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FREQUENCIES OF Ge—H STRETCHING MODES AND THE EFFECT OF d_π—p_π INTERACTION IN ORGANOGERMANIUM COMPOUNDS

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Summary

Frequencies of Ge—H stretching modes in triorganogermanes, R_3GeH, in which there is no d_π—p_π bonding between the R substituents and the germanium atom, have been studied. The frequency (ν) is related to the sum of the Taft σ^* constants of the substituents R ($\Sigma\sigma^*$) by the equation $\nu = 23\,\Sigma\sigma^* + 2015$. If R_3GeH molecules contain substituents which can form d_π—p_π bonds with the germanium atom, the frequency ν is determined not only by their I-effect, but also by d_π—p_π interaction. A germanium atom is shown to be less capable of d_π—p_π interaction than a silicon atom.

Introduction

One of the important problems of the chemistry of Group IVB organometallic compounds is that of the participation of vacant *nd*-orbitals of the Group IVB elements in conjugation. Unlike carbon, atoms of silicon, germanium, tin and lead have vacant *d*-orbitals. The energy of these orbitals is close to the *s*- and *p*-orbital energies of the outer electron shell. Therefore compounds of silicon subgroup elements, in contrast to carbon compounds, have physical and chemical properties stemming from available *d*-orbitals. One of these properties is d_π—p_π interaction in fragments M—X (M = Si, Ge, Sn and probably Pb; X is an atom with lone pairs of electrons). In this case, atom M becomes an acceptor of *p*-electrons of atom X thus forming a dative d_π—p_π bond. The principal regularities of d_π—p_π interaction are considered in a number of theoretical [1—6] and experimental works [7—9]. In spite of the great amount of information on this subject, many aspects of the phenomenon of d_π—p_π interaction are still not clearly understood and opinions differ on a number of details. This is because (*a*) the d_π—p_π interaction energy is relatively small, and (*b*) a great deal of investigation in this field has not been sufficiently careful. The same disadvantage is inherent in a number of spectroscopic investigations, as is shown in ref. 9. In spectroscopic studies of d_π—p_π interaction the fulfillment of some conditions [9] is required, including: (*i*) the changes of chemical bond polarity due to the inductive effect of substituents and conjugation effects other than d_π—p_π interaction must be taken into account; (*ii*) series of compounds must be used, in which spectroscopic parameters (a) depend only upon electron effects of substituents, and (b) are sufficiently sensitive to these effects. The above conditions are fulfilled in studies of the d_π—p_π interaction effect based on the investigation of the dependence of frequency and intensity of the Si—H stretching mode on the nature of X-substituents in organosilicon compounds X_3SiH [10—22]. The mode of the Si—H vibration is highly characteristic [23, 24]. The frequency of Si—H stretching mode, ν(Si—H), and intensity of this stretching mode, A(Si—H), are determined by the inductive effect of substituents X and conjugation effects in Si—X bonds [10—22]. By analysing ν(Si—H) and A(Si—H) values d_π—p_π interaction effect has been investigated [15, 18, 21] and σ,σ-, σ,π- and σ,p-conjugation effects in organosilicon compounds have been considered [18—21]. It is known [7—9, 19, 25] that the role of d_π—p_π interaction effect in organogermanium compounds is less significant than that in organosilicon compounds. Therefore for investigating this effect in organogermanium compounds the fulfillment of the conditions mentioned above is even more important. We consider the X_3GeH compounds to be the most convenient for investigating d_π—p_π interaction in organogermanium compounds. Therefore the purpose of the present work was to investigate the dependence of frequencies of the Ge—H stretching mode on the nature of the X substituents in X_3GeH compounds to obtain information about d_π—p_π interaction in Ge—X bonds, and to compare the capacity of silicon and germanium atoms for such interaction.

Results and discussion

The literature contains a number of works [26—31] dealing with study of the frequency of the Ge—H stretching mode. One of the most important conclusions of these is that, as in the case of organosilicon compounds, ν(Ge—H) increases with increase in the electron-attracting ability of X. To a first approximation the electron-attracting ability of X can be characterized by its inductive Taft σ^* constants. However correlation between ν(Ge—H) and $\Sigma\sigma^*$ of three substituents has proved to be no more than approximate [27, 28]. This could be expected *a priori*, as there are no reasons to believe that substituents attached to the germanium atom will affect ν(Ge—H) solely by an inductive mechanism. In addition to the inductive effect of electronegative substituents such as Hal and OAlk there is some d_π—p_π interaction. This accounts for the lack of a correlation between ν(Ge—H) in compounds with substituents and $\Sigma\sigma^*$ of those substituents, and also indicates the necessity for taking correct account of the influence of the inductive effect of substituents on ν(Ge—H) in order to obtain information about d_π—p_π interaction.

TABLE 1

THE FREQUENCIES OF Ge—H BOND STRETCHING IN TRISUBSTITUTED GERMANES CONTAINING SUBSTITUENTS WHICH DO NOT PARTICIPATE IN d_π—p_π INTERACTION

Compound	ν(Ge—H) (cm^{-1})	$\Sigma\sigma^*$
$[(CH_3)_2CH]_3GeH$	1998 [a]	−0.57
$(C_6H_{13})_3GeH$	2008 [b]	−0.486
$(n\text{-}C_4H_9)_3GeH$	2008 [b]	−0.375
$(n\text{-}C_3H_7)_3GeH$	2008 [c]	−0.345
$(C_2H_5)_3GeH$	2008 [d]	−0.3
$(CH_3)_2(C_2H_5)GeH$	2018 [e]	−0.1
$(n\text{-}C_4H_9)_2(CH_2{=}CH{-}CH_2)GeH$	2012 [f]	−0.007
$(n\text{-}C_4H_9)_2(HOCH_2CH_2)GeH$	2014 [g]	−0.05
$(n\text{-}C_4H_9)_2(C_6H_5CH_2)GeH$	2014 [c]	−0.035
$(n\text{-}C_3H_7)_2(HOCH_2CH_2)GeH$	2014 [g]	−0.03
$(C_2H_5)_2(C_6H_5CH_2)GeH$	2014 [e]	+0.015
$(n\text{-}C_7H_{15})(C_6H_5CH_2)GeH$	2015 [c]	+0.268
$(n\text{-}C_4H_9)(C_6H_5CH_2)_2GeH$	2015 [c]	+0.3
$(CH_3)_2(CH_2Br)GeH$	2040 [e]	+1.00
$(CH_3)_2(CH_2Cl)GeH$	2040 [e]	+1.05
$(CH_3)_2(CHCl_2)GeH$	2060 [e]	+1.94

[a] Ref. 33. [b] Ref. 30. [c] Ref. 27. [d] Ref. 31. [e] The present work. [f] Ref. 34. [g] Ref. 35.

The influence of the I-effect of substituents on ν(Ge—H)

As stated above, the calculations indicate that the mode of the Si—H vibration is highly characteristic [23, 24]. Such peculiarity of ν(Si—H) also results from the overall regularity that characterizes the vibrational spectra of organometallic compounds of Group IVB and is known as the "barrier effect" [28]. The atoms of silicon, germanium and tin are a "barrier" for kinematic interactions of radicals or atoms bound to them. Therefore, although theoretical calculations for ν(Ge—H) are absent, the (Ge—H) stretching mode is thought [28, 32] to be highly characteristic, as is ν(Si—H). This is, in fact, the basis of correlations between ν(Ge—H) and Taft-Hammett σ-constants. Thus, based on experimental data, Ge—H stretching is thought to involve almost exclusively Ge—H coordinate variation. The mass of X substituents does not influence the Ge—H stretching in X_3GeH, and mechanical Ge—H bond interactions with vibrations of X substituents are absent. Now, the electronic effects of X substituents are responsible for ν(Ge—H) variations. We think that correct conclusions about d_π—p_π interaction, as one of these effects, can be drawn only from studies of a series of compounds. The series must be selected in such a way that there would be a possibility of dividing total electronic influence of substituents into separate contributions: inductive and conjugative (d_π—p_π interaction). The simplest way of solving this problem lies in the choice of compounds, with substituents which exert only an inductive influence on ν(Ge—H). For this purpose compounds $(CH_3)_2XGeH$ were synthesized, where X = CH_2Cl, CH_2Br and $CHCl_2$. The germanium and halogen atoms in these compounds are separated by a carbon atom, so that the normal d_π—p_π interaction effect is absent. All compounds, the substituents of which do not exhibit normal d_π—p_π bonds with a germanium atom, are listed in Table 1. It is found that ν(Ge—H) values and $\Sigma\sigma^*$ sums of σ^* inductive constants substituents in these compounds are connected by the linear equation 1. Some comments should be made about eqn. 1:

$$\nu = 23\,\Sigma\sigma^* + 2015 \qquad (r = 0.978) \tag{1}$$

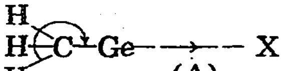
(*a*) Correlation between ν(Ge—H) and $\Sigma\sigma^*$ is quite reasonable in cases when the angles of a germanium atom remain tetrahedral to all substituents, and the influence of substituents on Ge—H bond is transferred uniformly and independently. In the presence of highly branched substituents at a germanium atom deviations from linearity take place.

(*b*) Strictly speaking, the linear relation should not be between ν(Ge—H), and $\Sigma\sigma^*$, but between the force constant of the Ge—H bond (K) and $\Sigma\sigma^*$ [36]. However, as shown by the example of organosilicon compounds X_3SiH, the quadratic equation [36]:

$$K = 4\pi^2 C^2 \mu\nu^2 = \text{const.} \cdot \nu^2$$

can be replaced by a linear equation at small values of K and ν. A linear relation between K and ν also leads to a linear relation between ν and $\Sigma\sigma^*$.

(*c*) Some compounds in Table 1 have methyl groups, bound to a germanium atom. In these compounds in addition to the I-effect one more electronic effect, hyperconjugation (σ,σ-conjugation) (A) may take place. It was shown



(A)

[18, 19] that for organosilicon compounds of the type $(CH_3)_nSi(X)_{4-n}$ σ,σ-conjugation can be detected by IR and NMR spectroscopy only in the case when Si—X bonds are of d_π—p_π character. Similar data are not available in the literature for organogermanium compounds. It may only be presumed, that the larger size of the electron shell of a germanium atom in comparison with that of silicon atom, as well as the larger polarizability of the Ge—C bond will lead to a more prominent role of σ,σ-conjugation effects in organogermanium compounds. Nevertheless, the influence of σ,σ-conjugation on ν(Ge—H) in compounds in Table 1, seems to be small.

(*d*) It was shown earlier [11], that the ν(Si—H) frequencies in organosilicon compounds of X_3SiH are related to $\Sigma\sigma^*$ of substituents X, which do not form d_π—p_π bonds with silicon by the equation $\nu = 23.1\ \Sigma\sigma^* + 2112$. So, straight lines $\nu = a\,\Sigma\sigma^* + b$ for organosilicon and organogermanium compounds have practically identical slopes. Similarly the chemical shifts of the methyl protons, τ, in methylsilanes $(CH_3)_nSiX_{4-n}$ and methylgermanes $(CH_3)_nGeX_{4-n}$ (if M—X bonds are not of d_π—p_π character) are connected with $\Sigma\sigma^*$ by the relations:

$$\tau = 10.00 - 0.140\ \Sigma\sigma^* \text{ and } \tau = 9.90 - 0.146\ \Sigma\sigma^*,$$

respectively [19]. The ν_s(Si—C) and ν_s(Ge—C) frequencies in ethyl-derivatives $(C_2H_5)_nSiX_{4-n}$ and $(C_2H_5)_nGeX_{4-n}$ are related to the electronegativities χ of substituents X, which do not form d_π—p_π bonds, by the equations [25]:

$$\nu_s(\text{Si—C}) = 30.4\,\chi + 530 \text{ and } \nu_s(\text{Ge—C}) = 30.3\,\chi + 474$$

Consequently, if silicon and germanium atoms do not form d_π—p_π bonds, their substituents have a very similar inductive influence.

The d_π—p_π interaction effect in organogermanium compounds

The validity of relation 1 for compounds whose substituents do not form

TABLE 2

THE FREQUENCIES OF Ge—H BOND STRETCHING IN TRISUBSTITUTED GERMANES CONTAINING SUBSTITUENTS CAPABLE OF d_π—p_π INTERACTION

Compound	ν_{calc} (cm^{-1})	ν_{exp} (cm^{-1})	$\Delta\nu$ (cm^{-1})
$(C_2H_5)_2ClGeH$	2077	2064 [a]	13
$(n\text{-}C_4H_9)_2ClGeH$	2075	2060 [a]	15
$(C_2H_5)Cl_2GeH$	2146	2108 [b]	38
$(n\text{-}C_4H_9)Cl_2GeH$	2145	2105 [b]	40
Cl_3GeH	2114	2151 [b]	63
$(C_2H_5)_2BrGeH$	2075	2055 [a]	20
$(n\text{-}C_4H_9)_2BrGeH$	2073	2056 [a]	17
$(C_2H_5)_2IGeH$	2064	2047 [a]	17
$(n\text{-}C_4H_9)_2IGeH$	2063	2048 [a]	15
$(C_6H_5)(C_6H_{11})_2GeH$	2017	2009 [b]	8
$(C_6H_5)Cl_2GeH$	2161	2116 [b]	46
$(C_6H_5)ClBrGeH$	2159	2110 [c]	49
$(C_6H_5)Br_2GeH$	2157	2100 [b]	57
$(C_6H_5)_2FGeH$	2213	2178 [d]	35
$(C_6H_5)_2BrGeH$	2107	2073 [b]	34
$(C_6H_5)_2IGeH$	2097	2065 [b]	32
$(C_6H_5)_3GeH$	2056	2038 [b]	18
$(C_6F_5)_3GeH$	2290	2153 [d]	137
$(C_2H_5)_2(C_6H_5O)GeH$	2065	2038 [d]	27
$(C_2H_5)_2(CH_3O)GeH$	2045	2013 [d]	32
$(C_2H_5)_2GeH$ $\quad\vert$ $OCH_2CH{=}CH(CH_3)$	2045	2014 [d]	81
$(C_2H_5)_2GeH$ $\quad\vert$ $OCH_2CH(CH_3)_2$	2045	2014 [d]	31
$(n\text{-}C_4H_9)_2(C_6H_{11}O)GeH$	2043	2013 [b]	30
$(C_6H_5)(CH_3O)FGeH$	2133	2120 [c]	13
$(C_6H_5)(CH_3O)ClGeH$	2128	2095 [c]	33
$(C_6H_5)(CH_3O)BrGeH$	2126	2090 [c]	36
$(C_6H_5)(CH_3O)IGeH$	2116	2073 [c]	43
$(C_6H_5)(CH_3O)_2GeH$	2095	2064 [c]	31
$(C_6H_5)(C_6H_5CH_2O)ClGeH$	2130	2097 [c]	33
$(C_6H_5)(C_6H_5CH_2O)BrGeH$	2171	2091 [c]	40
$(C_6H_5)(C_6H_5CH_2O)_2GeH$	2097	2067 [c]	30

[a] Ref. 31. [b] Ref. 29. [c] Ref. 40. [d] The present work.

d_π—p_π bonds with a germanium atom makes it possible to evaluate the strictly inductive effect of any substituents (including those capable of d_π—p_π interaction) upon ν(Ge—H). In this case it is necessary to assume that the inductive effect of substituents incapable of d_π—p_π interaction, as well as the inductive effect of groups forming d_π—p_π bonds with a germanium atom, are subject to the same relation 1. The rigorous theoretical substantiation of such an assumption is at present absent. Such an assumption has been shown not to be arbitrary in the chemistry of organophosphorus compounds [37]. In any case, it is no more random, than the assumptions made for separating inductive and resonance constants in aromatic series, which do not prevent the successful use of these constants [38].

The frequencies $\nu_{calc.}$ (Table 2) were calculated according to equation $\nu = 23\ \Sigma\sigma^* + 2015$ for organogermanium compounds having substituents capable of d_π—p_π interaction. The values of ν_{calc} were found to be more than the experimentally measured frequencies $\nu_{exp.}$ in all cases. The differences $\Delta\nu = \nu_{calc.} - \nu_{exp.}$ are positive. d_π—p_π interaction in Ge—X bonds acts in the opposite direction to the action of the I-effect of X. Formally this is equivalent to decreasing the I-effect

TABLE 3

$\Delta\nu$ VALUES FOR COMPOUNDS R′R″R‴MH, (cm^{-1})

No	Substituents R′R″R‴	M	
		Si [a]	Ge
1	Alk_2Ph	9	7
2	Alk_2I	10	16
3	Alk_2Br	15	18
4	$AlkPh_2$	18	14
5	Alk_2PhO	18	27
6	$Alk_2(MeS)$	22	25
7	Alk_2Cl	22	15
8	Ph_3	27	20
9	Ph_2Br	35	34
10	Ph_2F	37	34
11	$AlkCl_2$	38	39
12	$Alk_2(AlkO)$	38	31
13	$AlkBr_2$	42	41
14	$PhCl_2$	48	46
15	Cl_3	55	56
16	$PhBr_2$	62	57
17	$(C_6F_5)_3$	161	137

[a] $\Delta\nu$ values are taken from refs. 11—21.

of X. In this case the force constant of the Ge—H bond decreases. Consequently $\nu_{exp.}$ decreases in comparison with $\nu_{calc.}$, i.e. $\Delta\nu$ values increase (Table 2). Thus, conjugation effects between a germanium atom and an X substituent are responsible for the increase in $\Delta\nu$. The largest of these effects is d_π—p_π interaction. This conclusion is confirmed by the following. Previously, values of $\Delta\nu$ that indicate d_π—p_π interaction in organosilicon compounds have been obtained [11—21, 36]. In Table 3 we give these together with $\Delta\nu$ values for organogermanium compounds.

The relationship between these two sets of values is given by the straight line equation (see Fig. 1):

$$\Delta\nu_{Si} = 1.17\ \Delta\nu_{Ge} - 4 \qquad (r = 0.988) \qquad (2)$$

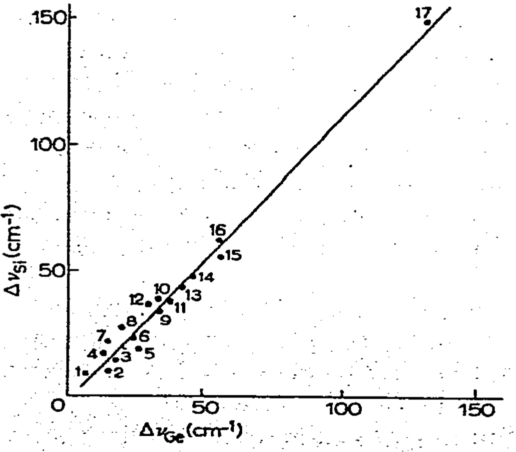


Fig. 1. The interdependence of $\Delta\nu_{Si}$ and $\Delta\nu_{Ge}$. The numbering of the points is in accordance with Table 3.

Equation 2 shows that the straight line correlation between the $\Delta\nu$ values for organosilicon and organogermanium compounds passes very close to the origin, especially when the accuracy of the $\Delta\nu$ values is considered. Besides giving the slope, eqn. 2 reveals that $\Delta\nu$ values are smaller in organogermanium compounds than those in organosilicon compounds. This is indicative of a lower ability of a germanium atom to take part in d_π—p_π interaction. In addition the linear character of relation 2 and rather high correlation coefficient show that the main features of d_π—p_π interaction with silicon and germanium atoms are the same. Yet it is clear that in organogermanium compounds in principle some other types of conjugation involving *d*-orbitals can be realized as well; for example d_π—d_π interaction. We propose to investigate this later.

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 spectra. Previously studied compounds containing Ge—H bond were used to check the calibration.

Diethylbenzylgermane was prepared by action of benzylmagnesium chloride in excess upon diethylgermane (4g) in tetrahydrofuran. After boiling (5 h), hydrolysis and evaporation of the solvent in vacuo, the residue was distilled in vacuo. Diethylbenzylgermane (2.16 g, 50%) was isolated, b.p. 110°/12 mm, n_D^{20} = 1.5250.

Dimethyl(chloromethyl)germane was prepared by a published method [41].

Dimethyl(dichloromethyl)germane was obtained by reducing dimethyl(dichloromethyl)chlorogermane with lithium aluminium hydride. Dimethyl(dichloromethyl)chlorogermane was formed along with dimethyl(chloromethyl)chlorogermane by chlorination of trimethylchlorogermane according to the procedure given in ref. 42. Dimethyl(dichloromethyl)germane was isolated as an admixture with 10% dimethyl(chloromethyl)germane.

Dimethyl(bromomethyl)germane was prepared by a procedure described for the synthesis of similar silicon compounds [43]. The method includes bromination of trimethylchlorogermane by a Cl_2/Br_2 mixture. Dimethyl(bromomethyl)germane formed by bromination and subsequent reduction with $LiAlH_4$ contained 20% of dimethyl(chloromethyl)germane.

Diethylphenoxygermane was obtained by interaction of diethylmethoxygermane with phenol, b.p. 116—117°/18 mm, n_D^{20} = 1.5192.

Diethyl(isobutyoxy)germane was prepared by the interaction of diethylmethoxygermane with isobutyl alcohol, b.p. 63°/14 mm, n_D^{20} = 1.4322.

Diethylmethoxygermane [44], diethyl(3-methylallyloxy)germane [45], diphenylfluorogermane [40], and tris(pentafluorophenyl)germane [46] were all prepared as described in the literature.

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