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Effect of d_π–p_π Interaction in Organic Compounds of Group IVB Elements

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The behaviour of organic derivatives of Group IVB elements is markedly influenced by d_π–p_π interaction in the ground and excited states. Chemical and physical techniques are nowadays widely used to investigate d_π–p_π interaction. This review deals with the results of certain spectroscopic (NMR and infrared) studies on this effect. The experimental data obtained by NMR and infrared spectroscopy have been compared in a number of cases with the results obtained by other research techniques. The bibliography includes 222 references.

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I. INTRODUCTION

Silicon, germanium, tin, and lead atoms have vacant d orbitals in contrast to carbon. The orbitals have energies close to those of the s and p orbitals in the outer electronic shell. As a result, organic derivatives of these elements have some chemical and physical properties which are not typical of the carbon analogues with the same structures and are due to the presence of d orbitals in the central atom[1]. Of these properties, the present review deals only with the phenomenon of d_π–p_π bonding. The formation of a bond of this type is possible only if the substituent X in the M–X (M = Si, Ge, Sn, or Pb) group is an atom with lone electron pairs (F, Cl, O, N, etc.) or a group with multiple bonds (CH=CH$_2$, C≡C–H, etc.). The atom M in the M–X group may be regarded as an acceptor of the p electrons of the atom X, the electron transfer process resulting in the formation of a dative d_π–p_π bond. The idea of partial double bonding involving silicon using d levels was put forward by Brockway and Wall[2]. The concept of d_π–p_π conjugation was introduced by Pauling[3], who suggested this phenomenon in order to account for the shortening of the Si–Hal and Si–O bonds. d_π–p_π interaction was considered theoretically by Craig[4–7] Jaffé[8], Moffitt[9], and Cruickshank[10,11]. Calculation of the overlap integrals shows[4,5,8,9] that the outer d orbitals can form a strong directed π bond. The degree of double bonding can then be considerable only in the presence of a partial positive charge at the silicon atom. Moreover, the degree of d_π–p_π interaction depends markedly on the steric disposition of the d orbitals relative to the σ bonds. Fairly effective overlap can be achieved only when the σ bond coincides with the plane of the maximum density of the d orbital. This is indicated by the significant dependence of the d_π–p_π overlap integrals on molecular geometry[8]. We may also note quantum-chemical data[12–14] indicating the occurrence of d_π–p_π interaction in Si–aryl and Si–vinyl bonds.

The reviews by Stone and Seyferth[15], Bürger[16], Ebsworth[1], and Attridge[17] deal with the problems of the experimental study of d_π–p_π interaction involving elements of the silicon subgroup. In these reviews the problem of d_π–p_π interaction has been considered as a whole, but, because of the large amount of new spectroscopic data on this problem, these reviews have become to a large extent obsolete. We decided to examine the results obtained by NMR and infrared spectroscopic methods, since we believe that these procedures are the most fruitful in spectroscopic studies on d_π–p_π interaction. We confined ourselves to the consideration of studies which appear to be the most significant. At the same time we may note that a fairly large number of publications have appeared in which the effect of d_π–p_π interaction is either ignored or is taken into account incorrectly. The reasons for the incorrect or invalid conclusions concerning d_π–p_π interaction are failure to take into account all the factors influencing the chemical shift in ^{1}H NMR spectra[18,19], the complex mode of the C=C stretching vibration in the infrared spectra of the vinyl derivatives of Group IVB elements[20–22], incomplete allowance for the factors influencing the frequencies of the C=O stretching vibrations and =CH$_2$ deformation vibrations in the vibrational spectra of organic derivatives of the elements[23–28], failure to take into account other conjugation effects[29,30], and low sensitivity of spectroscopic parameters to the effect of substituents[31,32]. Thus the necessary conditions for a correct interpretation of d_π–p_π interaction include the following: (1) allowance for the polarity of the chemical bond influenced by the inductive effect of substituents and conjugation effects other than d_π–p_π interaction; (2) the availability of fairly large series of compounds in which the spectroscopic parameters of the molecular fragments (a) depend only on the electronic effect of the substituents and (b) are fairly sensitive to these effects.

So far there have been no Russian reviews of spectroscopic studies on d_π–p_π interaction.

II. NMR STUDY OF d_π–p_π INTERACTION

There have been three main trends in studies of the effect of d_π–p_π interaction in organic derivatives of Group IVB elements by NMR: (1) analysis of the spin–spin coupling constants; (2) analysis of the chemical shifts in the proton magnetic resonance (^{1}H NMR) spectra; (3) the study of the basic and acidic properties of organic derivatives of Group IVB elements. We shall examine the results of studies of each type.

1. Analysis of the Spin–spin Coupling Constants

The extensive data accumulated on the spin–spin coupling constants (SSCC) between the nuclei of the ^{13}C and ^{1}H isotopes in compounds of the type $CH_{4-n}X_n$ show that the constants $J(^{13}C-^1H)$ are proportional to the amount of s

character of the carbon orbital in the direction of the C–H bond. However, the relation between $J(^{13}C-^{1}H)$ and the parameters of the polarisation of the C–H bond under the influence of substituents X (for example, the electronegativity of X) does not hold for all substituents without exception[33]. Moreover, it has been shown that, for strongly electronegative substituents (X, Y, and Z) in the molecules CHXYZ, the experimental values of the SSCC differ from the constants calculated assuming additivity on the basis of the SSCC for compounds of the type CH_3X, CH_3Y, and CH_3Z. The above remarks should be borne in mind in the interpretation of the ^1H NMR data for organic derivatives of Group IVB elements within the framework of $d_\pi-p_\pi$ interaction. We shall now consider certain SSCC data in the Table.

Spin–spin coupling constants.

Compound	$J(^{13}C-^{1}H)$, Hz	Compound	$J(^{13}C-^{1}H)$, Hz
$(CH_3)_4Si$	118.0	$(CH_3)_3SiOPb(CH_3)_3$	115.0
$(CH_3)_3SiOLi$	116.0	$(CH_3)_3SiSSi(CH_3)_3$	119.5
$(CH_3)_3SiONa$	115.0	$(CH_3)_3SiSeSi(CH_3)_3$	120.5
$(CH_3)_3SiOSi(CH_3)_3$	118.0	$[(CH_3)_3Si]_3N$	118.0
$(CH_3)_3SiOGe(CH_3)_3$	117.8	$[(CH_3)_3Si]_2NGe(CH_3)_3$	118.0
$(CH_3)_3SiOSn(CH_3)_3$	116.8	$[(CH_3)_3Si]_2NSn(CH_3)_3$	118.0

The constancy of the SSCC on passing from tetramethylsilane to hexamethyldisiloxane, despite the replacement of the methyl groups by the electronegative oxygen atom, is striking. These data are usually regarded as evidence of a strong effect of $d_\pi-p_\pi$ interaction in the Si–O bond[34]. In compounds with Si–O–M groups, the variation of M in the series Ge–Sn–Pb results in a lowering of the amount of s character of the C–H bond in the $(CH_3)_3Si$ fragment and the contribution of $d_\pi-p_\pi$ interaction to the Si–O bond increases. The degree of double bonding in the Si–O fragment increases also on passing from hexamethyldisiloxane to alkali metal trimethylsilanoxides[35].

The characteristics of the $d_\pi-p_\pi$ interaction in the Si–O bonds of heterosiloxanes have been investigated by NMR and infrared spectroscopic methods also in other studies[36–41].

In the compounds $(CH_3)SiXSi(CH_3)_3$, the SSCC increase in the series O < S < Se (in opposition to the variation of the electronegativities of the X), which indicates a decrease of $d_\pi-p_\pi$ interaction on passing from oxygen to selenium derivatives[34]. Comparison of the SSCC for methoxysilanes and their carbon analogues also confirms the occurrence of $d_\pi-p_\pi$ interaction in the Si–O bond[42]. The low values of the SSCC for compounds with Si–N bonds, despite the considerable electronegativity of the nitrogen atom have been interpreted on the basis of the $d_\pi-p_\pi$ interaction in the Si–N bond[34,43]. Analysis of the $^{13}C-1H$ SSCC for the $N-CH_3$ fragment in the compounds $(CH_3)_3MN(CH_3)_2$ and $M[N(CH_3)_2]_4$ showed[43] that the inductive effect of the $(CH_3)_3M$ group diminishes when M varies in the series Si > C ≥ Ge > Sn. Comparison of the effective electronegativities, which vary in the same sequence, with Batsanov's electronegativities[44] which do not take into account the effect of π bonding (C > Ge ≃ Sn > Si) shows that the capacity of Group IVB elements for $d_\pi-p_\pi$ interaction diminishes in the series Si > Ge > Sn. In the monohalogeno-derivatives $(CH_3)_3SiX$ with X varying in the series F–Cl–Br–I, the SSCC increase correspondingly (118.8, 120.5, 121.0, and 121.5) in a sequence opposite to that in the variation of the I effect of the halogen atom. According to Schmidbaur[34], this indicates a decrease of the capacity of the halogens for $d_\pi-p_\pi$ interaction in the series F > Cl > Br > I. However, this conclusion is not entirely correct, since in methyl halides the SSCC also increase from the fluoride to the iodide derivative[45].

The effect of the $d_\pi-p_\pi$ interaction in the Si–N bond was investigated by Zuckerman and coworkers[46–48], who showed that the $J(^{15}N-^{1}H)$ SSCC for the compounds $(CH_3)_3M^{15}NHC_6H_5$, where M = Si, Ge, or Sn, and for aniline are similar but differ from the SSCC for the pyridinium ion, the orbitals of the nitrogen atom of which are sp^2 hybridised. On this basis, it was concluded that there is no stereochemical evidence for $d_\pi-p_\pi$ interaction in M–N bonds. However, according to other data[13,49], sp^3 hybridisation of the orbitals of the nitrogen atom by no means rules out its $d_\pi-p_\pi$ interaction with the silicon atom.

2. Analysis of Chemical Shifts in ^1H NMR Spectra

^1H NMR is mainly employed to investigate organic derivatives of Group IVB elements (however, ^{19}F NMR also yields information about the $d_\pi-p_\pi$ interaction[50]). The attempts to isolate the contributions to chemical shifts associated with the $d_\pi-p_\pi$ interaction encountered considerable difficulties. This is because the chemical shift is a function of a large number of intramolecular factors[51] the most important of which are the inductive effects of the substituents and the effects of the anisotropy of the magnetic susceptibility and of the intramolecular electric field[52]. Therefore experimental chemical shifts must be treated with much caution in attempts to obtain information about $d_\pi-p_\pi$ interaction. We shall consider certain data obtained after approximate allowance for the above factors.

The idea of the first series of studies[53–55] consisted in a comparison of the relations in the ^1H NMR spectra of organic derivatives of silicon, germanium, and tin with the similar relations for carbon compounds. It was shown that in the series $(CH_3)_{4-n}MR_n$, where M = Si, Ge, or Sn and R = Cl, Br, I, OAlk, C_6H_5, or $CH=CH_2$, there is a linear correlation between the chemical shifts and the inductive constants σ^* of the substituents R for each R and M. Similar relations hold also for carbon compounds. Therefore the points corresponding to different R for carbon compounds on the plot of τ_{CH_3} against $\Sigma\sigma^*_R$ were transferred onto the chloride straight line in the direction parallel to the $\Sigma\sigma^*$ axis. The values of σ^*_{eff} were then obtained for each R. When the σ^*_{eff} were used for correlation with the τ_{CH_3} for silicon, germanium, and tin derivatives, the points corresponding to certain compounds deviated from the correlation owing to $d_\pi-p_\pi$ interaction. Analysis of the deviations indicates a considerable contribution of $d_\pi-p_\pi$ interaction to the τ_{CH_3} for R = OCH_3, OC_2H_5, and $CH=CH_2$. Bromine and iodine apparently enter into $d_\pi-p_\pi$ interaction less than does chlorine. Together with their advantages, these studies suffer from the evident disadvantages due to the assumption that the intramolecular factors influencing the chemical shifts in organic derivatives of Group IVB elements do not differ from those in carbon compounds.

Therefore in a second series of studies[56–58] an attempt was made to take into account these factors for methyl and ethyl derivatives of silicon and germanium more rigorously. The chemical shifts τ for the CH_3 and CH_2 groups in

compounds with substituents incapable of d_π–p_π interaction, in which there is almost no contribution to τ due to the anisotropy of the magnetic susceptibility and of the electric field, were considered initially. A linear correlation between the τ and the inductive constants σ^* of the substituents was found for these compounds. This made it possible to take into account accurately the changes in bond polarities in compounds with any substituents and hence to calculate the values of τ due solely to the I effect. Subsequently corrections were applied to these chemical shifts, taking into account approximately, on the basis of the appropriate formulae, the magnetic anisotropy and the electric field of the substituents, and the τ_{calc} were obtained. The discrepancies between the τ_{calc} and τ_{exp} were attributed to the effect of d_π–p_π interaction, decreasing in the series F > OCH_3 > Cl > C_6H_5 > Br and Si > Ge.

Because data concerning the involvement of the vinyl group in π bonding with elements of the silicon subgroup were contradictory [28], a series of studies were undertaken to investigate this problem by ^{1}H NMR. [59-61] Analysis of the chemical shifts in the ^{1}H NMR spectra of the compounds $(CH_3)_3MCH{=}CH_2$, $(C_2H_5)_2M(CH{=}CH_2)_2$ (M = C, Si, Ge, or Sn), and $Cl_3MCH{=}CH_2$ (M = Si or Ge) taking into account the effects of the magnetic anisotropy and the electric field showed that the capacity of Group IVB elements for d_π–p_π interaction with the vinyl group diminishes in the sequence Si > Ge > Sn. This conclusion was confirmed by infrared spectroscopy [62].

In some studies conclusions concerning the d_π–p_π interaction were reached on the basis of a simple analysis of the experimental chemical shifts. Although, owing to the complex nature of the chemical shift, the results of these investigations cannot pretend to a high objectivity, we shall examine some of the most important of them. Despite the failure to take into account intramolecular factors influencing the proton chemical shifts, the data for d_π–p_π interaction obtained in these studies agree qualitatively with the results of the investigation of this effect by other physical and chemical methods. The reason for this is probably as follows. It has been shown [58] for the compounds R_nMX_{4-n} (where R = CH_3 or C_2H_5, M = Si or Ge, and X = F, Cl, Br, OCH_3, or C_6H_5) that the principal factors affecting the proton chemical shift in the Group R are the inductive I effect of X and the intramolecular electric field of X (except for the case where X = C_6H_5, the effect of the anisotropy of the magnetic susceptibility of the M–X bond is extremely small). Both factors lead to a decrease of proton screening in the groups R. d_π–p_π interaction between M and X is opposed to the I effect and increases the screening of the protons in R. Therefore the conclusions concerning d_π–p_π interaction based on the anomalously high chemical shifts in certain methyl and ethyl derivatives of Group IVB elements can agree qualitatively with the results of more exact investigations. In studies of this type, a decrease of the capacity of Group VI elements for d_π–p_π interaction with Group IVB elements in the series O > S > Se > Te was established [34, 63, 64]; the occurrence of d_π–p_π interaction in bonds formed by silicon with oxygen, nitrogen, fluorine, and chlorine was discovered [65-73]; it has been shown that the amount of π character of the Sn–Cl bond is less than that of the Si–Cl bond [74] and a decrease of d_π–p_π interaction in Si–O bonds with increasing number of such bonds in the molecule was established [75, 76].

We shall now consider the results of studies in which the specific features of molecular structure make it possible to arrive at conclusions about d_π–p_π interaction without introducing corrections into the experimental chemical shifts for magnetic anisotropy and the electric field. In a study of the chemical shifts in the compounds $(CH_3)_nCl_{3-n}SiOR$, where n = 0–3 and R = alkyl group, Brune [77] demonstrated the occurrence of d_π–p_π interactions in the Si–O bond [77]. In the compounds $R'Cl_nSi(OR)_{3-n}$, d_π–p_π interaction in the Si–O fragment diminishes as chlorine atoms or alkoxy-groups accumulate; the chlorine atom is more actively involved in d_π–p_π interaction than oxygen [78-80]. Analysis of the effective electronegativities of the oxygen atoms in alkoxydisilanes showed that the delocalisation of the lone electron pairs of oxygen in the Si–Si–O fragment is accompanied by a strong d_π–d_π–p_π interaction [81]. Subsequently the characteristics of d_π–p_π interaction in organic derivatives of ethoxysilanes and also in aminoalkoxysilanes were studied by Voronkov and Pestunovich [82-85], who showed, in particular, that the conclusions [77] concerning the greater capacity of chlorine compared with oxygen for d_π–p_π interaction is erroneous. The distribution of electron density in aminoalkoxysilane molecules depends both on d_π–p_π interaction and on the effect of p, σ conjugation.

The aromatic systems of benzene, furan, and thiophen containing organometallic substituents have also been studied by ^{1}H NMR. It has been established both experimentally [86] and theoretically [87] that in compounds of this type the chemical shifts of certain ring protons are almost independent of the magnetic anisotropy and the electric field of the substituents. Therefore in many cases it is possible to relate these chemical shifts to the electronic effects of the substituents and to obtain information about the d_π–p_π interaction in the bond between the Group IVB element and the ring. Analysis of the ^{1}H NMR and ^{19}F NMR spectra of the compounds $XC_6H_4M(CH_3)_3$ (where M = Si, Ge, or Sn [88]) and $(FC_6H_4)_nSn_{4-n}$ (where R = CH_3, C_2H_5, [89] or C_6H_5 [90]) established that d_π–p_π interaction occurs in the M–ring bond, the interaction being a minimum for M = Sn and almost absent in lead derivatives [90].

As in other investigations [91-95], Angelelli et al. [96] concluded on the basis of the dipole moments of aryl derivatives of elements of the silicon subgroup that π bonding increases with increasing electron-donating properties of the *para*-substituent X, completely ignoring the contributions of the effects due to direct polar conjugation. The linear relation between the chemical shifts of the *para*-protons and Hammett's σ_n constants [97] showed that the d_π–p_π interaction between the phenyl ring and the atom M in the $M(C_2H_5)_3$ group diminishes in the sequence Si > Ge ≃ ≃ Sn > Pb as M is varied [98]. However, for compounds with the substituents MCl_3 the degree of d_π–p_π interaction in the M–Ph bond varies in a different sequence: Sn > > Ge > Si, which the authors explain [98] by a decrease of the capacity of silicon and germanium atoms for d_π–p_π interaction with the ring owing to their involvement in the energetically more favourable interaction with chlorine atoms. Reikhsfel'd and coworkers [99-105] showed that the d_π–p_π interaction in Si–Ph bonds competes with the intermolecular interaction involving the d orbitals of the silicon atom.

That the bonds between silicon subgroup elements and the phenyl ring are of the π type is also indicated by the ^{19}F NMR data for substituted fluorobenzenes [106] and the ^{14}N data for *p*-trimethylsilylnitrobenzene [107]. The problems of d_π–p_π interaction were examined in greater detail for organosilicon derivatives of furan and thiophen [108-110]. The trialkylsilyl group linked to the furan [108] or thiophen [108] ring behaves as a typical electron acceptor. At the same time the $(CH_2)_nSiAlk_3$ fragment is an electron donor. This demonstrates the occurrence of d_π–p_π inter-

action in furyl- and thienyl-silanes in which the silyl group is linked directly to the ring. It has been shown that the silicon atom in the $SiCl_3$ and $Si(OHAlk)_3$ groups is less strongly conjugated to the ring than the silicon atom in the $SiAlk_3$ group [110] owing to the competing $d\pi-p\pi$ interaction in the Si–Cl and Si–O bonds.

According to infrared spectroscopy [111] and electron diffraction [112] data, the lone electron pairs of the oxygen atom in compounds of the type $C_6H_5OSiH_3$ are involved in two conjugation processes—with the ring π electrons and the silicon 3*d* orbitals. This conclusion has also been confirmed by ^1H NMR. [113]

It has been shown by ^1H NMR that the $d\pi-p\pi$ character of the Si–N bond reduces the barrier to conformational transitions via an intermediate sp^2 state in *N*-trimethylsilyl derivatives of aziridine [114] and piperidine [115] compared with their carbon analogues. The $d\pi-p\pi$ interaction of silicon and germanium atoms with the nitrogen atoms of the pyrazole rings has also been established by ^1H NMR. [116]

3. The Basic and Acidic Properties of Organic Derivatives of Group IVB Elements

As already mentioned above, the chemical shift in the NMR spectra is a complex function of a large number of intramolecular and intermolecular factors. Therefore, in correlating the acid–basic properties of organic derivatives of the elements with molecular structure, correct experiments are necessary. In studies on basicity, the formation of hydrogen bonds between molecules having bonds of the type M–X (where M = Si, Ge, or Sn and X = O or N) and proton donors was investigated. Chloroform was mainly employed as the proton donor. The chemical shift of the proton in chloroform at infinite dilution or the $^{13}C-^1H$ spin–spin coupling constant of chloroform served as a measure of the strength of the hydrogen bond (and hence of the basicity of X).

It was found that the basicity of siloxanes and alkoxysilanes is much lower than that of their carbon analogues [117], which indicates, in agreement with infrared spectroscopic data [118], a strong $d\pi-p\pi$ interaction in the Si–O bond. The basicity of various compounds with M–N bonds has been investigated [43,119] and a decrease of $d\pi-p\pi$ interaction on passing from M = Si to M = Sn has been established, which in broad outline is also consistent with the results of earlier infrared spectroscopic studies [120].

The study of the acidic properties of alcohol derivatives of the elements is based on the finding [121] that alcohols form very stable [H-bonded (Ed. of Translation)] complexes with dimethyl sulphoxide. Other possible types of association are then suppressed and therefore the chemical shift of the OH proton is a measure of the acidity of the alcohol (we may note that this method has been recently criticised [122]). Organosilyl alcohols containing the $\rangle SiOH$ fragment are more acidic than their carbon and germanium analogues [123]. Comparison of the chemical shifts of the OH protons in silyl-substituted benzoic acids and phenols with their carbon analogues indicates $d\pi-p\pi$ interaction between the aromatic ring and the silicon atom, which is more pronounced in phenols [124]. The $(CH_3)_3SiSi(CH_3)_2$ group is a more powerful acceptor of π electrons from the aromatic ring than the trimethylsilyl group [125]. An appreciable $d\pi-p\pi$ interaction in the Si–O bond is also indicated by the greater strength of the hydrogen bonds in $(CH_3)_3SiOH$ than in $(CH_3)_3COH$; [122,126] for the Si–Cl bond, this follows from a comparison of the proton-donating properties of chloroform [127].

The greater capacity of silicon for $d\pi-p\pi$ intera tion compared with germanium follows from data obtained in a ^1H NMR study of the hydrogen bond in compounds of the type $(CH_3)_3M-C\equiv CH$. [128] For M = Si, the hydrogen of the $\equiv CH$ group is more mobile than for M = Ge owing to the reduced electron density in the multiple bond as a result of the interaction of the π electrons of this bond with the *d* orbitals of the silicon atom. The acidic properties of certain other acetylene derivatives of Group IVB elements have been studied by Petrov et al. [129]

The ^1H NMR study of the hydrogen bond between compounds of the type $(C_2H_5)_3MXH$ (where M = Si or Ge and X = S or Se) and proton-accepting solvents showed that silicon forms stronger $d\pi-p\pi$ bonds than germanium. The effect of the $d\pi-p\pi$ interaction in M–S bonds is more appreciable than in M–Se bonds [130].

III. STUDY OF $d\pi-p\pi$ INTERACTION BY VIBRATIONAL SPECTROSCOPIC METHODS

The effect of $d\pi-p\pi$ interaction in organic derivatives of Group IVB elements has been studied in three different ways by vibrational spectroscopic methods (infrared and Raman spectroscopy): (1) the study of the basic and acidic properties of the compounds; (2) the study of the vibration frequencies and intensities for certain bonds in organic derivatives of the elements, (3) analysis of the stretching vibration frequencies of the Si–H bond in substituted silanes.

1. The Basic and Acidic Properties of Organic Derivatives of Group IVB Elements

On formation of the hydrogen bond, organic derivatives of the elements can behave both as acids and bases. When compounds with a bond between a Group IVB element and a Group VI element form a hydrogen bond with proton donors (alcohols, pyrrole, chloroform), the compound behaves in the hydrogen bond as a base. On formation of a hydrogen bond between compounds with fragments of the type O–H, S–H, and N–H linked to a Group IVB element and hydrogen bond acceptors (dioxan, tetrahydrofuran, ethyl ether), the compound behaves as an acid. In studies of this kind it is assumed that the shift of the X–H frequency of the proton donor in the hydrogen bond on passing from the non-associated to the associated state is proportional to the hydrogen bond energy [131,132]. (In a more rigorous treatment, a linear relation was demonstrated between the νO-H frequency shift and the square of the hydrogen bond energy in phenol–base systems [133]. This is probably true also of other proton donors [133].) On the other hand, it is clear that the hydrogen bond energy is closely related to the electron density at the Group VI atom of the base or at the X atom of the X–H group of the proton donor in the hydrogen bond. The electron density at these atoms in turn depends directly on the contribution of the $d\pi-p\pi$ interaction in the M–X bond, where M is an element of the silicon subgroup. The stronger is the $d\pi-p\pi$ interaction, the lower the electron density at the atom X. Study of hydrogen bonding showed [131] that the silanols $(C_6H_5)_2SiH(OH)$ and R_3SiOH (where R = CH_3, C_2H_5, or C_6H_5) are much more acidic but only slightly less basic than the corresponding carbinols. This is evidence of $d\pi-p\pi$ interaction in silanols involving only one of the two lone electron pairs of oxygen. In the compounds $(C_6H_5)_3MOH$ (where M = C, Si, Ge, Sn, or Pb), the silanol is much more acidic

than the other hydroxy-derivatives[134,135]. In the absence of d_π–p_π interaction the acidity of the hydroxides should be determined by the electronegativity of the element M. This fact and also data for the basicity of the hydroxides leads to the following sequence in terms of capacity for d_π–p_π interaction: Si > Ge > Sn ≃ Pb. On passing to the alcohols $(C_6H_5)_3MCH_2OH$ (where M = C, Si, or Ge), one would expect that the carbinol would be the most acidic, since carbon is the most electronegative of the three elements M. However, the following acidity series was obtained experimentally: $(C_6H_5)_3GeCH_2OH > (C_6H_5)_3SiCH_2OH > > (C_6H_5)_3CCH_2OH$,[122] which according to the authors is evidence of intramolecular coordination between the oxygen and germanium atoms due to the *d* orbitals of the latter. In the silyl analogue this effect is less pronounced and in the carbinol it is absent altogether. It probably occurs in 2-substituted cyclohexanones and cyclohexanols[136] and also in the compound $H_3GeCH_2OCH_3$.[137] In the alcohols $(C_6H_5)_3MCH_2CH_2OH$ the effect is probably absent. The acidity of such alcohols is almost independent of the nature of the element M,[122] since the *I* effect of the $(C_6H_5)_3MCH_2CH_2$ group changes little as M is varied. In a study of intramolecular hydrogen bonding in the hydroperoxides $(C_6H_5)_3MOOH$ (where M = C, Si, Ge, or Sn) and their hydrogen bonding with tetrahydrofuran, it was established that the acidity of the hydroperoxides diminishes in the following sequence as M varies: Si > Ge > C > Sn.[138] This is evidence of a decrease of d_π–p_π interaction in the M–O bond in the series Si > Ge > Sn and it is consistent with the results obtained for the hydroxides $(C_6H_5)_3MOH$.[135] The effect of d_π–p_π interaction in the M–C_6H_5 bond is much less than in the M–O bond. Therefore the main factor determining the energy of the intramolecular (as well as intermolecular) hydrogen bond is the acidity of the hydroperoxides.

Studies of a series of ethers, siloxanes[118,139], alkoxysilanes, and alkoxygermanes[140-142] led to the discovery that the basicity of the oxygen atom diminishes in the series C–O–C > C–O–Si > Si–O–Si. The decrease of basicity was interpreted as a result of a shift of the oxygen *p* electron to the silicon *d* orbital. The difference between the basicities of monoethoxygermane and monoethoxysilane corresponds to a greater d_π–p_π interaction in the Si–O bond than in the Ge–O bond. On the other hand, tetraethoxygermane is only slightly more basic than tetraethoxysilane. This is because in tetraethoxysilane π-bonding with each of the oxygen atoms is weaker compared with the d_π–p_π interaction in monoethoxysilane[142]. Evidence for stronger π-bonding of oxygen to silicon than to germanium or tin was also obtained in other studies[143,144]. Thus the following series of decreasing basicity of organic derivatives of the elements with an M–O bond have been established:: SiOC > $Si(OC)_2$ > $Si(OC)_3$ > SiOSi, GeOGe > > GeOC > $Ge(OC)_2$ > $Ge(OC)_3$, and SnOSn > SnOC > > $Sn(OC)_2$.[145] It has also been shown[146] that the low basicities of compounds with the $(CH_3)_3SiO$ and $(CH_3)_3CO$ fragments is due not only to d_π–p_π interaction in the Si–O bond but also to steric hindrance to the formation of a hydrogen bond generated by the $(CH_3)_3C$ and $(CH_3)_3Si$ groups.

The force constants of the Group IVB element–Group VI element bonds have been analysed[147-149] on the basis of the vibrational spectra of compounds containing such bonds. Thus an enhanced multiplicity of the Si–O and probably Sn–S bonds has been established[147,148] but data supporting the π character of Si–S, Ge–S, Pb–S, and Sn–O bonds were not obtained[147-149]. In view of the large number of factors influencing the force constants (this is discussed in greater detail in the next section of the review), the reliability of these data[147-149] for d_π–p_π interaction is low. Studies on the basicity of organic derivatives of the elements with a Group IVB element–Group IV element bond are therefore of considerable interest. The problem of d_π–p_π interaction between elements M of the silicon subgroup and oxygen and sulphur (as well as nitrogen) atoms has been discussed[150] in a study of the basicity of compounds containing bonds involving these elements. The study showed that the capacity of M for d_π–p_π interaction with nitrogen or oxygen atoms decreases in the sequence Si > Ge > Sn. An appreciably weaker d_π–p_π interaction was observed in the Si–S bond. The authors' view that the d_π–p_π interaction of germanium with sulphur is more pronounced than with oxygen appears to be supported by insufficient evidence.

The order of the acidities of silanethiols and mercaptans, $(C_6H_5)_3SiSH \gg C_6H_5SH > (CH_3)_3SiSH > (C_6H_5)_3CSH > > (CH_3)_3CSH$,[151] proved to be similar to that obtained previously for the acidities of oxygen-containing compounds: $(C_6H_5)_3SiOH \gg C_6H_5OH > (CH_3)_3SiOH > (C_6H_5)_3COH > > (CH_3)_3COH$.[131] In the two pairs of compounds with the same structures $(C_6H_5)_3SiSH$–$(C_6H_5)_3CSH$ and $(CH_3)_3SiSH$–$(CH_3)_3CSH$ the silicon compounds are more acid. This is consistent with dative Si–S π bonding in silanethiols, which makes them stronger acids than mercaptans.

Whereas only one lone electron pair of the oxygen atom is involved in the d_π–p_π bonding in the Si–O–C group and to such pairs in the Si–O–Si group[118], the sulphur atom is probably capable of giving up only one electron pair in all cases[150].

These studies were developed further in an investigation[152] of the basicity of compounds of the type $(C_2H_5)_3MXM'(C_2H_5)_3$ (where M and M' = Si, Ge, or Sn; X = O, S, Se, or Te) and also the compounds $(C_2H_5)_3MXH$ (where M = Si or Ge; X = S or Se). The shift of the stretching vibration frequency of the C–D bond in non-associated deuterochloroform on formation of a hydrogen bond with the above compounds was studied. The shift $\Delta\nu$ was treated as a measure of the basicity of organic derivatives of the elements. Bearing in mind that (1) the basicity of organic derivatives of Group VI elements decreases in the sequence O > S > Se > Te[132] (the capacity of these elements for d_π–p_π interaction with Group IVB elements decreases in the same sequence), (2) the capacity of the elements for d_π–p_π interaction diminishes in the sequence Si > Ge > Sn,[63,111,130] and (3) the d_π–p_π interaction in the Si–Te bond (and even more so in the Ge–Te and Sn–Te bonds) is extremely weak[111,153], the authors[152] interpreted the results as follows. For all the tellurides $[(C_2H_5)_3M]_2Te$, the values of $\Delta\nu$ are similar. This shows that the steric hindrance and the d_π–p_π interaction have only a slight effect on the basicity. Nevertheless $\Delta\nu$ is a minimum for $[(C_2H_5)_3Si]_2Te$. The contribution of d_π–p_π interaction to the Si–Te bond is small, but it can be detected in the measurement of the basicity, since the latter is directly related to the electron density at the tellurium atom.

For organic derivatives of the elements with the general formula $[(C_2H_5)_3M]_2X$, the following sequences of decreasing basicity were obtained: O > Te > Se > S for M = Sn, O > Te > Se > S for M = Ge, and Te > Se > S > O for M = Si. None of them is identical with the O > S > Se > Te sequence quoted above for the series of carbon compounds. The reason for this is that the relatively small effect of d_π–p_π interaction, which, however, increases systematically in the sequence Te < Se < S, influences the basicity of the Group VI elements even in the series of organotin compounds. For the series $[(C_2H_5)_3Ge]_2X$, the

d_π–p_π interaction in the Ge–X bonds plays a more significant role. The basicity $[(C_2H_5)_3Ge]_2S$ and $[(C_2H_5)_3Ge]_2Se$ is lower than that of the corresponding tin derivatives. This is evidence of d_π–p_π interaction in the Ge–Se bond, which becomes even more pronounced in the Ge–S bond. In the series of compounds $[(C_2H_5)_3Si]_2X$, the values of $\Delta\nu$ are much lower than in the organogermanium and organotin series. This shows that the d_π–p_π interaction with silicon is stronger than with germanium or tin. From this point of view, examination of the series of compounds $[(C_2H_5)_3M]_2O$, $[(C_2H_5)_3M]_2S$, and $[(C_2H_5)_3M]_2Se$ yields striking results. In each of these series the basicity falls on passing from M = Sn to M = Ge and Si, which is also evidence of a decrease of the capacity of Group IVB elements for d_π–p_π interaction in the sequence Si > Ge > Sn. The degree of d_π–p_π interaction in the Si–O, Si–S, and Si–Se fragments varies approximately in the proportions 4 : 2 : 1, as shown by the analysis of the infrared spectra of substituted silanes containing these fragments[111]. Therefore the extremely low basicity of hexaethyldisiloxane is a result of a more pronounced effect of d_π–p_π interaction in silicon derivatives in general and in the Si–O bonds in particular. Moreover, as already mentioned[146], $\Delta\nu$ for $[(C_2H_5)_3Si]_2O$ is low also because of steric hindrance to the formation of a hydrogen bond due to triethylsilyl groups.

A strong d_π–p_π interaction in the Si–N groups was established in a study of the basicity of a series of organosilicon amines[120]. It was shown that the shift $\Delta\nu_{C-D}$ of the stretching vibration frequency of the C–D bond in mixtures of Cl_3CD with silylamines, characterising the basicity of the nitrogen atom, is in the range 50–80 cm^{-1} for compounds of the type $(CH_3)_3SiNR_2$, 30–35 cm^{-1} for the cyclic compounds $[(CH_3)_2SiNR]_3$, and 15 cm^{-1} for $(CH_3)_3SiNHPh$, $(CH_3)_3SiNPh_2$, and $[(CH_3)_3Si]_2NPh$. If one assumes that with decrease of basicity the effect of d_π–p_π interaction increases, then in the last of compounds the effect is a maximum. In trisilylamines the $\Delta\nu_{C-D}$ effect was not observed, which is evidence of an extremely low basicity of the nitrogen atom. However, the basicity data conflict with the conclusion of Randall and Zuckerman[46] that there is no stereochemical evidence for d_π–p_π conjugation in the Si–N bond, which was based on a study of the infrared and NMR spectra of *N*-trimethylsilyl-, *N*-trimethylgermyl, and *N*-trimethylstannyl-derivatives of aniline. This apparent contradiction can be resolved if one remembers that the lone electron pair of the nitrogen atom can interact both with *nd* orbitals and with the phenyl ring. While the data of Abel et al.[120] indicate conjugation of the lone pair of the nitrogen atom and those of Randall and Zuckerman[46] demonstrate the absence of d_π–p_π interaction, a common conclusion of both investigations is that the interaction of the lone electron pair of the nitrogen with the phenyl ring is much stronger than with *nd* orbitals.

The results obtained in the determination of the basicities of two series of compounds, $(CH_3)_3MN(CH_3)_2$ and $M[N(CH_3)_2]_4$ (where M = C, Si, Ge, or Sn), show that the silicon derivatives form weak hydrogen bonds: this is due to the delocalisation of the *p* electrons in the Si–N bond. According to Mack and Yoder[43], d_π–p_π interaction is more pronounced in silicon derivatives, is much weaker in germanium derivatives, and is probably absent in tin derivatives. The study of the basicity of ethyl(dimethylamino)germanes also indicates a smaller contribution of d_π–p_π interaction to the Ge–N bond compared with Si–N.[154]

Infrared spectroscopic data for silylamines[155] and trimethylsilyldiazomethane[156] as well as the results obtained in a study of the relative basicities of disilazanes[157] have been interpreted on the basis of the d_π–p_π interaction in the Si–N bond.

It was established by infrared spectroscopy[158,159] that the basicities of arylsilanes and organosilicon derivatives of thiophen are much lower than those of their carbon analogues. This is a consequence of d_π–p_π interaction, as a result of which the SiR_3 (R = alkyl or H) substituents in the benzene or thiophen rings become less effective electron donors than the corresponding substituent CR_3. The basicity of the vinyl derivatives of Group IVB elements is much lower than that of the corresponding carbon analogues; with increase of the atomic number of the Group IVB element, the basicity increases[160]. This is caused by the effect of d_π–p_π interaction, which decreases in the sequence Si > Ge > Sn.

The infrared spectra of compounds of the type $(CH_3)_3M{-}C{\equiv}CH$, where M = C, Si, Ge, Sn, or Pb, have been studied in various electron-donating solvents. It has been noted[161–162] that all the compounds except carbon derivatives form hydrogen bonds with the solvent, which is evidence of a considerable acidity of the hydrogen atom in the $-C{\equiv}CH$ fragment. The acidity of organic derivatives of the elements increases as a result of intramolecular interaction of the π electrons of the triple bond with the *nd* orbitals of the Group IVB element. Thus the presence of d_π–p_π interaction in ethynyl derivatives of the elements has been convincingly confirmed by NMR[128,129] and infrared spectroscopic[161,162] methods.

2. Vibration Frequencies and Absorption Band Intensities of Certain Bonds in Organic Derivatives of Group IV Elements

Since the contribution of the effect of d_π–p_π conjugation in the M–X fragment to the total MX bond energy is comparatively small, considerable caution must be exercised in drawing conclusions concerning d_π–p_π interaction on the basis of an analysis of the force constants. For such conclusions to be valid, it is necessary to have rigorous proof that the changes in force constants (including the changes under the influence of the d_π–p_π conjugation) are caused by electronic effects. As a rule it is necessary to carry out a theoretical analysis of the vibrations of the molecules investigated and to obtain proof that the vibration, on the basis of the changes in frequency of which conclusions concerning intramolecular effects of the type of d_π–p_π interaction are arrived at, is characteristic. Unfortunately the latter requirement has not been fulfilled in all the studies dealing with this problem.

It has been established that the bonds formed by silicon with elements such as N, O, F, and Cl have relatively high force constants[147,163]. On this basis, Kriegsman[147,164] concluded that d_π–p_π interaction must play an important role in compounds containing such bonds. According to Kriegsmann[165], the order of the Si–N bond in hexamethyldisilazane is 0.18. The Ge–N and Sn–N bonds also have partial double bond character, which is indicated by the M–N force constants in the compounds $M[N(CH_3)_2]_4$.[166]

Subsequently the vibrational spectra of compounds of the type $(H_3Si)_nX$ and $[(CH_3)_3Si]_nX$, where X is an element in Groups IV–VI and *n* is the valence, were studied systematically by Bürger (see Bürger's review[167] and the paper summarising his results[168]). In the analysis of the force constants of the Si–X bonds of these compounds, account was taken of the contribution of the d_π–p_π interaction in the bonds between silicon and elements in Groups V–VII. The effect of d_π–p_π interaction was studied on the basis of the

vibration spectra of the compounds SiX_4 and Si_2X_6,[169] where X = Cl, Br, or I. Detailed studies of the d_π–p_π interaction in compounds with Si–O–Si and Si–O bonds and related germanium derivatives were made by Lazarev and coworkers[170-174].

Investigation of the stretching frequencies of the C=O bond in the compounds $R_3MOC(O)R'$ (R and R' = CH_3, C_2H_5, or C_6H_5; M = silicon subgroup elements) showed[175] that in the compounds with M = Si or Ge there is competition between πp conjugation (R_3M–O–C(=O)–R') and d_π–p_π interaction. As a result, the d_π–p_π conjugation in the Ge–O bonds of these compounds proved to be comparatively weak; theSi–O bond has a much greater amount of π character. In tin and lead derivatives, the amount of ionic character of the M–O bond is very high, owing to the transition of the M element to the sp^3d or sp^3d^2 valence states and the formation of M...O coordinate bonds.

The Si_3N skeleton of trisilylamines is planar, which is believed to be a result of the delocalisation of the lone electron pair of nitrogen to the silicon *d* orbitals, i.e. d_π–p_π interaction in the Si–N bond[176-178]. In contrast to trisilylamines, the heavy atoms in trigermylamines are not coplanar[179], since the d_π–p_π interaction in the Ge–N bonds is weaker than in Si–N bonds. Analysis of infrared spectroscopic and electron diffraction data for silicon and germanium compounds led to the conclusion that germanium has a smaller capacity for d_π–p_π interaction[179].

Contradictory data concerning the possibility of d_π–p_π interaction between the silicon atom and the carbonyl group were obtained in a study of silyl ketones[23-27,180]. Thus, according to Brook and coworkers[23-27], the stretching frequencies of the C=O bond indicate the presence of intramolecular coordination in α- and γ-silyl ketones. In β-silyl ketones, such interaction is prevented by steric hindrance. However, physicochemical studies on 1-trimethylsilylpropan-2-one[180] indicate the occurrence in this compound of coordination between the carbonyl oxygen and the silicon atom even in the gaseous state. The above investigations[23-27,180] are closely related to later studies[122,136,137] indicating the possibility of intramolecular coordination between the germanium (and also probably silicon) atoms and oxygen in organic derivatives of the elements with alcoholic groups of the type R_3MCH_2OH, where M = Ge or Si. However, it is noteworthy that this type of expansion of the valence shell of the silicon subgroup element as a result of the involvement of their *d* orbitals in the formation of additional bonds may differ significantly from the d_π–p_π interaction between atoms which are linked directly by a chemical bond. This is indicated also by experiment. Indeed, it has now been finally established that in the M–X fragment (where M is an element of the silicon subgroup and X an element of Groups V–VII or an α-unsaturated hydrocarbon substituent) the capacity of the atoms M for d_π–p_π interaction with X increases in the sequence Sn < Ge < Si, i.e. has a maximum for silicon. The *d* orbitals of the atoms M of the type d_ϵ (d_{xy}, d_{xz} d_{yz}) are used for π bonding[8]. The element M can also be involved in the formation of additional σ bonds on passing to the quinquevalent and hexavalent state (sp^3d and sp^3d^2). Bonds of this kind are achieved with the aid of *d* orbitals of the type d_γ (d_{z^2}, $d_{x^2-y^2}$). The capacity of the element M for σ bonding increases in the sequence Si < Ge < Sn.[1] Data on the acidic properties of the alcohols $(C_6H_5)_3MCH_2OH$ show[122] that intramolecular coordination is most characteristic of germanium (the tin derivative was not studied) and is least pronounced for the silyl analogue. These results suggest that intramolecular coordination is achieved with participation of d_γ orbitals. We may also note that, since silicon exhibits a comparatively weak capacity for coordination of the above type, the data for silyl ketones[23-27] must be interpreted with much caution. Thus, in order to isolate the contribution associated with intramolecular coordination to the stretching vibration frequency of the C=O bond in the β-silyl ketones $R_3SiCH_2C(=O)-R'$, one must take into account rigorously not only the inductive effect of the substituent R_3SiCH_2 but also the effect of σ, π conjugation.

Infrared and NMR spectroscopic data for dialkoxydialkylstannanes were accounted for on the basis of the hypothesis of d_π–p_π interaction between the tin and oxygen atoms[181]. However, in a study of the vibrational spectra of compounds of the type R_3Sn–O–SnR_3, where R = alkyl or C_6H_5, the double bond character of the Sn–O fragment was not demonstrated[148]. The contradictory nature of the results of these investigations arises because the d_π–p_π bonds in tin compounds are energetically fairly weak. Therefore experimental accuracy for these compounds constitutes a particularly urgent task. Even for silicon compounds, where d_π–p_π bonds play a much more important role, allowance for all the factors influencing the force constant, necessary for the estimation of the contribution of d_π–p_π interaction, has not yet been finally achieved[167,168]. However, the literature shows that the search for a solution of this problem is being continued. A study[182] where it was established that in the absence of d_π–p_π interaction in M–X bonds the ν_{M-C} frequencies for the compounds $[(C_2H_5)_3M]_nX$ (M = Si or Ge; X = element in Groups I–VII; *n* = valence of X) are linearly related to the electronegativities of the substituents X is particularly instructive in this respect. An increase in the electronegativity of X increases the amount of *p* character of the M–X bond and the amount of *s* character of the M–C bond[183]. The ν_{M-C} frequencies in the compounds where the M–X bonds have π character are reduced compared with the values expected on the basis of the above linear relations. Analysis of the deviations leads to the following sequence in terms of the capacities of the substituents X for d_π–p_π interaction with the silicon or germanium atom: F ≥ O > Cl > Br > I ≃ S > Se > Te > Sb > Bi. The deviations for silicon derivatives are greater than for germanium derivatives, which indicates a greater capacity of silicon for d_π–p_π interaction compared with germanium. Thus the fact that in different Groups of the Periodic System the capacity of the elements for d_π–p_π interaction decreases with increasing atomic number of the element was confirmed yet again in this investigation. This applies both to elements which behave as lone electron pair donors (elements in Groups V–VII) and to Group IVB elements with vacant *d* orbitals.

Numerous studies have been made on the effect of d_π–p_π interaction in compounds with an α-unsaturated hydrocarbon substituent linked to a Group IVB element[184-193]. It has been shown that in compounds of the type $(CH_3)_3M$–C≡CH (where M = C, Si, Ge, Sn, or Pb) d_π–p_π interaction decreases on passing from silicon to lead derivatives. In compounds with several ethynyl groups, $(CH_3)_{4-n}Si(C{\equiv}CH)_n$, one may expect that the vibrations of the individual ethynyl groups will be independent and therefore the intensities of the absorption bands of the ≡C–H and –C≡C– bonds will increase additively with increasing number of such bonds. The experimental deviations from these expectations

were accounted for by two types of intramolecular interactions—the inductive effect and the effect of the d_π–p_π interaction[185]. The conclusion that the π electrons of the acetylenic bonds interact with the 5*d* orbitals of the tin atom was based on a study of the vibrational spectra and the measurement of the integral intensities of certain absorption bands of the ethynyl compounds $(C_2H_5)_3SnC{\equiv}CX$, where X = H, CH_3, $CH{=}CH_2$, C_6H_5, or $Si(CH_3)_3$.[186] The results of these studies agree with the data obtained in the study of the acidic properties of the hydrogen atom in the ethynyl group by NMR[128,129] and infrared spectroscopy[161,162].

The conclusion that there is d_π–p_π interaction between the silicon atom and the π electrons of the triple bond was arrived at in a series of studies of Zeil and coworkers[187–190] of the vibrational and microwave spectra as well as NQR spectra of the compounds $(CH_3)_3MC{\equiv}CX$ and $(CH_3)_3MC{\equiv}CM(CH_3)_3$, where M = Group IVB element and X = H or Cl. The electron-accepting properties of the silicon atom linked directly to the triple bond are also indicated by NMR[191] and infrared spectroscopic[192] data and studies on the vertical ionisation potentials[192] of compounds of the type $R_3MC{\equiv}CH$ and $R_3M(C{\equiv}C)_nMR_3$, where M = C or Si, R = H, CH_3, or C_6H_5, and n = 1–3.

Thus in the M–C≡C system (where M = Si, Ge, or Sn) there is d_π–p_π interaction between the *d* orbitals of M and the π electrons of the triple bond, although in lead derivatives such interaction was not detected by infrared spectroscopy[193].

Many studies have been made on the d_π–p_π interaction between the *d* orbitals of Group IVB elements M and the π electrons of the ethylenic bond in compounds containing the M–C=C grouping. It has been shown that the vibration attributed to the presence of the C=C bond in the molecules has a wave-number of about 1650 cm^{-1} in alkenes, while in the corresponding vinylsilanes it is reduced by about 50 cm^{-1}. According to the authors of these investigations[20–22], this indicates the existence of a structure of the type $\overset{-}{Si}\!\!\curvearrowright\!\!C{=}\overset{+}{C}$ in which the electron density in the double bond is reduced owing to d_π–p_π interaction. Subsequently Bock and Seidl[194,195] carried out a series of studies on silyl-substituted ethylenes and butadienes by physical methods among which they examined in detail the $\nu_{C=C}$ frequencies in these compounds. Comparison of these results with the vibrational spectra of alkylbutadienes enabled them[194,195] to conclude that trimethylsilyl substituents exhibit electron-accepting properties in consequence of the d_π–p_π interaction in the Si–C=C fragments. Therefore the force constants and the ν_{C-C} frequencies in silyl derivatives are reduced. Despite the agreement between the data for π bonding and the results obtained by other methods, Egorov and coworkers[28] showed that the complex mode of vibration with a wave-number of about 1600 cm^{-1} does not permit correct conclusions concerning d_π–p_π interaction on the basis of changes in the frequency of this vibration. It was noted that the intensity of the absorption bands corresponding to this vibration in the compounds $(CH_3)_3MCH{=}CH_2$ decreases in the following sequence as M is varied: Si > Ge > Sn. On the other hand, in allyl derivatives the intensity of this vibration actually increases in the same sequence. This type of variation of the intensity was tentatively interpreted[21,22,196] within the framework of the d_π–p_π interaction between the vinyl group and the Group IVB elements. However, according to Leites et al.[28] the intensity data can also be accounted for by the involvement in the above vibrations of all the coordinates of the $\diagdown C{=}C \diagup_{M}$ fragment.

Analysis of the absorption bands due to the fanwise vibrations of the $=CH_2$ group in substituted vinylsilanes led Eisch and Trainor[197] to the conclusion that there is d_π–p_π interaction in these compounds. Other workers[20–22,194,195,198] support this view. The spectra of vinyl derivatives were interpreted from a different standpoint by Leites et al.[28] The frequency shift of the $=CH_2$ fanwise vibrations of the vinyl group when the central carbon atom is replaced in succession by silicon, tin, and germanium was explained primarily by the inductive effect of the atom M. Leites et al.[28] believe that, even if a d_π–p_π interaction effect exists, it is so weak that it does not influence the parameters of the vibrational spectra. Egorov[30,199] examined the optical properties of methyl and vinyl derivatives of Group IVB elements on the hypothesis that such elements have a duel function—both electron-donating and electron-accepting ("C-effect"). Since the "C-effect" and d_π–p_π interaction act in the same direction, it is believed[200] that it is difficult to obtain information about the d_π–p_π interaction in vinyl and phenyl derivatives in Group IVB elements. The problems of the d_π–p_π interaction in vinyl derivatives of Group IVB elements were examined in greater detail by Egorochkin and coworkers[62,201]. The frequencies ωCH_2 of the out-of-plane deformation vibrations of the CH_2 group in the compounds $CH_2{=}CHX$ are known to be highly characteristic[28] and sensitive to the electronic effects of the substituents X.[202] Therefore if X is not conjugated with the vinyl group, the ωCH_2 are linearly related to the inductive constants of X.[62] The points corresponding to compounds with substituents capable of conjugation with the vinyl group deviate from this linear relation. Analysis of the deviations established[62,201] (1) an analogy between the effects of conjugation with the vinyl group and the phenyl ring, (2) a decrease of d_π–p_π interaction in the M–vinyl bonds in the sequence Si > Ge > Sn, (3) a competition between the d_π–p_π interaction in the M–vinyl and M–halogen bonds in the compounds $Hal_3MCH{=}CH_2$,[203] and (4) a decrease of the effect of σ,π conjugation in the allyl derivatives $R_3MCH_2CH{=}CH_2$ in the sequence Sn > Ge > Si and the dependence of this effect on the nature of the substituent R. These data are consistent with the results obtained by the ^1H NMR method[59–61].

Petrov and coworkers[204,205] showed that the vibrational spectra and dipole moments of silyl-substituted 1,3-dienes indicate a shift of the electron clouds of the substituent towards the silicon atom. The d_π–p_π interaction has a significant influence also on the reactivities of compounds of this class.

A number of studies[88–97,206,207] indicate the occurrence of d_π–p_π interactions between the Group IVB element and the aromatic ring. The majority of data suggest that this effect diminishes in the sequence Si > Ge > Sn. The changes in the positions and intensities of certain characteristic vibrations of the phenyl group in the phenylsilane derivatives C_6H_5SiXYZ indicate the occurrence of d_π–p_π interaction between the *d* orbitals of the silicon atom and the π electrons of the phenyl ring[31]. However, a similar study of phenylgermanes did not yield a direct answer to the question of the possibility of π bonding in the Ge–C_6H_5 fragment[32]. The reason for the contradictory nature of the results[31,32] is low sensitivity of the spectroscopic parameters of the phenyl group to the electronic effects of the substituents. The study of Egorochkin et al.[208], where conclusions concerning the electronic effects of the aryl substituents C_6H_4X were based on an analysis of the stretching vibration frequencies of the Si–H bond (these investigations are considered in greater detail below) in

compounds with the H–Si–C_6H_4X fragments, was free from this defect. The degree of $d\pi$–$p\pi$ interaction in the Si–aryl bond varies over a wide range and increases approximately linearly with increasing inductive effect of the aryl substituent at the silicon atom, i.e. with increase of the positive charge of the central element.

The linear correlation between the stretching frequency of the C=O bond in substituted acetophenones and the Brown–Okamoto σ^+ constants of the substituents[209] was used in an investigation of the electronic properties of the substituents X in the compound $CH_3CO-C_6H_4-X$, where X = $(CH_3)_3Si$, $(CH_3)_6SiSi(CH_3)_2$, $(CH_3)_3SiO$, or $(CH_3)_3SiSi(CH_3)_2O$.[125] It was established that the group $(CH_3)_3SiSi(CH_3)_2$ has a more pronounced $+I$ effect than the trimethylsilyl group but at the same time the pentamethyldisilyl group forms more stable $d\pi$–$p\pi$ bonds than does the trimethylsilyl group with both the aromatic ring and the oxygen atom. This investigation[125] was not the only one in which the enhanced electron-accepting capacity of the pentamethyldisilyl group in relation to the trimethylsilyl group was demonstrated. A similar phenomenon was observed, for example, also by Brune[81] in a study of the NMR spectra of alkoxydisilanes. Probably, in compounds with Si–Si–O or Si–Si–C_6H_5 fragments, the lone electron pairs or π electrons are probably not delocalised solely over the d orbitals of the nearest silicon atom. Both silicon atoms are involved in this process with formation of a single d_π–d_π–p_π interaction system.

3. Analysis of the Stretching Vibration Frequencies of the Si–H Bonds in Substituted Silanes

As already mentioned frequently in this review, in a spectroscopic study of the effect of $d\pi$–$p\pi$ interaction it is particularly important to select a series of compounds such that their molecular fragments are sensitive to the electronic effects of substituents; on the other hand, it is desirable that the spectroscopic parameters should depend only on electronic effects. The vibrational spectra of substituted silanes are particularly interesting from this point of view. The vibration of the Si–H bond involves almost exclusively changes in the Si–H coordinate. The mass of the substituents R in the silanes R_3SiH does not affect the Si–H stretching vibration frequency (ν_{Si-H}) and there is no mechanical interaction between the Si–H bond and the vibrations of organic substituents[210]. Thus the vibration of the Si–H bond is highly characteristic. Moreover examination of the literature data for the vibrational spectra of substituted silanes[211–214] reveals a significant dependence of ν_{Si-H} on the nature of the substituent. On the basis of the foregoing, substituents influence ν_{Si-H} only via their electronic effects. All these factors make silanes with organic substituents ideal objects for the investigation of the effect of substituents (in particular the effect of $d\pi$–$p\pi$ interaction) on the stretching frequency of Si–H bonds. However, for a long time little attention was paid to this problem in the literature.

In the first studies dealing with the effect of substituents on the ν_{Si-H} frequency in vibrational spectra, the frequency change was attributed exclusively to the inductive effect of substituents[211–214]. Thus Thompson[212] obtained the equation $\nu_{Si-H} = 17.5\,\Sigma\sigma^* + 2106$ relating the ν_{Si-H} frequency to the sum of Taft's inductive constants σ^* for the three substituents in the silanes R_3SiH. The substituents R were both alkyl groups and groups potentially capable of $d\pi$–$p\pi$ interaction with the silicon atom (for example, halogens and the phenyl group). The accumulated experimental data on the vibrational spectra of silanes revealed that inductive hypotheses alone are clearly insufficient to describe the variation of the ν_{Si-H} frequency as the substituents are varied. It was shown that the analysis of the ν_{Si-H} frequency in the silanes $R_{3-n}X_nSiH$, where X is a substituent capable of $d\pi$–$p\pi$ interaction with the silicon atom, yields information about the double-bond character of the Si–X fragment. It was established in this way that the amount of double-bond character in the linkage between the vinyl or phenyl groups and the silicon atom is considerable even in the presence of three such groups in the molecule. Another situation is observed in alkoxysilanes. The ν_{Si-H} frequency in monoalkoxysilanes differs little from the frequency in trialkylsilanes owing to the considerable contribution of $d\pi$–$p\pi$ interaction between the oxygen and silicon atoms. In di- and tri-alkoxysilanes the ν_{Si-H} frequency is higher mainly because of the inductive effect of the alkoxy-groups. The contribution of each alkoxy-group to the $d\pi$–$p\pi$ interaction with the silicon atom becomes less than in monoalkoxysilanes[198]. Attridge[215] observed that, for each series of silanes $R_{3-n}X_nSiH$ [R = alkyl; X = $N(CH_3)_2$, C_6H_5Cl, or OCH_3], the plot of $\Sigma\sigma^*$ against ν_{Si-H} is linear.

The presence of several straight line correlations was explained by the transfer of electron density from X to the silicon d orbitals. The anomalously high ν_{Si-H} frequencies in alkoxychlorosilanes, which could not be accounted for on the basis of earlier correlations[211–213], were interpreted as due to a decrease of $d\pi$–$p\pi$ electron donation caused by the competition between substituents for the silicon d orbitals. However, the series of substituents in terms of their capacities for $d\pi$–$p\pi$ interaction proposed by Attridge does not agree satisfactorily with the current hypotheses in this field.

These studies were developed further[58,111,208,216–222]. It was shown[216,217] that, for trisubstituted silanes R_3SiH with substituents R incapable of $d\pi$–$p\pi$ interaction with the silicon atoms and exerting only an inductive effect on the ν_{Si-H} frequency, we have $\nu_{Si-H} = 23.1\,\Sigma\sigma^* + 2112$. This equation relates the ν_{Si-H} frequency to the sum of Taft's inductive constants $\Sigma\sigma^*$ for three substituents. It was used to calculate the frequencies ν_{calc} in the silanes $R_{3-n}X_nSiH$ with substituents X capable of $d\pi$–$p\pi$ interaction with the silicon atom. It was found that the ν_{calc} are higher than the experimental frequencies ν_{exp}. Under the influence of the effect of $d\pi$–$p\pi$ interaction operating in a direction opposed to that of the I effect of X (this can be conventionally treated as a decrease of the inductive effect of X), the force constant and the stretching vibration frequencies of the Si–H bond decrease. The differences $\Delta\nu = \nu_{calc} - \nu_{exp}$ are a result of the $d\pi$–$p\pi$ interaction in the Si–X bonds. The values of $\Delta\nu$ in several series of compounds have been analysed: R_2XSiH, RX_2SiH, and X_3SiH, where X = F, Cl, Br, I, OAlk, SAlk, SeAlk, $NAlk_2$, PH_2, $CH{=}CH_2$, $C{\equiv}CH$, C_6H_5, C_4H_3O, C_4H_3S, OC_6H_5, SC_6H_5, $OCOCH_3$, $C{\equiv}N$, $NH(C_6H_5)$, NCS, and N_3. Next it was established[218] that the following equations are valid for di- and mono-substituted silanes R_2SiH_2 and $RSiH_3$ with substituents R incapable of $d\pi$–$p\pi$ interaction: $\nu_{Si-H} = 23.1\,\Sigma\sigma^* + 2121$ and $\nu_{Si-H} = 23.1\,\Sigma\sigma^* + 2132$, relating the ν_{Si-H} frequency to the sum of the inductive constants σ^* for the three substituents. The ν_{exp} frequencies in the silanes $RXSiH_2$, X_2SiH_2, and $XSiH_3$ with substituents X capable of $d\pi$–$p\pi$ interaction with the silicon atom differ from the ν_{calc} calculated from these equations. The differences $\Delta\nu = \nu_{calc} - \nu_{exp}$ for di- and mono-substituted

silanes agree with the corresponding $\Delta\nu$ obtained from the spectra of trisubstituted silanes[216,217]. Analysis of the values of $\Delta\nu$ in halogenosilanes[219], in compounds with silicon–Group VI element bonds[111], and silanes with Si–N and Si–P bonds[220] showed that the capacity for d_π–p_π interaction with the silicon atom decreases within the Groups of the Periodic System from above downwards. It was established[203] that in silanes having only one substituent entering into the d_π–p_π conjugation with the silicon atom, the values of $\Delta\nu$ are related to the constants $\sigma_n - \sigma'$, characterising the conjugation of these substituents with the phenyl ring, by the linear equation $\Delta\nu = -65.6(\sigma_n - \sigma') + 3$. These data and also the results of Egorochkin et al.[62] are evidence of a considerable analogy between the effects of conjugation with the silicon atom, the phenyl ring, and the vinyl group. In compounds of the type C_6H_5–X–SiH_3, where X = O, S, or NH, there is competition between two conjugation effects: p,π and d_π–p_π.[111,220] Since the dominant effect is that of p,π conjugation, the values of $\Delta\nu$ for these compounds are appreciably lower than the $\Delta\nu$ in silanes of the type Alk–X–SiH_3, where X = O, S, or NH.

It was also shown that the points corresponding to the compounds Alk_2NSiH_3 deviate markedly from the linear equation $\Delta\nu = -65.6(\sigma_n - \sigma') + 3$ towards lower values of $\Delta\nu$.[220] This is caused by the effect of p,σ conjugation in $Alk_2\overset{\curvearrowright}{N}-Si\begin{smallmatrix}H\\H\end{smallmatrix}$, which leads to a decrease of $\Delta\nu$. The effect of p,σ conjugation in this compound is associated with the unique properties of the Alk_2N group: a low-I effect and a high capacity for conjugation. The effect of p,σ conjugation is observed also in the compounds $(Alk_2N)_2ClSiH$ and $(Alk_2N)Cl_2SiH$, as shown by the deviation of the experimental $\Delta\nu$ from the values calculated assuming an additive contribution of the dialkylamino-groups and chlorine atoms to $\Delta\nu$.[220] A similar phenomenon has been observed also in chloromethoxysilanes[217]. Likewise it was established that the degree of d_π–p_π interaction in the Si–N bond increases with the increasing $-I$ effect of the substituent having a nitrogen atom in the α-position relative to the silicon atom[220]. In agreement with theoretical postulates[4–8], this is caused by the increase of the capacity of the silicon atom for d_π–p_π interaction when its positive charge increases. The latter relation can be clearly seen also in the study of the d_π–p_π interaction in silanes having several substituents capable of such interaction[221]. A positive charge may be induced on the silicon atom by electronegative substituents. It would appear that the introduction of a second substituent X should stabilise the d_π–p_π linkage between the silicon atom and the first substituent X. However, by virtue of its $-I$ effect, the second substituent X decreases the σ electron density at the silicon atom, but, being involved simultaneously in the d_π–p_π conjugation, it increases the π electron density at the central atom. Thus, depending on the relative contributions of the electron-donating and electron-accepting properties of the substituents, their effect on the d_π–p_π conjugation in the silane molecule can be extremely varied. This problem was investigated by Egorochkin and Vyazankin[221]. The values of $\Delta\nu$ in two series of compounds were determined: $(C_2H_5)_2XSiH$ and $(C_2H_5)X_2SiH$, where X = C_6H_5, CH_2=CH, Br, Cl, F, CH_3S, or CH_3O. The compounds $(C_2H_5)X_2SiH$ may be regarded as products of the substitution of the ethyl group in $(C_2H_5)_2XSiH$ by X. The effective charge of the silicon atom in $(C_2H_5)_2XSiH$ depends both on the $-I$ effect of X and on the electronic effect of the d_π–p_π conjugation in the Si–X bond, which is opposed to it. The strength of the second d_π–p_π linkage between Si and X and hence the overall effect of the d_π–p_π interaction in molecules of the type $(C_2H_5)X_2SiH$ are determined by the magnitude and sign of this effective charge. These studies explain the experimental finding that the series of relative capacities for d_π–p_π interaction in the silanes R_2XSiH (AlkO > F > $CH_3S \simeq$ Cl > Br > CH_2=CH > C_6H_5), RX_2SiH (Br > Cl > F > CH_3S > C_6H_5 > CH_2=CH > AlkO), and X_3SiH (Br > Cl > CH_3S > C_6H_5 > CH_2=CH > F > AlkO) are not the same. The extent of d_π–p_π interaction in the molecule depends on the inductive and mesomeric effects of the substituents which alter the charge of the silicon atom. Therefore in silanes with several substituents the extent of the electron-donating properties of each substituent is determined significantly by the number and nature of its partners in d_π–p_π interaction.

The equation $\nu_{Si-H} = 23.1\,\Sigma\sigma^* + 2112$, relating the ν_{Si-H} frequency to the sum of Taft's inductive constants σ^* of substituents incapable of d_π–p_π conjugation was used to determine the values of σ^* for the groups C_2H_5Te (+0.4),[153] $(CH_3)_3Si$ (−0.9), $(C_2H_5)_3Si$ (−1.1), and $(C_2H_5)_3Ge$ (−0.8).[222] The higher electronegativity of germanium compared with silicon in the absence of the effects of d_π–p_π conjugation involving these elements was thereby confirmed.

By taking into account rigorously the inductive effects of the substituents on the infrared spectra of substituted silanes and on the ^1H NMR spectra of alkylsilanes and alkylgermanes, it was possible to establish the effect of σ,σ conjugation in methyl derivatives of silicon and germanium[58].

The data described show that considerable advances have been achieved in the study of the effect of d_π–p_π interaction in organic derivatives of Group IVB elements. Summarising the principal results of studies in this field, the following conclusions may be formulated. In compounds containing one M–X bond (M = Si, Ge, or Sn; X = element or Groups V–VII) or a group M–X–M (X = O, S, or Se), the capacity for d_π–p_π interaction between the atoms M and X in a given Group of the Periodic System decreases with the atomic numbers of the elements M and X. The decrease of the capacities for d_π–p_π interaction between the atoms M and X in the given Group on passing from a substituent X in the Second Period to one in the Third Period is greater the lower the number of the group to which X belongs. The mechanism of the d_π–p_π interaction between the atoms Si and X is formally similar to the effects of the conjugation of the substituent X with an aromatic ring or the vinyl group. In compounds containing one Si–H bond, the relative capacity for the formation of d_π–p_π linkages with the silicon atom is correlated with their Hammet resonance constants. In silane derivatives containing two or three similar substituents X capable of d_π–p_π interaction, the extent of the latter is determined by the effective charge of the silicon atom, which depends on the inductive and mesomeric effects of X.

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