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INFRARED STUDY OF SOME SPECIFICITIES OF THE d_π—p_π INTERACTION IN ORGANOGERMANIUM COMPOUNDS

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Summary

The analysis is presented for the frequencies of stretching modes ν(Ge—H) in the IR spectra of organogermanium compounds R_2XGeH, RX_2GeH, RXYGeH, X_2YGeH and $XYGeH_2$ (where R is a substituent which does not make a d_π—p_π bond with germanium, and X and Y are groups capable of d_π—p_π interaction with germanium). It is shown that ν(Ge—H) in these compounds is dependent on both the —*I* effect of R, X and Y, and the d_π—p_π interaction in Ge—X and Ge—Y bonds. If only one substituent capable of d_π—p_π interaction with germanium is present, the value of such an effect is determined by its σ_R constant. However, when germanium is bound to several substituents capable of d_π—p_π interaction its magnitude depends on the effective charge at germanium which is determined by the inductive and mesomeric effects of X and Y. The data obtained are compared to the dependences observed in the IR spectra of similar organosilicon compounds.

Introduction

Unlike the carbon atom which may produce p_π—p_π multiple bonds the silicon subgroup elements afford no such bonds under normal conditions. However, unlike carbon, such elements may expand their valence shells owing to their *d* orbitals generating additional chemical bonds [1-3]. These bonds may be of σ- or π-type. If σ-bonds are formed the silicon subgroup elements become penta- or hexavalent. Such bonds are found in $MX_4 \cdot L_2$ and $MX_4 \cdot L$ compounds, where

M is an element of the silicon subgroup and L is a ligand possessing a lone electron pair. If π-bonds are formed the silicon subgroup elements become formally tetravalent but the multiplicities of M—X bonds in MX_4 increase. The M—X bond multiplicity will increase only when the X substituent has lone electron pairs or if it is an α,β-unsaturated hydrocarbon radical. In this case the p-electrons are partially delocalized over the vacant nd-orbitals of M (d_π—p_π interaction). The data available [1] demonstrate that the ability towards additional σ-bonds formation increases with the atomic number of M. On the other hand the d_π—p_π interaction effect decreases with increasing atomic number. Thus, this effect is probably absent for lead derivatives.

d-Orbital participation may essentially affect the chemical and physical properties of Group IVB organometallics (e.g. refs. 1-9). The role of d-orbitals in chemical bond formation is obviously different in the ground and excited electronic states [1].

The present paper is concerned with one aspect of this vast problem: the effect of d_π—p_π interaction on the strength of the chemical bond in the ground states of organogermanium compounds. The authors' aim was to study the d_π—p_π interaction of germanium atom with one, two and three substituents, to compare the results obtained with dependences observed in similar organosilicon compounds, and to provide further information on the nature of the d_π—p_π interaction effect. IR spectroscopy was employed as the investigation tool.

It should be noted that the energy of the d_π—p_π interaction effect is rather small. Correct investigation techniques should thus be used. It has been shown [3,10] that the following conditions should be satisfied in a spectroscopic study of the d_π—p_π interaction. *(a)* Besides the d_π—p_π interaction, account should be taken of the chemical bond polarity in the presence of inductive and other conjugation effects. *(b)* Sets of compounds should be used with spectroscopic parameters (i) depending only upon substituent electronic effect, (ii) sufficiently sensitive to the action of such effects. These conditions are entirely satisfied by organosilicon and organogermanium compounds of the type X_3MH (M = Si, Ge). It has been shown that the shapes of Si—H [11,12] and Ge—H [10,13] stretching modes are highly characteristic. The M—H vibrations occur with the change of practically only the M—H coordinate. Mechanical interaction of the M—H bond with substituent X vibrations are virtually absent in X_3MH, and the mass of X does not affect the M—H vibration. However, the frequency of the M—H stretching mode, ν(M—H), and its intensity, A(M—H), do not remain constant when X is varied. This may be explained by the inductive effect of X and conjugation effects in the Si—X and Ge—X bonds [10,13-26]. The influence of inductive and conjugation effects on ν and A may be separated by means of correlational analysis. For such purposes it is necessary to have a sufficiently large series of X_3MH compounds where the X substituents display only an inductive effect on ν and A. This technique has been used in the study of d_π—p_π interaction with one [19] or more [20,21,25] substituents, in elucidating the nature of the d_π—p_π interaction effect [19,22,25] and in the study of σ,σ-, σ,π- and σ,p-conjugation [22-25] in organosilicon compounds. A study of ν(Ge—H) in the IR spectra of organogermanium compounds demonstrated that the effect of d_π—p_π interaction in such compounds in smaller than in their organosilicon analogs [10]. The present paper is a continuation of these investigations.

Results and discussion

Earlier we showed [10,13] that ν(Ge—H) in triorganogermanes, R_3GeH, where R produces no d_π—p_π bonds with the germanium atom, is proportional to the sum of Taft's σ^*-constants of the R substituents ($\Sigma\sigma^*$) (eqn. 1). By assuming [10] that for substituents capable of d_π—p_π interaction with germanium, the inductive effect obeys eqn. 1 as well, one may estimate with sufficient accuracy the influence of the —*I* effect of such substituents on ν(Ge—H). The values ν_{ind} estimated from eqn. 1 are greater than experimental frequencies (ν_{exp}).

$$\nu_{ind} = 23\Sigma\sigma^* + 2015 \qquad (1)$$

The inductive —*I* effect of X and the d_π—p_π interaction in the Ge—X bond act in opposite directions. Thus the presence of a d_π—p_π interaction in a Ge—X bond effectively decreases the —*I* effect of X. In terms of eqn. 1 this is a decrease of ν_{exp} with respect to ν_{ind} estimated for a purely inductive effect of X on ν(Ge—H). The difference $\Delta\nu = \nu_{ind} - \nu_{exp}$ may be assigned to the influence of conjugation effects. In Ge—X bonds the main effect is d_π—p_π interaction. We have previously analyzed values of $\Delta\nu$ for some organogermanium compounds [10]. It was found that $\Delta\nu_{Ge}$'s of germanium derivatives and $\Delta\nu_{Si}$'s values determined by a similar method [10,13] for organosilicon compounds show a linear relationship (eqn. 2). It follows from eqn. 2 that *(a)* the character of d_π—p_π interaction for silicon and germanium atoms is the same, and *(b)* germanium is less capable of d_π—p_π interaction than silicon.

In the present paper the similarities and differences between $\Delta\nu_{Ge}$ and $\Delta\nu_{Si}$ are analyzed in more detail. Apart from compounds of the type X_3GeH we decided to consider ν(Ge—H)'s in X_2GeH_2 compounds in order to include $\Delta\nu$'s for a greater number of compounds.

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

The influence of —I effect of substituents on ν(Ge—H) in diorganylgermanes

In the case of $(R_i)_2GeH_2$ compounds isolation of the contribution to ν(Ge—H) of the d_π—p_π interaction is more complicated than determination of the value of $\Delta\nu$ for $(R_i)_3GeH$ compounds. This is explained by the fact that not many $(R_i)_2GeH_2$ compounds were investigated whose R_i substituents were incapable of a d_π—p_π interaction with germanium. We compared ν_{exp} in six diorganylgermanes to ν_{calc} from eqn. 1 which is valid in the case of triorganylgermanes $(R_i)_3GeH$ in the terms of the above discussion. One of the hydrogen atoms in $(R_i)_2GeH_2$ was considered to be a substituent.

It follows from Table 1 that the values ν_{calc} computed from eqn. 1 for diorganylgermanes were below experimental values ν_{exp} on average by 14 cm^{-1}. This demonstrates that the lines obtained from eqn. 1 and ν(Ge—H) vs. $\Sigma\sigma^*$ are parallel for $(R_i)_2GeH_2$ compounds. This is also specific in the spectra of organylsilanes. The shift between correlation curves in diorganylsilanes and triorganylsilanes is 9 cm^{-1} [30]. Hence the frequency of the stretching mode ν(Ge—H) in $(R_i)_2GeH_2$ is linearly dependent on the sum of the inductive Taft constants of the three substituents: $\Sigma\sigma^* = \sigma^*_{R'} + \sigma^*_{R''} + \sigma^*_{H}$.

$$\nu_{ind} = 23\Sigma\sigma^* + 2029 \qquad (3)$$

TABLE 1

THE FREQUENCIES OF STRETCHING MODES ν(Ge—H) IN THE IR SPECTRA OF DIORGANYLGERMANES WITH SUBSTITUENTS INCAPABLE OF d_π—p_π INTERACTION WITH GERMANIUM

No.	Compound	$\Sigma\sigma^*$	ν_{exp} (cm^{-1})	ν_{calc} (cm^{-1})	$\Delta\nu^a$ (cm^{-1})
1	$(C_7H_{15})_2GeH_2$	0.17	2033^b	2019	14
2	$(C_6H_{13})_2GeH_2$	0.17	2033^b	2019	14
3	$(C_4H_9)_2GeH_2$	0.23	2036^c	2020	16
4	$(C_2H_5)_2GeH_2$	0.29	2037^c	2022	15
5	$(C_2H_5)(CH_3CH{=}CHCH_2)GeH_2$	0.52	2040^d	2027	13
6	$(C_2H_5)(HOCH_2CH_2)GeH_2$	0.59	2040^d	2028	12

[a] $\Delta\nu_{av}$ = 14 cm^{-1}. [b] Ref. 27. [c] Ref. 28. [d] Ref. 29.

Diorganylgermanes display the same behaviour as triorganylgermanes. Firstly the ν(Ge—H) mode is highly characteristic: ν(Ge—H) is unaffected by the mass of the variable substituent, and there is no mechanical link between ν(Ge—H) and substituent vibrations. Secondly on proceeding to substituents capable of d_π—p_π interaction with the germanium atom the experimental ν(Ge—H) values (ν_{exp}) are below ν_{ind} computed from eqn. 3. The differences $\Delta\nu = \nu_{ind} - \nu_{exp}$ are a quantitative measure of the conjugation effect between germanium and the X substituent. Analogously to triorganylgermanes [10] the d_π—p_π interaction is predominant. Some $\Delta\nu$ values of diorganylgermanes will be discussed later.

d_π—p_π interaction of the germanium atom with one substituent

Theoretical studies [4,8,22] demonstrate that the value of the d_π—p_π

TABLE 2

THE FREQUENCIES OF STRETCHING VIBRATIONS ν(Ge—H) IN THE IR SPECTRA OF ORGANYLGERMANES

No.	Compound	ν_{ind} (cm^{-1})	ν_{exp} (cm^{-1})	$\Delta\nu$ (cm^{-1})	σ_R
1	$(C_4H_9)_2(C_6H_5)GeH$	2022	2015^a	7	−0.09
2	$(C_6H_{11})_2(C_6H_5)GeH$	2017	2009^a	8	−0.09
3	$(C_2H_5)(C_6H_5)GeH_2$	2053	2045^b	8	−0.09
4	$(C_4H_9)_2IGeH$	2063	2048^c	15	−0.20
5	$(C_2H_5)_2IGeH$	2064	2047^c	17	−0.20
6	$(C_2H_5)IGeH_2$	2093	2075^d	18	−0.20
7	$(C_2H_5)_2BrGeH$	2075	2055^c	20	−0.22
8	$(C_4H_9)_2BrGeH$	2073	2056^c	17	−0.22
9	$(C_2H_5)BrGeH_2$	2103	2084^a	19	−0.22
10	$(C_2H_5)_2(C_2H_5S)GeH$	2037	2017^a	20	−0.22
11	$(C_2H_5)ClGeH_2$	2106	2091^a	15	−0.24
12	$(C_4H_9)ClGeH_2$	2105	2090^a	15	−0.24
13	$(C_4H_9)_2ClGeH$	2075	2059^a	16	−0.24
14	$(C_2H_5)_2ClGeH$	2077	2059^f	18	−0.24
15	$(C_2H_5)_2(C_6H_5O)GeH$	2065	2037^f	28	−0.41
16	$(C_2H_5)_2(CH_3O)GeH$	2045	2014^f	31	−0.52
17	$Alk_2(AlkO)GeH$	2045	2014^f	31	−0.53

[a] Ref. 31. [b] Ref. 32. [c] Ref. 33. [d] Ref. 34. [f] This work.

interaction effect (if the d_π- and p_π-orbital overlap integrals of Ge and X are taken to be a measure of such an effect) depends on the charge at the germanium atom and on the number of X substituents bound to germanium. Thus it is reasonable to start the analysis of d_π—p_π interaction with the most simple case, i.e. only one X substituent bound to the germanium atom and capable of a d_π—p_π interaction (Table 2).

It has been shown previously that the mechanism of d_π—p_π interaction of some substituents with a silicon atom is formally similar to their conjugation with an aromatic ring or vinylic group [19,35]. Germanium is the closest analog to silicon in Group IVB of the Periodic Table. Thus there is great similarity between the chemical bonds in organosilicon and germanium compounds. On the other hand some differences may be due to e.g. the higher polarizability of germanium with respect to silicon [1]. It was of interest to compare the specificities of d_π—p_π interaction in the organosilicon and germanium compounds.

Table 2 lists the values of $\Delta\nu'_{\mathrm{Ge}}$ estimated from eqns. 1 and 3. The compounds shown in Table 2 have only one X substituent producing d_π—p_π bonds with germanium. Thus it is natural to suggest that the value of the d_π—p_π interaction effect in these compounds should be determined by the ability of the X substituent to release its lone pair electron to the vacant germanium d-orbitals. It is already known [36] that σ_R constants are a quantitative measure of the ability of a substituent to conjugate with the benzene ring. The constants σ_R are related to the Hammett σ_p constants (specifying the inductive and mesomeric substituent effects) by the equation $\sigma_R = \sigma_p - \sigma_I$. σ_R constants are widely used in correlating chemical reactions and physical properties [37] since it has been found e.g., that they govern the substituent ability to conjugate with vinylic groups [35] and to participate in d_π—p_π interaction with the silicon atom [19,22,25]. We demonstrate that the values of $\Delta\nu'_{\mathrm{Ge}}$ characterizing the d_π—p_π interaction effect in the compounds of Table 2 depend linearly on the σ_R constants of substituents producing d_π—p_π bonds with germanium (eqn. 4) (least squares method, $r = 0.961$) (Fig. 1). Earlier it was shown [19] that in organosilicon compounds with a single substituent capable of d_π—p_π interaction with the silicon atom the values $\Delta\nu'_{\mathrm{Si}}$ and σ_R obey the relation:

$$\Delta\nu'_{\mathrm{Ge}} = -53\sigma_R + 4 \qquad (4)$$

$$\Delta\nu'_{\mathrm{Si}} = -66\sigma_R + 3 \qquad (5)$$

Attention may be drawn to the lower gradient in eqn. 4 in comparison with eqn. 5. This indicates that in producing d_π—p_π bonds with its substituents the germanium atom is less electron attracting than silicon. Thus when one substituent capable of d_π—p_π interaction is bound to germanium or silicon then the interaction is weaker in the organogermanium.

Let us now consider d_π—p_π interaction with several substituents at the germanium atom capable of forming d_π—p_π bonds.

d_π—p_π interaction of the germanium atom with two identical substituents

Let us analyze the values of $\Delta\nu$ in RX_2GeH compounds containing two substituents X capable of d_π—p_π interaction with the germanium atom (Table 3). On going from R_2XGeH to RX_2GeH $\Delta\nu$ varies depending on X. For $X = C_6H_5$,

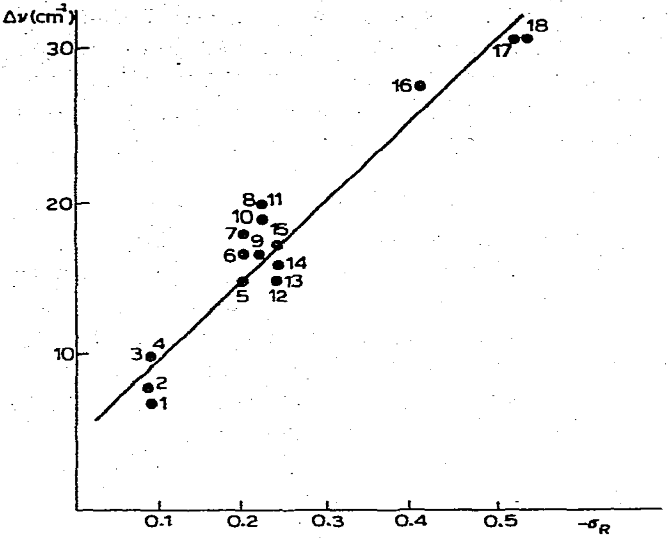

Fig. 1. The interdependence of $\Delta\nu_{Ge}$ and σ_R of substituent X in the compounds Alk_nXGeH_{3-n}.

Cl, Br and I the values of $\Delta\nu$ are increasing, while for X = OC_6H_5 these values decrease. These observations may be explained in the following manner. Theory states [4,8,22] that the d_π—p_π interaction is enhaced in the presence of an effective positive charge at the atom possessing vacant *d*-orbitals. A charge on the germanium atom may be induced by the introduction of typical electron attracting substituents into the germane. However, these substituents, owing to their —*I* effect, may induce a positive charge at the germanium atom whilst at the same time participating in d_π—p_π interaction with the germanium *d*-orbitals. In this case a shift of electron density to the germanium atom occurs with the appearance of some negative charge at the germanium. The value and sign of the resultant effective charge at germanium atom (in the case of two or more such substituents) depend on the relative role of the inductive and mesomeric effects of the substituents. Thus the effect of X substituents on the total d_π—p_π interaction effect in the molecule is determined by the relation of the donor and acceptor properties of these substituents. Thus, series of the relative ability of X substituents to produce d_π—p_π interaction drawn on the basis of a simple comparison of $\Delta\nu_{exp}$ are not the same in the two types of compound, R_2XGeH and RX_2GeH.

Hence, the primary reason for the values $\Delta\nu$ in RX_2GeH compounds not being additive of $\Delta\nu'$'s observed in R_2XGeH compounds must be the change in the effective charge at the germanium atom. The second reason for deviation from additivity is the dependence of group overlap integrals on molecular geometry. The strength of the d_π—p_π bonds generated is determined by p_π- and d_π-orbital overlap integrals of X and Ge [8]. If the bond angles of germanium are almost tetrahedral then the group overlap integrals of GeX_2 and the two-centre overlap integrals (*s*) of Ge—X bonds obey the relation $\sqrt{4/3}s$ [8]. The following conclusion is drawn. If the degree of d_π—p_π interaction in the molecule were independent of the effective charge at germanium then it would be expected that the experimental values $\Delta\nu_{exp}$ in RX_2GeH compounds and the values $\Delta\nu'_{Ge}$

TABLE 3

THE VALUES $\Delta\nu$ IN THE IR SPECTRA OF RX_2GeH ORGANYLGERMANES

No.	Compound	ν_{ind} (cm^{-1})	ν_{exp} (cm^{-1})	$\Delta\nu_{exp}$ (cm^{-1})	$\Delta\nu'_{Ge}$ (cm^{-1})	$\Delta\nu_{calc}$ (cm^{-1})	$\Delta(\Delta\nu)_{Ge}$ (cm^{-1})	σ_p
1	$(C_2H_5)(C_6H_5O)_2GeH$	2123	2110[a]	13	28	32	−19	−0.32
2	$(C_6H_{13})(C_6H_5)_2GeH$	2039	2025[b]	14	7	8	6	0.01
3	$(C_4H_9)(C_6H_5)_2GeH$	2040	2025[b]	15	7	8	7	0.01
4	$(C_2H_5)I_2GeH$	2121	2095[c]	26	16	18	8	0.18
5	$(C_2H_5)Cl_2GeH$	2147	2108[d]	39	18	21	18	0.22
6	$(C_4H_9)Cl_2GeH$	2145	2105[d]	40	18	21	19	0.22
7	$(C_2H_5)Br_2GeH$	2141	2100[c]	41	19	22	19	0.23
8	$(C_4H_9)Br_2GeH$	2140	2098[d]	42	19	22	20	0.23

[a] This work. [b] Ref. 32. [c] Ref. 34. [d] Ref. 31.

in R_2XGeH obey the relation: $\Delta\nu_{exp} = \sqrt{4/3}\Delta\nu'_{Ge}$. However, a deviation from this relation is observed. The expected values ($\Delta\nu_{calc}$) computed from eqn. 6 (where $\Delta\nu'_{Ge}$ are values of $\Delta\nu$ for compounds R_2XGeH) deviate from those obtained experimentally for compounds RX_2GeH (Table 3). The differences

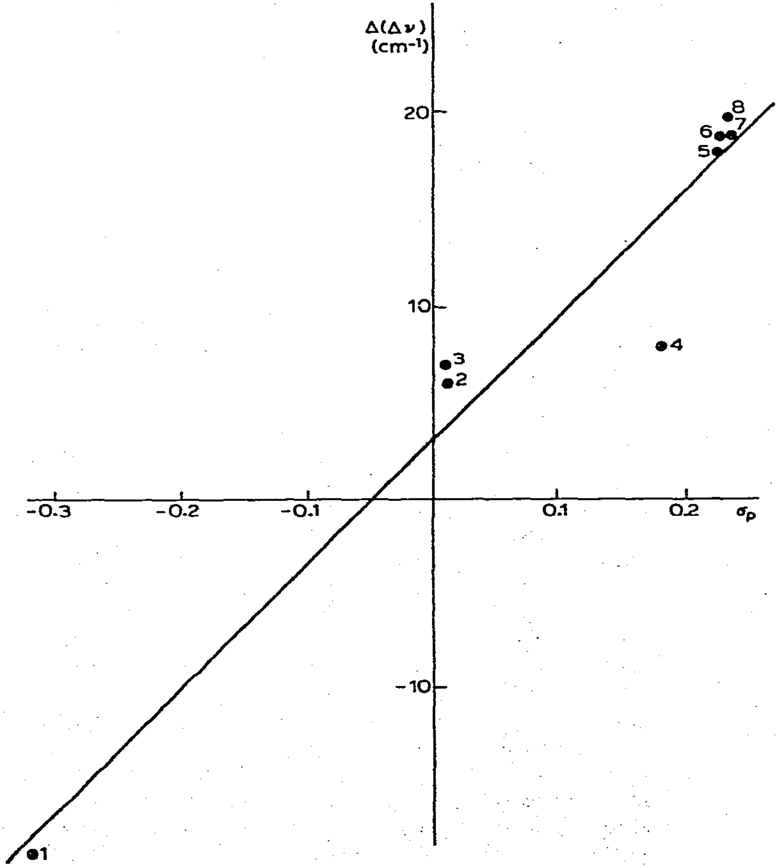

Fig. 2. The interdependence of $\Delta(\Delta\nu)$ and σ_p of substituent X in the compounds $AlkX_2GeH$.

$\Delta(\Delta\nu)_{Ge} = \Delta\nu_{exp} - \Delta\nu_{calc}$ that occur in RX_2GeH compounds are a result of the change of effective charge at the germanium atom when X is varied. The charge at germanium induced by the X substituent may be accounted for by the Hammett σ_p constant. It is known that $\sigma_p = \sigma_R + \sigma_I$. The σ_I constant specifies the $-I$ effect of the X substituent while σ_R characterizes the ability of this substituent to conjugate. Hence the values $\Delta(\Delta\nu)_{Ge}$ and σ_p are linearly dependent (eqn. 7) (least squares method, $r = 0.963$) (Fig. 2). For similar organosilicon compounds the following relation is observed:

$$\Delta\nu_{calc} = \sqrt{4/3}\,\Delta\nu'_{Ge} \tag{6}$$

$$\Delta(\Delta\nu)_{Ge} = 67\sigma_p + 3 \tag{7}$$

$$\Delta(\Delta\nu)_{Si} = 92\sigma_p \text{ [20]} \tag{8}$$

Thus the degree of d_π—p_π interaction in RX_2MH (M = Si, Ge) compounds is determined by the effective charge at M. With an increase of positive charge on M (i.e. an increase of σ_p's) the d_π—p_π interaction is enhanced. The greater gradient of the line in eqn. 8 with respect to eqn. 7 indicates that, unlike organogermanium compounds, in the organosilicon compounds the same increase of positive charge on M results in the greater d_π—p_π interaction. This may due to the fact that silicon d-orbitals are less diffuse. Thus in organosilicon compounds overlap of the p_π-orbitals of X with the d_π-orbitals of silicon is more favourable.

TABLE 4

THE VALUES OF $\Delta\nu$ IN THE IR SPECTRA OF ORGANYLGERMANES X_2YGeH, RXYGeH AND $XYGeH_2$

No.	Compound	ν_{ind} (cm^{-1})	ν_{exp} (cm^{-1})	$\Delta\nu_{exp}$ (cm^{-1})	$\Delta\nu_{add}$ (cm^{-1})	$\delta(\Delta\nu)_{Ge}$ (cm^{-1})	$\Sigma\sigma_p$
1	$(C_6H_5)_2(CH_3O)GeH$	2076	2065[a]	11	39	—28	—0.25
2	$(C_6H_5)(CH_3O)GeH_2$	2088	2064[a]	24	38	—14	—0.26
3	$(C_2H_5)(CH_3O)ClGeH$	2113	2076[b]	37	49	—12	—0.05
4	$(C_2H_5)(CH_3O)BrGeH$	2110	2070[b]	40	50	—10	—0.04
5	$(C_6H_5)(CH_3S)GeH_2$	2082	2061[a]	21	31	—10	—0.04
6	$(C_2H_5)(CH_3O)IGeH$	2100	2060[b]	40	47	—7	0.00
7	$(C_6H_5)ClGeH_2$	2122	2097[c]	25	25	0	0.23
8	$(C_6H_5)BrGeH_2$	2118	2089[c]	29	26	3	0.24
9	$(C_6H_5)IGeH_2$	2109	2083[c]	26	23	3	0.28
10	$(C_6H_5)_2ClGeH$	2109	2077[c]	32	26	6	0.24
11	$(C_6H_5)_2BrGeH$	2107	2073[c]	34	27	7	0.25
12	$(C_6H_5)Cl(C_6H_{13})GeH$	2092	2060[a]	32	25	7	0.23
13	$(C_6H_5)_2IGeH$	2097	2065[c]	32	24	8	0.29
14	$(C_6H_5)Cl_2GeH$	2162	2116[c]	46	28	18	0.45
15	$(C_6H_5)Br_2GeH$	2156	2100[c]	56	29	27	0.47
16	$(C_6H_5)I_2GeH$	2137	2077[c]	60	25	35	0.55
17	Cl_2BrGeH	2212	2144[d]	68	40	28	0.67
18	$ClBr_2GeH$	2210	2135[d]	75	40	35	0.68
19	$(C_6H_5)FGeH_2$	2125	2102[a]	23	34	—11	0.07
20	$(C_6H_5)_2FGeH$	2113	2082[c]	31	35	—4	0.09
21	$(C_6H_5)F_2GeH$	2171	2135[c]	36	38	—2	0.13

[a] Ref. 32. [b] Ref. 38. [c] Ref. 31. [d] Ref. 39.

d_π—p_π *interaction of the germanium atom with various substituents*

The data available on ν(Ge—H)'s in compounds of the type RXYGeH, X_2Y-GeH and $XYGeH_2$ [31,32,38,39], where X and Y are different types of substituent, enable us to discuss the changes in d_π—p_π interaction upon variation of X and Y. Let us compare $\Delta\nu_{exp}$'s in these compounds with calculated $\Delta\nu_{add}$'s (Table 4).

The values $\Delta\nu_{add}$ were obtained in the following manner. For compounds of the type RXYGeH and $XYGeH_2$ the values $\Delta\nu_{add}$ are simply an addition of $\Delta\nu$'s observed in R_2XGeH and R_2YGeH. (R's are substituents incapable of d_π—p_π interaction with germanium). Taking account of overlap integrals mentioned above $\Delta\nu_{add}$ values for X_2YGeH were estimated from the formula:

$$\Delta\nu_{add} = \sqrt{4/3}\Delta\nu(\text{Ge—X}) + \Delta\nu(\text{Ge—Y})$$

where $\Delta\nu$(Ge—X) and $\Delta\nu$(Ge—Y) are the values of $\Delta\nu$ in R_2XGeH and R_2YGeH. This shows that the $\Delta\nu_{add}$ values are more approximate than those values found in the previous section. It can be seen from Table 4 that in most cases the values $\Delta\nu_{add}$ differ considerably from $\Delta\nu_{exp}$'s in the compounds with more than one type of substituent. Thus, if different types of substituents are present in the molecule the degree of d_π—p_π interaction depends essentially on the nature of X and Y substituents.

In the previous section it was shown that d_π—p_π interaction is determined by the donor or attractor properties of substituents and thus the change of the charge at the germanium atom. It is evident from the above discussion that the

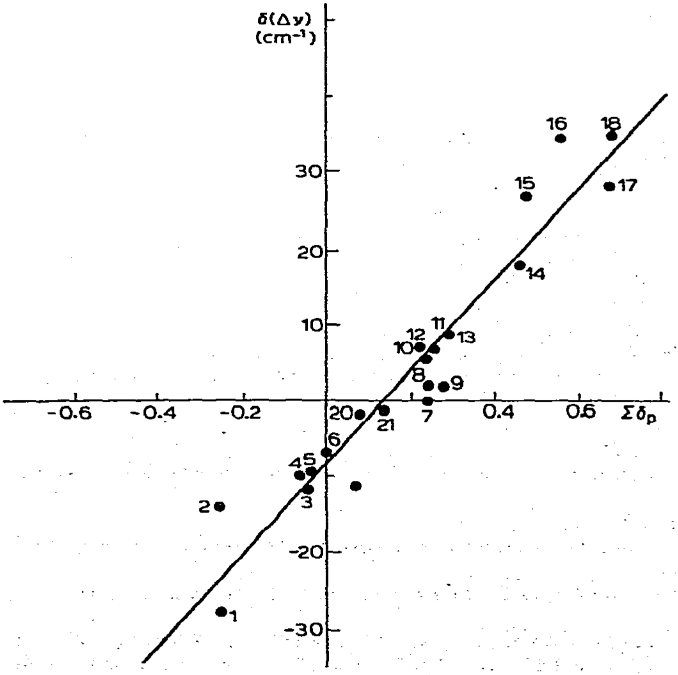

Fig. 3. The interdependence of $\delta(\Delta\nu)$ and $\Sigma\sigma_p$ of substituents in the compounds X_2YGeH, AlkXYGeH and $XYGeH_2$.

sum of the σ_p constants for the substituents participating in d_π—p_π bonds gives values which are proportional to the charge at the germanium atom. It is seen from Table 4 that the values of $\Sigma\sigma_p$ are proportional to the values $\delta(\Delta\nu)_{Ge} = \Delta\nu_{exp} - \Delta\nu_{add}$. Figure 3 shows the dependence of $\delta(\Delta\nu)_{Ge}$ on $\Sigma\sigma_p$ which is governed by eqn. 9 (least squares method, $r = 0.965$). In spite of the fact that no ν(Ge—H) values for R_2FGeH compounds are available it is possible to estimate the d_π—p_π interaction in compounds containing a Ge—F bond. The value $\Delta\nu'_{Ge}$ of R_2FGeH (27 cm^{-1}) was computed from eqn. 4 to obtain σ_R for fluorine. Using experimental values of ν(Ge—H) (compounds 19-21, Table 4) we obtained the values $\Delta\nu_{exp}$, $\Delta\nu_{add}$ and $\delta(\Delta\nu)_{Ge}$. It may be seen from Fig. 3 that $\delta(\Delta\nu)$ vs. $\Sigma\sigma_p$ in compounds 19-21 also obeys eqn. 9.

$$\delta(\Delta\nu)_{Ge} = 61\Sigma\sigma_p - 8 \tag{9}$$

Equation 10 holds for organosilicon compounds with different types of substituents. Thus d_π—p_π interaction in compounds with different types substituents, in analogy to those with one type of substituent, is determined essentially by the charges at the silicon and germanium atoms. A comparison of eqns. 9 and 10 shows that increase of the positive charge at the central atom results in a greater d_π—p_π interaction in the organosilicon than the germanium compound.

$$\delta(\Delta\nu)_{Si} = 89\Sigma\sigma_p - 19 \text{ [25]} \tag{10}$$

In conclusion it may be pointed out that some differences in the parameters of linear eqns. 7 and 9 and in eqns. 8 and 10 may be due to different numbers of compounds investigated with identical and different substituents as well as to the result of less accurate determinations of $\delta(\Delta\nu)$'s (with respect to $\Delta(\Delta\nu)$'s) in the compounds with different substituents.

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