p_π interaction effect and inductive $-I$ effect are opposed to each other. Therefore the influence of the d_π—p_π interaction effect on A(Ge—H) can be formally regarded as lowering the $-I$ effect. As a result the negative charge on hydrogen in the Ge—H bond increases slightly, the polarity of the bond increases, the $A_{\text{exp.}}$ value rises, and the $\Delta A^{1/2}$ difference appears.

TABLE 1

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

No.	Compound	$A^{1/2}$	$\Sigma\sigma^*$
1	$(C_2H_5)_3GeH$	1.37	—0.3
2	$(C_2H_5)_2C_6H_5CH_2GeH$	1.29	0.015
3	$(CH_3)_2CH_2ClGeH$	1.20	1.05
4	$(CH_3)_2CHCl_2GeH$	1.07	1.94

As can be seen from Table 2 the $\Delta A^{1/2}$ values for $Alk_{3-n}X_nGeH$ compounds vary over a rather wide range depending on the nature and the number of substituents, X, capable of d_π—p_π interaction with the germanium atom. Information on the d_π—p_π interaction in organometallic compounds of Group IVB available from the literature makes it possible to establish a relationship between $\Delta A^{1/2}$ and the electronic effects of the substituents linked with germanium. Authors of theoretical works [23—25] on the d_π—p_π interaction have shown that the extent of such an interaction depends on the effective charge on the atom-acceptor (germanium atom in our case). The effect of the d_π—p_π interaction is enhanced when the effective positive charge on the atom-acceptor increases. Determination of the absolute value of the effective charge is a complicated problem. It is much simpler to calculate values proportional to the effective charge, as has been done for organosilicon compounds [8,10,26]. Such calculations are based on the properties of the d_π—p_π interaction effect known at present. Substituents forming d_π—p_π bonds with the elements of the silicon subgroup can be characterized by two electronic effects, electron-accepting and electron-releasing. When such substituents as C_6H_5, CH_3S, Cl and Br are attached to germanium they behave as acceptors, because they possess the inductive —*I* effect characterized quantitatively by Taft σ_I constants. Due to the —*I* effect

TABLE 2

VALUES OF $A_{exp.}^{1/2}$, $A_{calc.}^{1/2}$ AND $\Delta A^{1/2}$ IN THE IR SPECTRA OF THE COMPOUNDS STUDIED

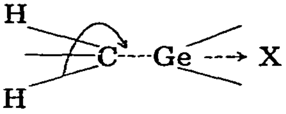
No.	Compound	$A_{exp.}^{1/2}$	$A_{calc.}^{1/2}$	$\Delta A^{1/2}$	$\Sigma\sigma_p$
1	$CH_3(C_6H_5)_2GeH$	1.19	1.18	0.01	—0.15
2	$(CH_3)_2ClGeH$	0.98	0.97	0.01	—0.12
3	$(C_4H_9)_2BrGeH$	1.05	1.01	0.04	—0.09
4	$(C_2H_5)_2ClGeH$	1.05	1.00	0.05	—0.08
5	$(C_6H_5)_2(CH_3S)GeH$	1.12	1.03	0.09	—0.03
6	$(C_6H_5)_3GeH$	1.19	1.10	0.09	0.03
7	$(C_6H_5)_2ClGeH$	1.08	0.83	0.25	0.24
8	$(CH_3)Cl_2GeH$	0.82	0.62	0.20	0.27
9	$(C_2H_5)Cl_2GeH$	0.87	0.65	0.22	0.29
10	$(C_3H_7)Cl_2GeH$	0.90	0.65	0.25	0.31
11	$(C_6H_5)BrClGeH$	0.89	0.56	0.33	0.46
12	$(C_6H_5)Br_2GeH$	0.91	0.58	0.33	0.47
13	Cl_3GeH [a]	0.73	0.28	0.45	0.66
14	$(C_2H_5)_2(CH_3O)GeH$	1.37	1.17	0.20	—0.57
15	$(C_2H_5)_2(C_6H_5O)GeH$	1.23	1.06	0.17	—0.21

[a] The IR spectra of a mixture of $HGeCl_3$ and $GeCl_4$.

the positive charge on the germanium atom increases. On the other hand, participating in the d_π—p_π interaction these substituents behave as donors of electrons thus creating some negative charge on the germanium atom. An analysis of the frequencies of M—H stretching modes in organosilicon [5] and organogermanium [15] compounds indicates that the mechanism of the d_π—p_π interaction of a certain substituent with silicon or germanium atoms is formally similar to the conjugation mechanism of this substituent with an aromatic ring or vinyl group. Hence, σ_R constants of the substituent are a quantitative measure of its ability for d_π—p_π interaction [5,15].

Thus, a change in the effective charge on the germanium atom due to the influence of C_6H_5, Hal, CH_3S type substituents is proportional to the sum of σ_I and σ_R of these substituents. This sum is known as the σ_p Hammett constant. Therefore, to obtain values proportional to the effective charge on the germanium atom the σ_p constants of the substituents bonded to the central atom should be summed. It should be noted that this is valid only for the case when the substituents change the effective charge on the germanium atom independently of one another.

Some of the compounds in Table 2 contain alkyl groups as substituents. Changes of the effective charge on the germanium atom due to the effect of the alkyl groups have been characterized in this work by σ_p Hammett constants. Alkyl groups possess the +*I* effect. In addition, these substituents seem to possess a resonance effect and participate in the σ,σ-conjugation



The least squares method has revealed a linear relationship between $\Delta A^{1/2}$ and $\Sigma\sigma_p$ in compounds 1—13:

$$\Delta A^{1/2} = 0.53\ \Sigma\sigma_p + 0.09\ (r = 0.96;\ s = 0.05) \qquad (6)$$

For similar organosilicon compounds the following relationship was observed [18]:

$$\Delta A^{1/2} = 1.47\ \Sigma\sigma_p + 0.12 \qquad (7)$$

It follows from eq. 6 and 7 that the extent of the d_π—p_π interaction in a molecule increases with the effective positive charge on the silicon and germanium atoms (hence with $\Sigma\sigma_p$). A comparison of the slopes of the straight lines of eq. 6 and 7 indicates a greater increase of the d_π—p_π interaction in organosilicon compounds with identical rise of a positive charge on germanium and silicon atoms. A similar conclusion was drawn [15] from the analysis of frequencies of (M—H) stretching modes.

The effect of σ,σ-conjugation in organogermanium compounds

At first sight the experimental data given above can be interpreted without involving σ,σ-conjugation (hyperconjugation). Indeed, the straight line of eq. 6 has a relatively high correlation coefficient in spite of the fact that some of the compounds 1—13 have alkyl substituents potentially capable of σ,σ-conjugation. The points on the plot (Fig. 1) representing compounds with alkyl substituents do not deviate considerably from the correlation straight line eq. 6.

The data obtained when studying the integrated intensity of M—H bands can be compared with those supplied by other methods of investigation of organosilicon and organogermanium compounds. As has been shown earlier [11,27] the straight lines $\nu = a\Sigma\sigma^* + b$ relating ν(M—H) to the sum of the inductive constants, $\Sigma\sigma^*$, of substituents not forming d_π—p_π bonds with M have identical slopes for both M = Si and Ge. The ν(M—C) frequencies and electronegativities, χ, of substituents R_i not forming d_π—p_π bonds with M in $(C_2H_5)_n$-$M(R_i)_{4-n}$ type compounds, are also related by linear relationships $\nu = a\chi + b$ which have identical slopes [11,28] in the cases when M = Si and Ge. The straight lines $\tau = a - b\Sigma\sigma^*$ representing the relationship between ^{1}H chemical shifts in CH_3 groups and the $\Sigma\sigma^*$ constants of substituents in the PMR spectra of methylsilanes and methylgermanes have practically identical slopes [11,29]. Thus, infrared frequencies and PMR chemical shifts suggest that, in the absence of substituents forming d_π—p_π bonds, (1) silicon and germanium have essentially similar abilities to transfer the inductive effect of substituents, and (2) the σ,σ-conjugation plays an insignificant role, if any, both in organosilicon and organogermanium compounds. The intensity data on M—H bands add a great deal to the above conclusions. As was shown in refs. 16 and 17, $A^{1/2}$ (Si—H) values in $(R_i)_3SiH$ compounds that do not contain d_π—p_π bonds between R_i and silicon are related to $\Sigma\sigma^*$ of the substituents R_i by the linear equation

$$A_{\text{ind.}}{}^{1/2} = 1.35 - 0.19\ \Sigma\sigma^* \qquad (8)$$

A comparison of eq. 8 with eq. 5 shows that the linear relation between $A^{1/2}$ and $\Sigma\sigma^*$ has a much smaller slope for organogermanium compounds than for their silicon analogs. This may be attributed to the influence of σ,σ-conjugation on the intensity. It is known [18,19] that intensity is more sensitive to intramolecular interaction than frequency, thus, according to ref. 19, one of the most convenient methods to study the σ,σ-conjugation in the ground state is a consideration of A(M—H) values. It is known [30] that a difference in the electronegativities of atoms A and B is a necessary conditions for the σ,σ-conjugation effect in the $A{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}B$ system to be markedly displayed. An enhancement of the σ,σ-conjugation effect should be expected upon replacement of one carbon atom by an element of the silicon subgroup possessing a greater polarizability. In the $H{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{M}}{-}X$ system (M = Si, Ge) the σ,σ-conjugation effect increases with the electron-attracting properties of the substituents X [9]. A similar enhancement of the σ,π-conjugation effect with the difference in donor—acceptor properties of conjugating bonds was demonstrated [31] by spectroscopy. The above consideration allows one to expect that (1) the σ,σ-conjugation will contribute more in organogermanium compounds than in their silicon analogs and (2) the extent of the σ,σ-conjugation in $H\overset{\curvearrowright}{\equiv C -}\underset{|}{\overset{|}{Ge}} \rightarrow R_i$ compounds will increase with increasing electron-attracting properties of R_i. Our experimental data, viz. a smaller slope of the straight line of eq. 5 as compared to eq. 8, are in accord with the above assumptions and are indicative of an increase of the σ,σ-conjugation effect in the compounds studied with the $\Sigma\sigma^*$ constants of

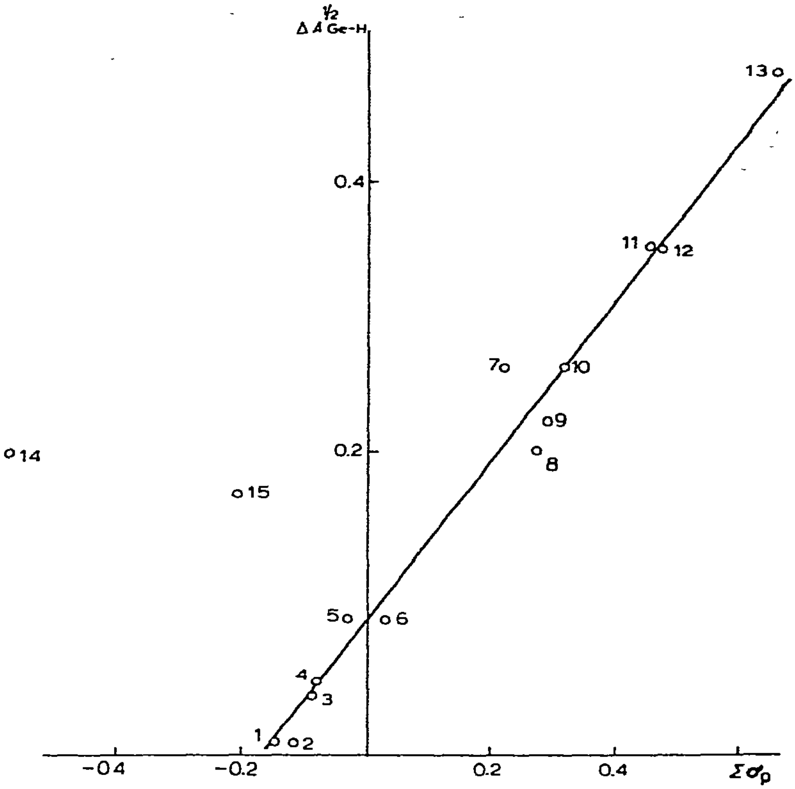


Fig. 1. The relationship between $\Delta A^{1/2}$ and $\Sigma\sigma_p$ of the substituents in triorganogermanes.

their substituents. Thus, the $A_{\text{calc.}}^{1/2}$ values in eq. 5 represent the sum of two electronic effects, the inductive effect and σ,σ-conjugation, with the latter increasing in magnitude with the $-I$ effect. Since the σ,σ-conjugation effect causes a rise in the electron-attracting properties of alkyl substituents the polarity of the Ge—H bond increases due to this effect and the $A^{1/2}$ values become greater. As a result the slope of the straight line of eq. 5 becomes smaller.

Proceeding from the above discussion the conclusion was drawn that eq. 5 takes into account the influence of the inductive and σ,σ-conjugation effects on $A^{1/2}$. Therefore the $A_{\text{calc.}}^{1/2}$ values for compounds 1—4 and 8—10 (Table 2) include the contribution from the σ,σ-conjugation while the differences $\Delta A^{1/2} = A_{\text{exp.}}^{1/2} - A_{\text{calc.}}^{1/2}$ characterize only the d_π—p_π interaction effect for compounds 5—7 and 11—13. Hence, the correlation line of eq. 6 describes the points corresponding to compounds with any substituents (including alkyl groups).

It is of interest that the points corresponding to organosilicon compounds with alkyl substituents deviate considerably from the straight line, eq. 7, towards greater $\Delta A^{1/2}$ values. The σ,σ-conjugation effect is smaller in organosilicon compounds than in organogermanes. The line of eq. 8 therefore manifests the influence of the I effect alone on $A^{1/2}$(Si—H), whereas the line of eq. 7 relates the $\Delta A^{1/2}$ values resulting from the d_π—p_π interaction to the $\Sigma\sigma_p$ constants. It is natural that the points corresponding to compounds in which besides the I

effect and d_π—p_π interaction also the σ,σ-conjugation effect is displayed deviate from the straight line of eq. 7.

In conclusion, we consider the data for diethylmethoxygermane and diethylphenoxygermane. The points for these compounds deviate sharply from the correlation line (eq. 6) towards greater $\Delta A^{1/2}$ values. This indicates anomalously high electron-releasing properties of the substituents, probably due to the σ,p-conjugation effect in the $\mathrm{R{-}\overline{O}\overset{\curvearrowright}{-}\underset{|}{\overset{|}{Ge}}\rightarrow H}$ fragments. A detailed investigation of this effect is in progress.

Experimental

The IR spectra were measured on a UR-20 "Zeiss" spectrometer. Heptane solutions (0.04—0.09 mole l^{-1}) were used to obtain the spectra. The integrated intensity of the Ge—H bands, A (mole^{-1} l cm^{-2} × 10^4), was measured by Jogansen's method [32]. Gas—liquid chromatography was used to check the purity of the compounds. The compounds were prepared using methods previously described [33].

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