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Spectroscopic Study of π-Acceptor Effects in Compounds of Silicon Subgroup Elements

A.N.Egorochkin and S.Ya.Khorshev

The general state of research into the π-acceptor properties of silicon subgroup elements (E) by spectroscopic methods is examined and the data obtained are surveyed. It is shown that the π-acceptor properties are weakened with increase of the atomic number of the element E, and the analogy between these properties and the conjugation effect in unsaturated carbon compounds is traced. The widespread interpretation of π-acceptor properties of these elements as a manifestation of the effect of the d_π-p_π interaction is justified.
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I. INTRODUCTION

The study of the nature of the chemical bond in compounds of silicon and the elements of its subgroup (E) is not only of great independent interest but is also of undoubted importance for the understanding of the characteristics of the chemical bond in organoelemental compounds of non-transition elements as a whole.

Despite the theoretical and practical importance of this problem (many of the compounds considered are used in the national economy), many of its aspects still remain controversial. These include primarily the problem of the mechanism of the π-acceptor effect of the atoms E, which is observed in M–X fragments, where X is an atom with unshared electron pairs (*n*-donor substituent) or an α,β-unsaturated hydrocarbon group (π-donor substituent) and is one of the causes of the sharp difference between the properties of compounds of carbon and the elements E.[1-6] The study of the intramolecular interaction between the E and X atoms not linked directly by chemical bonds has been studied vigorously in recent years[7]; it is evidently also a consequence of the manifestation of the acceptor properties of the atoms E.[8]

The traditional interpretation of the π-acceptor properties of the atoms E is based on the idea of the d_π–p_π interaction in E–X fragments caused by the presence of vacant *nd* orbitals in the atoms E.[9] The E–X bond then acquires a partial double bond character, the amount of double bond character depending on the ratio of the donor properties of X and the acceptor properties of E. The donor–acceptor properties depend on the nature of other substituents linked to the E and X atoms[3,6]. The hypothesis of vacant *nd* orbitals explains at least qualitatively all the properties of the compounds of silicon subgroup elements which significantly distinguish these derivatives from carbon compounds.

The possibility, in principle, of d_π–p_π binding has been demonstrated by a quantum-chemical method[10-12] and some of its aspects have been considered: the dependence of the overlap integrals of the p_π and d_π orbitals on the molecular geometry[3,11] and the enhancement of the double bond character with increase of the positive charge on the central element E.[11] The size of the *d* orbitals of the atom depends on the nature of the substituents linked to it[13]. For this reason, firstly, the atomic *d* orbitals can differ appreciably from molecular *d* orbitals[14] and, secondly, it is difficult to make an *a priori* estimate of the relative contribution of the d_π–p_π binding for compounds of different structure. At the same time critical analysis of the data obtained using various quantum-chemical computational methods showed that, in order to account for the nature of the bond in compounds of non-transition elements (particularly in silicon compounds), it is necessary to take into account the contribution of the 3*d* atomic orbitals of these elements[15]. We may note, however, that the opposite view has also been expressed[16].

The quantum-chemical data indicated above[10-16] and those quoted below in the present review should apparently be considered from two standpoints. On the one hand, the involvement of *nd* orbitals in the formation of bonds by the elements E is entirely possible. On the other hand, the actual degree of this involvement is in many cases so small that, although the effect produced by this can in fact be observed experimentally, their magnitude is comparable to the accuracy of the computational methods. For this reason, the application of modern quantum-chemical methods in many cases fails to yield an unambiguous result in the study of effects of this kind and, for reasons described above, the idea of the d_π–p_π interaction was partly in the nature of a working hypothesis from its very inception.

During the last decade other ideas have been invoked to account for the properties of compounds of silicon subgroup elements together with the *nd*-orbital hypothesis[17,18]. The more significant role of the hyperconjugation effects in organoelemental compounds compared with carbon derivatives, due to the greater polarisability of the bonds in the former compounds, has been known for a long time[19]. However, Pitt's attempt[17] to put forward the hyperconjugation effect as an alternative to the hypothesis of the decisive role of the d_π–p_π interaction in organosilicon compounds, maintained in some investigations (see, for example, Ponec and Chvalovsky[20,21]), was subsequently disproved by its author[22], who concluded that both effects are important: hyperconjugation and d_π–p_π interaction.

In 1969 Musher proposed the model of hypervalent bonds to account for the acceptor properties of Group V–VIII elements of the Periodic System in the highest valence states in compounds where the number of ligands is greater than four[18]; on the basis of this model, it was shown, in particular, that there is a transannular bond between the silicon and nitrogen atoms in silatranes[23]. With the exception of the study of Sidorkin et al.[23], there is no information about the applicability of this hypothesis to the study of compounds of silicon subgroup elements. This hypothesis cannot therefore be

recognised at present as an effective alternative to the idea of the d_{π}–p_{π} interaction[24,25].

Thus there are several points of view on the problem of the mechanism of the π-acceptor properties of the atoms E. While the possibility, in principle, of the involvement of the *d* orbitals of such atoms E in the formation of a bond is not to be denied, quantum-chemical methods do not yield unambiguous conclusions about the magnitude of the *d*-orbital contributions in specific compounds because of their approximate nature. At the same time, there are extensive literature data obtained in experimental studies of the π-acceptor effects of the E atoms by spectroscopic methods. A critical consideration of these data makes it possible to formulate the fundamental characteristics of the manifestation of these effects, which, as will be shown below, do not conflict with the hypothesis of the involvement of the *nd* orbitals of the E atoms in the formation of bonds of the d_{π}–p_{π} type. The present review deals only with those studies, among the large number described, in which the π-acceptor properties of the E atom have been studied by a correct method and which lead to generalisations and are of fundamental importance for the understanding of the subject of this review.

II. CHARACTERISTICS OF THE MANIFESTATION OF THE π-ACCEPTOR EFFECTS

We believe it to be most useful to arrange the literature data systematically on the basis of the type of E–X bonds. The π-acceptor effects of the elements of the silicon subgroup will be designated in the present review by the term d_{π}–p_{π} interaction (arguments justifying the legitimacy of this term are given in Section III).

1. The E-Group VII Element Bond

The E–X interatomic distances (X = halogen) in halogeno-derivatives of the E elements are in many cases shortened compared with the values calculated from the covalent radii of the E and X atoms after correction for their electronegativities. For example, the experimental[26] and calculated (given below in brackets) values are as follows for the compounds SiF_4, $SiCl_4$, $SiBr_4$, SiI_4, GeF_4, and SnF_4 respectively (in Å): 1.54 (1.69); 2.01 (2.05); 2.25 (2.22); 2.43 (2.44); 1.67 (1.75); 1.84 (1.94). These findings were used by Brockway and Wall[27] and also by Pauling[9] as a basis for the introduction of the concept of the d_{π}–p_{π} conjugation between the *d* orbitals of silicon and the unshared electron pairs of the halogens. A tendency has been observed towards a decrease of the discrepancy between the experimental and calculated E–X lengths in the series Si > Ge > Sn and F > Cl > Br > I; however, one should note that analysis of the discrepancies is complicated by the inadequate accuracy of the experimental E–X distances and some uncertainity in their calculated values.

The double bond character of the E–X fragments has been demonstrated more unambiguously by spectroscopic methods and by experiments designed to investigate the dipole moments. The occurrence of d_{π}–p_{π} binding between the E and X atoms is indicated by a whole series of facts.

1. The high valence force constants of the Si–X (X = halogen) indicating the partial double character of these linkages. A detailed examination of the dependence of the force constants on the electronic effects of the substituents led to the conclusion[2,28–32] that the force constants of the Si–X bonds cannot be described solely in terms of the inductive influence of X and other substituents.

2. The higher energies of the unshared electron pairs of the halogens in silicon compounds compared with the isostructural carbon compounds and the intermediate values of the germanium derivatives[33–36]. Thus the vertical ionisation potentials of the *np* orbitals of the halogens, determined by photoelectron spectroscopy, are 11.28, 11.61, and 11.34 eV for CH_3Cl, SiH_3Cl, and GeH_3Cl respectively and 10.70, 11.03, and 10.72 eV for CH_3Br, SiH_3Br, and GeH_3Br respectively[33]. It might have been expected that the replacement of a carbon atom by a less electronegative silicon or germanium atom would lead to an increase of the negative charge on the Cl and Br atoms and hence to a decrease of the ionisation potentials of the halogens. However, this is not observed experimentally owing to the manifestation of π-acceptor properties by the silicon atom (and to a lesser extent by the germanium atom).

3. The low-electron-donating capacity of chlorosilanes in the formation of a hydrogen bond[37]. In conformity with the ionisation potential data examined above, the compounds $(CH_3)_3MCl$ and $(CH_3)_2ECl_2$ (E = C, Si, Ge, or Sn), which are electron donors in the formation of a hydrogen bond with phenol, exhibit the lowest electron-donating capacity for E = Si. This also confirms the partial delocalisation of the unshared electron pairs of the chlorine atoms over the vacant 3*d* orbitals of the silicon atom.

4. The opposite signs of the conjugation contributions of the substituents R_i to the NQR frequencies of the halogens in the carbon derivatives $(R_i)_3CX$ and derivatives of the silicon subgroup elements $(R_i)_3EX$, where X = Cl or Br and E = Si, Ge, or Sn.[38] It has been observed that the NQR frequencies (characterising the state of the valence electrons and the type of chemical bond in which the halogens are involved) are correlated, within the limits of each of the above eight series of compounds, with the sums of the inductive Taft constant σ* of the substituents R_i. However, a more rigorous treatment leads to the conclusion that one must take into account not only the inductive but also the conjugation influence of R_i on the NQR frequency. Analysis of the correlation analysis data indicates an increased multiplicity of the E–X bonds and its dependence on the d_{π}–p_{π} interaction in the E–R_i fragments.

5. The reduced frequencies and increased intensities of the absorption bands associated with the stretching vibrations of the E–H bonds (E = Si or Ge) in the infrared spectra of halogenosilanes and halogenogermanes compared with the values expected on the hypothesis of a purely inductive influence of the halogens[39–42]. The transfer of electron density in the H–E–X fragment from the halogen atom to the E atom leads on the one hand, to a decrease of the acceptor properties of the halogen and a decrease of the force constant of the E–H bond and of its stretching vibration frequency and, on the other hand, it induces an increase of the negative charge on the hydrogen atom of the E–H bond and increases its polarity and the intensity of the E–H stretching vibration band in the infrared spectrum.

6. The increased shielding constants of the methyl and ethyl groups in the ^1H NMR spectra of alkylhalogeno-silanes and -germanes $R_{3-n}EX_n$ (R = CH_3 or C_2H_5; E = Si, or Ge; X = F, Cl, Br, or I).[43] Calculation taking into account the purely inductive influence of the substituents on the chemical shifts of the protons in the group R by the method of correlation analysis with corrections for magnetic anisotropy leads to a discrepancy between the calculated chemical shifts and their experimental values. The increased shielding of the groups R is a result of the weakening of the electron-accepting properties of the halogen atoms in consequence of the d_{π}–p_{π} interaction in the E–X fragments.

7. The smaller dipole moments of halogenosilanes compared with the corresponding halogenomethanes[3]. On the basis of

the lower electronegativity of silicon compared with that of carbon, a greater polarity of the Si–X bond compared with C–X might have been expected. However, experiment failed to confirm this. The example of the simplest silane derivatives shows that the polarity of the Si–X bonds[3] as well as the polarity of the E–X bonds in alkylhalogeno-derivatives of silicon, germanium, tin, and lead (see, for example, Sorriso et al.[44]) is reduced owing to the delocalisation of the unshared electron pairs of the halogen atoms over the *nd* orbitals of the E atoms.

2. The E–Group VI Element Bond

Among the compounds having this bond, the practically important derivatives containing the Si–O siloxane linkage and the Si–O–Si disiloxane linkages have been studied in greatest detail. Modern ideas about the nature of the siloxane linkage have been considered in a monograph[45]. The characteristic results of the manifestation of a strong d_π–p_π interaction in the Si–O bond are as follows[45]: the shorter length of the Si–O bond (~1.65 Å) compared with the sum of the covalent radii (1.83 Å) of the silicon and oxygen atoms; the greater Si–O–Si angle (105–180°); the high energy (100–120 kcal mol^{-1}) and high force constant[46] as well as the low polarity (dipole moment 1.2–1.6 D) of the Si–O bond; the weak-electron-donating properties of the oxygen atoms in alkoxysilanes, which are still further reduced in disiloxanes compared with the corresponding carbon analogues; the appreciably greater acidity of silanes compared with carbinols.

The strong d_π–p_π interaction in the Si–O bond is appreciably weakened on passing to the Ge–O fragment. The expected bond length in $(H_3Ge)_2O$ is therefore smaller by only 0.06 Å than the experimental value and the Ge–O–Ge angle (126°) is significantly smaller than the Si–O–Si angle in disilyl ether (144°).[47] The E–O–E angles in the $[(CH_3)_3Ge]_2O$ and $[(CH_3)_3Sn]_2O$ molecules, which are ~141°, indicate the important role of the effect of the d_π–p_π interaction also in the formation of the Sn–O bond[48].

Systematic studies of the dependence of the d_π–p_π interaction in the E–X fragment on the nature of the silicon sub-group elements E and the group VI elements X have been carreid out by infrared spectroscopy and ^{1}H NMR [40,43,46,49,50]. The use of correlation analysis methods showed that the frequency and intensity of the stretching vibrations of the E–H bond in the infrared spectra of compounds with the H–E–X (E = Si, or Ge; X = O, S, or Se) fragment are determined, apart from the inductive effect, also by the conjugation interactions in the E–X groups. The role of such interactions diminishes with increase of the atomic number of the elements E and X, i.e. in the sequences Si > Ge > Sn and O > S > Se > Te. The contribution of the d_π–p_π interaction to the Si–Te bond is extremely small if any.

A convincing confirmation of these conclusions was obtained by three independent methods: in the study of the relative electron-donating capacity of compounds with E–X–E groups in the formation of hydrogen bonds by them[51]; in the analysis of the chemical shifts in the ^{1}H NMR spectra of the protons of the CH_3E groups of the compounds $(CH_3)_3SiXCH_3$ (X = O or S) and $(CH_3)_3GeOCH_3$;[43] in the study of the variation of the stretching vibration frequency ν(E–C) as a function of the substituents X in organodielemental compounds of the type $[(C_2H_5)_3E]_nX$, where E = Si, Ge, or Sn and X is a Group I–VII element[52]. The following features of the spectroscopic parameters, which do not agree with the hypothesis of their dependence solely on the inductive influence of the various substituents, have been found using these three different methods: (1) the change in the electron-donating capacity of compounds with E–X–E groups, where E is a silicon subgroup element, as the Group VI elements X are varied is inconsistent with the sequence O > S > Se > Te known to hold[53] for carbon compounds. The differences diminish with increase of the atomic numbers of the elements E and X. The increase of the mobility of the hydrogen in the X–H group in structurally similar compounds with the E–X–H fragment corresponds to a decrease in the electron-donating capacity of the compounds with such a fragment[54,56]; (2) corrections for magnetic anisotropy and the inductive effect showed that the shielding constants of the protons of the CH_3E group in trimethylmethoxygermane and to an even greater extent in trimethylmethoxysilane are too high. The shielding constant of trimethylthiosilane has increased less than the constant of trimethylmethoxysilane[43]; (3) the points corresponding to compounds with E–Group VI element bonds deviate from the linear correlation between the ν(E–C) frequencies in the compounds $[(C_2H_5)_3E]_nX$ and the electronegativity of the elements X (where X is a Group I–III element); the deviations decrease in the sequence O > S > Se > Te.[52] However, they cease to be "anomalous" if one takes into account the effect of d_π–p_π interaction. In the E–X and E–X–E fragments this effect opposes the inductive effect of the atom X and therefore leads to the above deviations, which diminish with increase of the atomic numbers of the elements E and X

Specific aspects of the problem of the d_π–p_π interaction have been examined in a number of studies, in which details of the general relations discussed above were obtained. One of the most significant problems in this connection is competition between the effects of the d_π–p_π interaction and p,π conjugation in compounds containing groups of the type C_6H_5–X–Si< and R–C(=O)OE<. [49,57]. In $C_6H_5SiH_3$ both unshared electron pairs of the oxygen atom are involved in conjugation—one with the benzene ring and the other with the silicon atom[47][sic], [58]. In contrast to oxygen, the sulphur atom supplies only one electron pair for conjugation[59]. Therefore in $C_6H_5SSiH_3$ only the energetically more favourable conjugation with the benzene ring takes place, while there is no d_π–p_π interaction in phenylthiosilanes, in contrast to alkylthiosilanes[49]. The reduction of the electron density at the oxygen atom of the E–O–C fragment in benzoates and acetates in consequence of the R_3E–$\overset{\curvearrowright}{O}$–CR=$\overset{\curvearrowright}{O}$ conjugation is responsible for the small amount of the d_π–p_π character of the M–O bond in these compounds[57], compared with, for example, the alkoxy-derivatives of the elements E.

3. The E–Group V Element Bond

Fairly clear evidence in support of the operation of the effect of the d_π–p_π interaction in some of the E–Group V element bonds has been obtained in structural studies, selected results of which are presented in Table 1.

A classical example of the influence of the d_π–p_π interaction is the planar disposition of the heavy atoms in trisilylamine (with the Si_3N molecular skeleton), in contrast to the pyramidal structure of the C_3N fragment in trimethylamine. The delocalisation of the unshared electron pair of the nitrogen atom over the 3*d* orbitals of the silicon atoms leads to a sharp reduction of the basicity of trisilylamine compared with trimethylamine[3]. Solely on the basis of the smaller electronegativity of the silicon atom compared with the carbon atom, one would actually expect a greater basicity of trisilylamine compared with trimethylamine. The configuration of the bonds involving nitrogen atoms becomes nearly planar also in

the molecules of disilylmethylamine, silyldimethylamine, trigermylamine, and $Sn[N(CH_3)_2]_4$.[65] This shows that the effect of the d_π–p_π interaction contributes to the energy of not only the Si–N bond but also the Ge–N and Sn–N bonds. However, owing to the decrease of the contribution of the d_π–p_π interaction with increase of the atomic number of the elements E, the heavy atoms in trigermylamine are not entirely coplanar, unlike trisilylamine[63]. In contrast to derivatives with E–N bonds, the trisilylphosphine and trigermylphosphine molecules have a pyramidal configuration, while their E–P–E valence angles differ slightly from the C–P–C angle (~100°) in trimethylphosphine. The heavy atoms are also non-coplanar in trisilylarsine and trisilylstibine (Table 1).

Table 1. The bonds lengths and valence angles in derivatives of Group V elements.

Compound	E–X bond length, Å		E–X–E angle (°)	References
	experimental	calculated as the sum of covalent radii of E and X (Ref.60)		
$(H_3Si)_3N$	1.734	1.87	119.7	61
$(H_3Si)_2NCH_3$	1.726	1.87	125.4	61
$H_3SiN(CH_3)_2$	1.715	1.87	—	61
$(H_3Si)_3P$	2.246	2.27	96.8	62
$(H_3Si)_3As$	2.353	2.38	94.1	62
$(H_3Si)_3Sb$	2.555	2.58	89	62
$(H_3Ge)_3N$	—	1.92	116	63
H_3GeNCO	1.831	1.92	—	64
$(H_3Ge)_3P$	2.306	2.32	95.7	62
$(H_3C)_3N$	1.47	1.47	108	60
$(H_3C)_3P$	1.87	1.87	100	60
$(H_3C)_3As$	1.98	1.98	96	60

It follows from Table 1 that the Si–N and Ge–N interatomic distances deviate appreciably from the sum of the covalent radii of the E and N atoms. As in siloxanes, in silazanes the Si–N bond length is reduced (the bond length calculated from the covalent radii after introducing corrections for the amount of ionic character of the bond by the Schomaker–Stevenson method[66] is 1.80 Å) and the valence angles at the nitrogen atom are increased. These facts agree with the hypothesis of an increased order of the Si–N bond in silazanes due to the d_π–p_π interaction[67]. Thus structural data clearly indicate an increase of the E–N (E = Si, Ge, or Sn) bond orders. The amount of double bond character then decreases with increase of the atomic number of E.

On the other hand, the experimental E–X bond lengths (where E = Si or Ge and X = P, As, or Sb) virtually agree with the sum of the covalent radii of the E and X atoms. As stated above, compounds containing such bonds have a pyramidal structure like their carbon analogues (i.e.with E =C). Thus the structural data for derivatives containing elements of the phosphorus subgroup do not indicate an appreciable increase of the angles or a decrease of the interatomic distances which might be ascribed to the influence of the effect of the d_π–p_π interaction.

These facts, pointing to a significant weakening of the d_π–p_π interaction already on transiton from the E–N bond to the E–P bond were subsequently convincingly confirmed by infrared spectroscopy[68]. Analysis of the stretching vibration frequencies of the Si–H bond in the infrared spectra of compounds with the H–Si–N fragment showed that values of ν(Si–H) depend not only on the inductive influence of the three substituents at the silicon atom but are also determined by the influence of several mesomeric effects, the principal ones being those of the d_π–p_π interaction and the σ,p conjugation. In contrast to this, the frequencies ν(Si–H) in the infrared spectra of compounds containing the H–Si–P fragment depend solely on the inductive influence of the three substituents linked to the silicon atom[68].

The significant d_π–p_π character of the Si–N bond and the absence of double bond character in the Si–P group can be explained by assuming that the d_π–p_π interaction in the E–X bond has a profound analogy with conjugation effects in organic chemistry, for example, with the effect of ρ,π conjugation in the benzene derivatives C_6H_5–X (where X has the same substituents as in the organo-elemental compounds with the E–X bond). The possibility of drawing such an analogy is justified in detail in Section III of the present review.

The proposed approach makes it possible to regard d_π–p_π interaction as a process which depends on two factors: the electron-accepting properties of the atom E and the electron donating properties of the substituent X. It is well known[69] that, as a substituent in an aromatic ring, the dialkylamino-group exhibits an exceptionally high capacity for conjugation. This property of the dialkylamino-group is responsible for the considerable amount of the d_π–p_π character of the Si–N bond in fragments of the type $Si–N(CH_3)_2$.[68] The $P(CH_3)_2$ group has a low capacity for conjugation of the p,π type[70] due to the weak p character of the orbitals of the unshared electron pair of tervalent phosphorus[71]. This is the reason for the virtual absence of d_π–p_π character in the Si–P bond[68], which applies to an even greater extent, according to structural data, to other bonds of the type E–P and also to E–X bonds where X is a phosphorus subgroup element[52].

Important information about the π-acceptor properties of silicon subgroup elements E has been obtained in a systematic study of the electron-donating capacity of compounds containing E–N fragments[59,72–80]. The electron-donating capacity was estimated from the shift of the stretching vibration frequency of the C–D bond in deuterochloroform or the N–H bond of pyrrole in the infrared spectrum when the above compounds form a hydrogen bond with organoelemental compounds. The electron-donating capacity of organosilicon, organogermanium, and organotin amines depends significantly, like that of the usual organic amines, on the nature of the substituents linked to the Group IVb element; in the absence of appreciable steric hindrance, it decreases steadily with enhancement of the electron-accepting properties of the substituent. In isostructural series of compounds with a variable element E, the electron-donating capacity depends greatly on the nature of the atom E.[73–77,79].

In all cases, the electron-donating capacity of amines having one or several Si–N bonds is greatly reduced compared with that for the corresponding carbon compounds[59,72,75]. A typical example is provided by the extremely low electron-donating capacity of trisilylamine[3], while trimethylamine is a strong base. The electron-donating capacity of germanium-containing amines is also appreciably weakened compared with that of carbon compounds of analogous structure[75–77]. The relative electron-donating capacity of the nitrogen atoms in isostructural compounds is reduced to the sequence C–N–C > C–N–Ge > Ge–N–Ge > C–N–Si > Si–N–Si when the immediate environment of the nitrogen atom is altered[75]. This sequence is directly opposed to that expected on the basis of the electronegativities of the Group IV elements. The electronegativity varies in the sequence C > Ge > Si,[6] so that it might have been expected that carbon-based amines and silylamines would exhibit the minimum and maximum electron-donating capacities respectively. The experimentally observed opposite sequence of electron-donating capacities indicates the delocalisation of the unshared electron pairs of the nitrogen atoms over the vacant *nd* orbitals of the E atoms (i.e. d_π–p_π interaction occurs). This effect is enhanced on passing from germanium derivatives to silylamines and also with increase of the number of silicon atoms linked to the nitrogen atom[81].

The π-acceptor properties of the E atoms, which involve the transfer of electron density in the E–N fragments from the nitrogen atom to that of the silicon subgroup element, should lead to an increase of the mobility of the hydrogen atom in the E–N–H group compared with that expected on the basis of the inductive effect of the substituents linked to the nitrogen atom. The validity of this conclusion was demonstrated by comparing the relative acidities of amines and silylamines. It has been shown by infrared spectroscopy that, on formation of a hydrogen bond, silylamines exhibit much more pronounced electron-accepting properties than their carbon analogues in relation to electron donors to which they are linked by hydrogen bonds[74,75,82,83]. The effect of the d_π–p_π interaction in the Si–N bond leads to the appearance of electron-accepting properties in the R_3Si group, as a result of which the mobility of the hydrogen atom in compounds containing the R_3Si–N–H fragment increases sharply[83].

An extremely characteristic feature of compounds with an E–N fragment is the significant role of conjugation effects in the latter, which operate together with the d_π–p_π interaction. The specific features of the appearance of these effects are determined mainly by two factors: firstly, the exceptionally high capacity of the dialkylamino-group for conjugation, which has already been noted, and, secondly, the presence of only one electron pair at the nitrogen atom and the consequent possibility of competition between different conjugation effects involving this pair. If the conjugation effects are comparable in intensity, they do not appreciably weaken one another, acting independently. On the other hand, if one of the effects is energetically clearly preferable, its influence becomes dominant and that of the other effects is suppressed. The situation of the first type is characteristic of alkyl(dialkylamino)silanes and that of the second type is characteristic of *N*-trimethylsilyl, *N*-trimethylgermyl, and *N*-trimethylstannyl derivatives of aniline.

Analysis of the factors influencing the frequency and integral intensity of the stretching vibration of the Si–H bond in the infrared spectra of ethyl(diethylamino)silanes shows that, together with the d_π–p_π interaction, a second mesomeric effect—the σ, *p* conjugation $R_2\overset{\curvearrowright}{N}$–Si → H—plays a significant role in the Si–N bond in these compounds[84]. The manifestation of the σ, *p* conjugation is promoted by the small inductive effect ($\sigma_I \cong 0.1$) and the high capacity of conjugation ($\sigma_R = -0.8$) of the diethylamino-group. The introduction of second and third diethylamino-groups into the silane molecule is accompanied by the enhancement of the overall *-I* effect of the substituents, but the inductive effect is fully compensated by the electron-donating properties of the diethylamino-group via the d_π–p_π and σ, *p* conjugation mechanisms. Therefore, in contrast to any other silanes with functional groups, the frequencies ν(Si–H) decrease, and not increase, as the number of diethylamino-groups is increased. The dipole moment of the Si–H bond and the negative charge on the hydrogen atom in ethyl(diethylamino)silanes become greater than in trialkylsilanes as a result of the joint influence of the effects of the d_π–p_π interaction and the σ, *p* conjugation[84].

Typical systems in which the competition between the effects of the d_π–p_π interaction and the *p*, π conjugation induces a virtually complete suppression of the former effect are *N*-substituted anilines[85]. In the study of these compounds by infrared spectroscopic and NMR methods no stereochemical evidence for the occurrence of the d_π–p_π interaction in the E–N bonds was found. This is caused by the stronger *p*, π conjugation of the single unshared electron pair of the nitrogen atom with the aromatic ring in the fragment E–$\overset{\curvearrowright}{N}$–(E = Si, Ge, or Sn) compared with the d_π–p_π interaction in the E–N bonds[68]. A similar phenomenon has been observed, as already mentioned above, in phenylthiosilanes[49] where the involvement of the sulphur atom in *p*, π conjugation with the aromatic ring Si–$\overset{\curvearrowright}{S}$i– leads to the "switching off" of the d_π–p_π interaction between this atom and the 3*d* orbitals of silicon.

Thus, other conditions being equal, the d_π–p_π interaction is energetically less favourable than the *p*, π conjugation.

4. The E–Aromatic Ring Bond

The π-acceptor properties of silicon subgroup elements E in relation to an aromatic ring linked to them are indicated by numerous spectroscopic data. The principal data refer to the study of benzene derivatives; only a few have been concerned with aromatic heterocycles.

The electron-accepting properties of the E atoms linked to an aryl substituent are indicated by a series of data.

1. The higher energies of the first band in the photoelectron spectrum of phenylsilane compared with toluene, which indicate the stabilisation of the highest energy orbital in phenylsilane via d_π–p_π binding[86]. This has been confirmed by data for halogenotriphenyl derivatives of Group IV elements[87] and for the *p*-substituted derivatives of trimethylphenylsilane[88,89], which also indicate an appreciable transfer of electron density from the benzene ring to the silicon atom.

2. The enhanced electron-accepting properties of the substituents ER_3 compared with the corresponding carbon substituents (according to NMR data). ^1H NMR and particularly ^{19}F NMR of benzene derivatives constitute thoroughly developed methods for the estimation of the electronic effects of substituents linked to the benzene ring[90]. In particular, the secondary scale of Hammett constants is based on NMR data[90]. Derivatives of trimethylphenylsilanes containing different substituents in the *ortho*-, *meta*-, and *para*-positions have been studied by NMR [91]: compounds of the $(C_6H_5)_3EX$ series (E is a group IVB element and X are different substituents)[92]; the fluoro-derivatives *m*- and *p*-FC_6H_4E [93]; the pentafluorophenyl derivatives of Group IVB elements[94]; organotin compounds containing monofluorophenyl substituents[95–97]. The above investigations showed that, in the case of all the organoelemental substituents, including the organotin substituents, ideas based on the electronegativities of the silicon subgroup elements are insufficient for the description of the characteristic features of the variation of the chemical shifts and the spin–spin coupling constants. The electronic interactions between the organoelemental substituents and the aromatic ring proceed via a combined (inductive and resonance) mechanism (d_π–p_π interaction).

3. The increase, according to microwave spectroscopic data[98], of the potential barrier to the rotation of the silyl group in phenylsilane, compared with the analogous quantity for the methyl group in toluene, owing to the d_π–p_π binding between the silicon atom and the aromatic ring.

4. The smaller electron-donating capacity of silicon- and germanium-containing derivatives of benzene compared with their carbon analogues on formation by these compounds as π-donors of a hydrogen bond with electron acceptors[99,100]. This effect is caused by the reduced electron density in the benzene ring in organoelemental compounds in consequence of the d_π–p_π interaction in the E–C_6H_5 fragments.

5. The higher frequencies, ν_{CT}, of the charge-transfer bands in the electronic absorption spectra of charge-transfer complexes of phenylsilanes with tetracyanoethylene compared with their carbon analogues and the intermediate values of ν_{CT} in phenylgermane complexes[100–103]. Charge-transfer

complexes of the π,π type are formed between π-donors (aromatic compounds) and π-acceptors (for example, tetracyanoethylene). The absorption of a light quantum $h\nu_{CT}$ by such a complex causes the transition of the latter from the ground to an excited state. The energy $h\nu_{CT}$ is linearly related to the ionisation potential of the π-donor and the σ_n^+ constants of the substituents in the aromatic ring[100]. Analysis of the values of ν_{CT} in the spectra[100-103] and of the calculated Brown–Okamoto σ_n^+ constants shows unambiguously that the overall electronic effect of the substituents ER_3 in the ring (E is a silicon subgroup element) is the sum of two components—inductive and resonance (i.e. d_π–p_π interaction takes place). The d_π–p_π interaction is most pronounced in phenylsilanes.

6. The inadequacy of inductive ideas alone for the description of the nature of the changes in the frequencies and intensities of the stretching vibration bands of the E–H bond (E = Si or Ge) in the infrared spectra of silane and germane derivatives containing phenyl substituents[40-42,50,105]. This is caused by the effect of the d_π–p_π interaction in the E–C_6H_5 fragments. The dependence of the effectiveness of the d_π–p_π binding on the nature of the substituents in the aromatic ring will be specially considered in Section III of the present review in relation to arylsilanes[105].

7. Numerous data for the dipole moments of phenyl derivatives of Group IVB elements, which have been discussed in fair detail in a number of reviews[3,5,6] and surveys[106-110] have shown that the ER_3 fragments (E is a silicon subgroup element) manifest, together with a positive inductive effect, a negative mesomeric effect (d_π–p_π interaction), which diminishes on passing from organosilicon compounds to germanium and tin derivatives. The degree of d_π–p_π interaction depends on the nature of the substituents at the E atom and in the benzene ring. The presence of typically electron-donating substituents in the *para*-position in the ring leads to a direct polar conjugation effect in which the ER_3 fragment behaves as an acceptor centre.

As mentioned above, the d_π–p_π interaction between the E atoms and the aromatic ring has been studied mainly for benzene derivatives. However, it has been established in a number of studies[111-117] that significant π-binding is characteristic also of silylnaphthalenes.

Electronic spectroscopy of charge-transfer complexes has been used to investigate the π-acceptor effects of organoelemental substituents in thiophen[118] and furan[119] derivatives. Analysis of the frequencies of the charge-transfer bands in the spectra of charge-transfer complexes of these compounds (π-donors) with tetracyanoethylene (π-acceptor) and also comparison of these frequencies with proton chemical shifts in NMR spectra show convincingly that the electron-donating properties of the trimethylsilyl and trimethylgermyl groups are weaker than those of the t-butyl group owing to the d_π–p_π interaction. The decrease of the d_π–p_π character of the E–furyl bond as E is varied in the sequence Si > Ge > Sn [119] has been established in relation to furan derivatives and has been confirmed by NMR data[120].

Thus the sum total of the available spectroscopic data clearly indicates the d_π–p_π character of the E–aromatic ring bonds.

5. E–C = C and E–C ≡ C Systems

Numerous literature data have confirmed the involvement of the π electrons of an α,β-unsaturated hydrocarbon substituent linked to a silicon subgroup element (E) in d_π–p_π interaction with the vacant *nd* orbitals of the E atom. The most striking of these results are described below.

1. The smaller valence force constants of the C = C [112,121] and C ≡ C [122-124] bonds in organoelemental derivatives, compared with their carbon analogues, which is particularly pronounced for silicon derivatives. For example, the carbon–carbon bond orders in the compounds $H_3EC \equiv CH$ with E = C, Si, or Ge, are respectively 2.65, 2.47, and 2.53.[124] The maximum degree of delocalisation of the π electrons of the multiple bonds over the vacant *d* orbitals in the silicon compounds corresponds to the minimum order of the multiple bond in these compounds.

2. The lower electron-donating capacity of organoelemental compounds (as π-bases in the formation of hydrogen bonds with electron acceptors[122,125,126] and as π-donors in the formation of charge-transfer complexes of the π,π type[127,128]), linked indirectly to the lower force constant, as well as the greater mobility of the acetylenic hydrogen atom of the E–C = C–H fragment (E is a silicon subgroup element) compared with carbon analogues[129-132]. All these factors, caused by the π-acceptor properties of the E elements, are most strongly manifested in silicon compounds, while in lead derivatives they are virtually absent[129].

3. The inadequacy of inductive ideas alone for the description of the change in the frequency of the highly characteristic[133] out-of-plane deformation vibration of the $=CH_2$ group in the infrared spectra of ethylene derivatives $CH_2 = CH–ER_3$ containing organoelemental substituents ER_3 (E = Si, Ge, or Sn).[134] The frequency of this vibration is determined by the joint inductive and mesomeric (π,π and π,*p* conjugation as well as d_π–p_π interaction for organoelemental compounds) effects of the substituents.

4. The occurrence of a resonance interaction, together with the inductive effect, between the silicon atom and the C = C and C ≡ C fragments, which is manifested in the infrared spectra of silane derivatives containing such fragments[135]. The influence of the resonance effect (d_π–p_π interaction) is shown by the deviation of the stretching vibration frequencies of the Si–H bond from the values expected on the basis of allowance for the purely inductive effect of these fragments.

5. Analysis of the parameters of the NMR spectra[136-140] and the dipole moments[106,109,137] of organoelemental derivatives of ethylene and acetylene also demonstrate the necessity to take into account the π-acceptor properties of silicon subgroup elements in the interpretation of the experimental relations.

The experimental data considered in this section indicate unambiguously the presence of π-acceptor properties in silicon subgroup elements (E) with respect to the *n*- or *p*-donor type substituents linked to them (d_π–p_π interaction). In compounds having one E = X bond or one E–X–E fragment the capacity for d_π–p_π interaction is reduced with increase of the atomic numbers of the E and X atoms. The decrease of the capacity for d_π–p_π interaction with a constant E and a variable X is greater the smaller the number of the Group in the Periodic System to which X belongs. Other characteristics of the d_π–p_π interaction will be examined in Section III.

The results of the experimental study of the d_π–p_π interaction have been confirmed by quantum-chemical calculations by the molecular orbital method using various approximations. These calculations indicate an appreciable involvement of the vacant *d* orbitals in the formation Si–O,[141-143] Si–N,[144-146] Si–halogen[146-148], Si–aryl[143,149-155], Ge–C_6H_5,[152] and Si–C = C [155,156] bonds. However, as mentioned in the introduction, the conclusions reached in such calculations can depend on the accuracy of the method employed, which reduces sharply their value compared with experiment.

III. THE NATURE OF THE π-ACCEPTOR EFFECTS IN COMPOUNDS OF SILICON SUBGROUP ELEMENTS

Numerous literature data have shown that spectroscopic methods make it possible to investigate the fine details of the π-acceptor properties of silicon subgroup elements. Without going into the details of the mechanism of the π-effects, we adopted for these effects, following the majority of published studies, the terms d_π–p_π interaction (interaction between an E atom and a substituent X which is an *n*- or π-donor in the E–X fragment) and (p–d) σ-interaction (interaction through space between atoms E and X not linked by a valence bond). The use of these terms is absolutely correct only when it is demonstrated unambiguously that the *nd* orbitals of the E atoms are responsible for the manifestation of π-acceptor properties by the latter. There is no direct evidence for this at the present time, but there exist no firmly demonstrated alternative to the hypothesis of vacant *nd* orbitals.

At the same time extensive experimental data have been accumulated on the relations obeyed by the π-acceptor properties of silicon subgroup elements. Under these conditions, it is important to analyse the extent to which the conclusions reached on the basis of these experimental data are consistent with the postulates of the *nd*-orbital hypothesis. In the fundamental study by Jaffé [11] and in other investigations[3,10,12–15], it was shown that the d_π–p_π bonds in the E–X fragment are formed when the following three necessary and sufficient conditions are fulfilled: (1) the substituent X must possess *n*- or π-donor properties; the involvement of *d* orbitals should lead to effects similar to those arising on conjugation of π-bonds; (2) there should be a positive charge on the atom E, an increase of which should entail an enhancement of the d_π–p_π interaction; (3) the effect of the d_π–p_π interaction arises only in the presence of high overlap integrals of the p_π and d_π orbitals of the interacting X and E atoms.

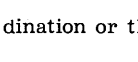
These conditions are inter-related. For example, the contraction of the *d* orbitals of the atom E and the decrease of the energy and electron affinity with increase of the positive charge on the E atom[13] create more favourable conditions for the interaction of the d_π orbitals of the E atom with the p_π orbitals of the X atoms, i.e. they increase the overlap integrals of the interacting orbitals of the E and X atoms[11]. Under these conditions, it is extremely significant that the molecular d_π orbitals are much less diffuse and have a much lower energy than the corresponding atomic orbitals[14] and their energy is therefore closer to that of the p_π orbitals of the X atom. In addition, the size of the molecular d_π orbitals, their energy, and the values of their overlap integrals with the p_π orbitals of the X atom depend also on the nature of the substituents at the E atom[13]. Electron-accepting substituents linked to E increase the positive charge of the latter and favour the d_π–p_π interaction[11]. Conditions (2) and (3) quoted above are therefore closely related.

At the same time condition (3) is of independent importance, particularly when not one but several X atoms involved in d_π–p_π interaction with tetrahedral E atoms are linked to the latter. Under these conditions, owing to the difference between the valence angles (~109.5°) and between the angles between the maximum intensity vectors of the d_π orbitals (90°), the interaction of E with several X proceeds when the orientation of the d_π orbitals is such that it does not lead to the maximum overlap integral in any of the E–X bonds[11]. In view of this, the overall effect of the d_π–p_π interaction in the molecule depends strongly and non-additively on the number of X atoms linked to E.[11,14].

The main task of the present section of the review is to examine to what extent the results of experimental studies of the d_π–p_π interaction are consistent with the above three conditions for the formation of d_π–p_π bonds and the conclusions arising therefrom.

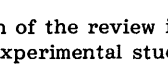
1. Analogy Between the π-Acceptor Effects of the Elements E and the Conjugation Effects in Carbon Compounds

Systematic studies of the π-acceptor properties of silicon subgroup elements E, carried out in relation to organosilicon and organogermanium compounds by infrared spectroscopy and ^{1}H NMR, [39,40,49,50,157,158], have shown unambiguously that the elements E exhibit π-acceptor properties only when they are linked by direct chemical bonds to the group X in the E–X fragment, where X can be an atom with unshared electron pairs (*n*-donor) or an α,β-unsaturated hydrocarbon radical (π-donor). On the other hand, if E and X are separated by a fragment of the type $(CH_2)_n$, then the carbofunctional substituent $(CH_2)_nX$ in the group $E(CH_2)_nX$ exhibits only an inductive effect.

Generally speaking, the claim that the mutual influence of the atoms E and X in the fragment $E(CH_2)_nX$ occurs solely via an inductive mechanism is not entirely rigorous. In reality, there can be interactions of at least two types between these atoms. The first involves intramolecular coordination or the so-called α-effect (for $n = 1$):  [7]

The results of a number of studies have shown[6,8,160] that this type of interaction takes place through space, but its mechanism continues to be the subject of a lively discussion[159].

A detailed examination of this type of interaction is of independent interest and is outside the scope of the present review. We shall only mention that the majority of the spectroscopic features of the manifestation of intramolecular coordination in the fragment $E(CH_2)_nX$ can be given a non-contradictory explanation if the following view on the mechanism of the effect is adopted[6]. Intramolecular coordination takes place between the atoms E and X. The X atom behaves as an *n*-donor by virtue of the presence of unshared electron pairs; the E atom then behaves as an acceptor by employing the vacant *nd* orbitals with the formation of a new weak bond of the (p–d) σ-type with the atom X. The principal difference between the bond thus formed and the σ-bond between E and D in compounds of the type EX_4D and EX_4D_2 is that the former has a much smaller energy. Thus the enthalpy of formation of the (p–d) σ-bond in dimethylchloromethylsilane is ~1 kcal mole^{-1}.[160] The low energy of bonds of the (p–d) σ-type is apparently largely caused by the impossibility of the mutual approach of the atoms E and X in the fragment ECH_2X to a distance close to the sum of the covalent radii. Such mutual approach would require a significant alteration of the geometry of the fragment ECH_2X, which involves a considerable expenditure of energy. Intramolecular coordination has almost no effect on the chemical shifts of the protons of the group R in the fragments R–E (C = CH_3 or C_2H_5; E = Si or Ge) in the NMR spectra of compounds with the groups $E(CH_2)_nX$,[48] and its influence on the frequency and intensity of the stretching vibration of the E–H bond in the infrared spectra of compounds with the fragment $H–E(CH_2)_nX$ is manifested distinctly only for $n = 1$ [160] and can be taken into account by correlation analysis[160].

The second type of resonance interaction in the groups $E(CH_2)_nX$ is the effect of the σ,π conjugation manifested for $n = 1$. A detailed study of the frequency and intensity of the ν(E–H) vibration in the infrared spectra of compounds with the groups $H–E(CH_2)_nX$ showed that the σ,π conjugation in benzyl  and allyl ($H–E–CH_2–CH=CH_2$)

derivatives has almost no influence on the above spectroscopic parameters[39-43,49,50,158], although this effect does influence the change in electron density in the aromatic ring and in the double bond[99,125,161,162]. This is probably caused by the comparatively small effect of the σ,π conjugation in the ground electronic state, which intensifies appreciably only in the presence of a positive charge in the benzene ring or in the double bond, which follows from theoretical considerations[163,164] and from the electronic spectra of the charge-transfer complexes of benzyl and allyl derivatives of silicon subgroup elements[100,128].

Taking into account the foregoing it is possible to formulate the requirements which must be met by the correct empirical method for the estimation of the π-acceptor properties of the silicon and germanium atoms (E) in the fragment E–X.[6] In the first place, it is necessary to have a sufficiently representative series of compounds whose spectroscopic parameters depend exclusively on the electronic effects of the substituents (inductive and conjugation effects) and are sufficiently sensitive to the influence of substituents. In addition, it is extremely important that the research method employed should make it possible to separate the overall influence of the electronic effects of substituents into components due to the influence of the inductive and conjugation effects. The inductive and conjugation effects can be separated by methods of correlation analysis, which have been thoroughly developed for the study of problems of this kind in unsaturated carbon compounds[90]. The application of this approach leads to the possibility of a quantitative study of the characteristics of the manifestation of the π-acceptor properties of the elements E.

All the requirements enumerated above are satisfied by silane and germane derivatives. Important information has been obtained in the analysis of the frequencies and integral intensities of the Si–H and Ge–H stretching vibration bands in the infrared spectra of these derivatives[39-43,49,50,157,158]. The stretching vibration of the E–H bond (E = Si or Ge) takes place virtually only along the bond. The mass of the substituents linked to the atom E does not affect these vibrations. The mechanical interactions of the vibration with other vibrations in the molecule are very weak, so that the stretching vibrations of the E–H bond are highly characteristic as regards mode. At the same time, when other substituents at the atom E are varied, the frequency and intensity of the ν(E–H) band vibrations vary over a wide range owing to the electronic effects of the substituents which alter the force constant and the polarity of the E–H bond.

The ν(Si–H) frequencies were first investigated in the infrared spectra of compounds containing the $Si(CH_2)_nX$ fragments where resonance interactions between the atoms Si and X are ruled out[39,43,49,132]; the substituents in these compounds exhibit only an inductive effect. The ν(Si–H) frequencies in the infrared spectra of the above compounds are therefore linearly related to the sums of the inductive Taft constants $\sum \sigma^*$. For tri-, di-, and mono-derivatives of silane, individual correlation straight lines parallel to one another are observed+:

$$\nu_{ind} = 23 \sum \sigma^* + 2112 \ (R_3SiH), \quad (1)$$

$$\nu_{ind} = 23 \sum \sigma^* + 2121 \ (R_2SiH_2), \quad (2)$$

$$\nu_{ind} = 23 \sum \sigma^* + 2132 \ (RSiH_3). \quad (3)$$

The existence of three correlation straight lines has been explained by the hyperconjugation effect (σ,σ conjugation).[132] If the molecule contains even one *n*- or π-donor atom or a fragment X linked to a silicon atom, then the experimental stretching vibration frequency of the Si–H bond (ν_{exp}) in the infrared spectrum of such a compound becomes smaller than the value calculated from the corresponding equation in system (1)–(3). The differences $\Delta\nu = \nu_{ind} - \nu_{exp}$ are in all cases positive[39,43,49]. The difference Δν is caused by the manifestation of π-acceptor properties by the silicon atom. The inductive -*I* effect of the substituent X and the π-acceptor effect of the silicon atom in relation to the substituent X act in opposite directions. The resultant electronic effect can therefore be interpreted as a decrease of the inductive effect of the substituent X, which causes a decrease of the values of ν_{exp} relative to ν_{ind}.

The differences Δν depend strongly on the nature of the substituents X. Even a qualitative examination[157] shows that the series corresponding to increasing Δν is the same as the series based on the increase of the capacity of the substituents X for conjugation with the benzene ring when the latter is characterised by the quantity σ_R ($\sigma_R = \sigma_n - \sigma_I$, where σ_I is the inductive component of the Hammett constant σ_n of the *para*-substituent in the benzene ring). Next it was shown[157] that the quantities Δν and σ_R are linearly related:

$$\Delta\nu = -66 \sigma_R + 3. \quad (4)$$

The data examined above show, firstly, that the silicon atom exhibits an acceptor effect only when the substituent linked to it is an *n*- or π-donor and, secondly, that the π-acceptor effect of silicon exhibits the features which are observed in conjugation in unsaturated carbon compounds.

As mentioned at the beginning of this review, these features constitute one of the conditions whose fulfillment confirms that *nd* orbitals are responsible for the manifestation of acceptor properties by the atoms E. Taking into account data[134] for conjugation in ethylene derivatives, one may conclude that the mechanism of the d_π–p_π interaction is similar to that of conjugation with an aromatic ring and the vinyl group. Thus the well known[19] analogy in the behaviour of the π,π-, π,*p*-, π,σ-, and σ,σ-conjugated systems extends also to d_π–p_π interaction. When the molecule contains several groups X capable of involvement in resonance interaction with E, the degree of d_π–p_π interaction depends on the positive charge on the atom E and on the group overlap integral of the d_π and p_π orbitals of the atom E and the substituents X in the fragment EX. This will be examined in detail in the next section.

Features similar to those observed for silane derivatives are characteristic also of germane derivatives. Thus the following parallel correlation straight lines are observed for tri- and di-substituted germanes containing substituents which do not form d_π–p_π bonds with the germanium atom[40,158]:

$$\nu_{ind} = 23 \sum \sigma^* + 2015 \ (R_3GeH), \quad (5)$$

$$\nu_{ind} = 23 \sum \sigma^* + 2029 \ (R_2GeH). \quad (6)$$

The introduction into the molecule of a substituent capable of d_π–p_π interaction with the germanium atom leads, as for silane derivatives[39,43], to a decrease of the experimental stretching vibration frequency of the Ge–H bond (ν_{exp}) relative to the value calculated from the corresponding equation [(5) or (6)] on the basis of the inductive effect (ν_{ind}). The differences $\Delta\nu = \nu_{ind} - \nu_{exp}$, which constitute a quantitative

+ Here and henceforth in this review the frequencies ν, Δν, etc. are expressed in cm^{-1} and the intensities 10^{-4} *A* are expressed in $mole^{-1}\ cm^{-2}$.

measure of the effect of the d_π–p_π interaction for the compounds R_2XGeH and $RXGeH_2$, are linearly correlated with the constants σ_R of the substituents X [158]:

$$\Delta\nu = -53\,\sigma_R + 4. \quad (7)$$

Comparison of the parameters of the linear equations (4) and (7) demonstrates a smaller capacity of the germanium atom for d_π–p_π interaction compared with the silicon atom. The latter is not characteristic only of silane and germane derivatives, containing a single substituent in the molecule capable of d_π–p_π interaction with the silicon or germanium atom, but is a general property of organoelemental compounds of Group IVB elements. This problem will be examined in greater detail in the next Section; here we shall only mention that the values of $\Delta\nu$ in the infrared spectra of organosilicon and organogermanium compounds ($\Delta\nu_{Si}$ and $\Delta\nu_{Ge}$), incorporating from one to three substituents capable of d_π–p_π interaction, are linearly related[40]:

$$\Delta\nu_{Si} = 1.17\,\Delta\nu_{Ge} - 4. \quad (8)$$

It follows from Eqn.(8) that (a) the principal features of the d_π–p_π interaction in organosilicon and organogermanium compounds are identical and (b) the germanium atom exhibits a smaller capacity for d_π–p_π interaction than the silicon atom.

The results obtained in the analysis of the stretching vibration frequencies of the E–H bond in the infrared spectra of silane and germane derivatives have been confirmed by the intensities of these absorption bands (the intensity data are quoted below).

Thus the mechanism of the π-acceptor effect of the E atoms (E = Si or Ge) in compounds with the fragments E–X has a profound analogy with the effects of the conjugation of the substituent X with an aromatic ring or the vinyl group. In conformity with Jaffé's work[11], this conclusion constitutes the first argument in support of the involvement of the vacant *nd* orbitals of the atoms E in the manifestation of π-acceptor properties by these atoms.

Experimental data consistent with theoretical postulates (2) and (3) of the *nd* orbital hypothesis are examined below.

2. Dependence of the π-Acceptor Effects on the Charge on the Atoms E

As already mentioned at the beginning of this section, the strength of the d_π–p_π bonds E–X increases with increase of the positive charge on the central element E.[11] The increase of the positive charge on E (for example, as a result of the addition of electron-accepting substituents Y to the given E) while the substituent X in the molecule XEY_3 remains unchanged induces a decrease of the energy of the d_π orbitals of the atom E, since the energy of the latter approaches that of the p_π orbitals of the atom X.[13] This entails an increase of the overlap integrals of the p_π and d_π orbitals of the atoms X and E and an increase of the strength of the d_π–p_π bond E–X.

We shall consider how well these theoretical postulates [(2) and (3)] of the *nd*-orbital hypothesis are consistent with the results of the spectroscopic study and the characteristics of the π-acceptor effects of the silicon and germanium atoms in organoelemental compounds. Silane and germane derivatives are convenient objects for the investigation of the dependence of the π-acceptor properties of the element E (Si or Ge) on its charge. As shown above, the difference $\Delta\nu = \nu_{ind} - \nu_{exp}$ between the stretching vibration frequencies of the E–H bond (E = Si or Ge) in the infrared spectra calculated by Eqns.(1) to (3), (5), and (6), on the one hand, and the experimental values ν_{exp}, on the other, is a quantitative measure of the electron-accepting properties of the atoms E.

In the study of the dependence of the π-acceptor properties of the atoms E on their positive charge a number of difficulties are encountered. They are associated with the fact that an increase of the positive charge on E is usually achieved by the addition to E of substituents X having a negative inductive $-I$ effect. However, such substituents X are as a rule *n*- or π-donors and are involved in resonance interaction with the atom E, which increases the electron density on the latter. The magnitude and sign of the resultant charge on the atom E (particularly in the presence of several substituents X of the type under consideration) are therefore determined by the ratio of the electron-accepting and electron-donating properties of the substituents, i.e. depend on the relative roles of the inductive and mesomeric effects of these substituents[135].

For the reasons described, the dependence of the π-acceptor properties of the atoms E on their effective charge can be conveniently investigated by considering the values of $\Delta\nu$ for a series of compounds with an increasing number of substituents. Here the simplest case is provided by compounds with a single substituent X of the type R_2XEH or (more specifically) of the type $(C_2H_5)_2XEH$.[157] These compounds can be regarded as products of the substitution of one ethyl group in triethylsilane or triethylgermane by a substituent X. Since the silicon and germanium atoms in triethylsilane and triethylgermane have quite definite effective charges, the π-acceptor effects of these atoms are determined largely by the ability of the substituent X to transfer its unshared electron pairs to the atom E (d_π–p_π interaction). It is therefore natural to compare $\Delta\nu_1$, characterising the π-acceptor effect, with the parameter characterising the ability of unshared electron pairs of the substituent X to participate in conjugation phenomena. As shown above, such parameters are the constants σ_R. The linear correlation between $\Delta\nu_1$ and σ_R in compounds with a single substituent X [see Eqns.(4) and (7)] now becomes entirely understandable.

Consider a compound RX_2EH containing two substituents X.[135,158] The values of $\Delta\nu_2$ for these compounds, which represent the differences $\nu_{ind} - \nu_{exp}$ and are calculated by the method already examined, differ from the values of $\Delta\nu_{add}$, which are equal to twice the values of $\Delta\nu_1$ for the corresponding compounds R_2XEH (Table 2). The compounds RX_2EH can be regarded as products of the substitution of an alkyl group R in R_2XEH by the substituent X. The effective charge on the atom E in R_2XEH depends both on the inductive $-I$ effect of X and on the opposed π-acceptor effect of E in relation to X (or, in other words, the π-donor effect of X in relation to E). The magnitude and sign of this effect determine the strength of the second d_π–p_π bond between E and X and hence the overall π-acceptor effect of the atom E in X_2EH.[135,158]. This is the first cause of the discrepancy between $\Delta\nu_2$ and $\Delta\nu_{add}$ for RX_2EH (Table 2).

The charge on the atom E induced by the substituent X can be taken into account by the sum of two constants $\sigma_I + \sigma_R$, where σ_I characterises the inductive effect of X and σ_R characterises, as shown above, the π-donor effect of X in relation to E. The sum of the constants $\sigma_I + \sigma_R$ represents the Hammett σ_n constant of the substituent X. The Hammett constants are known[90] to be proportional to the charges induced by the substituent on the reaction centre. The σ_n constant of the substituent X is therefore the simplest parameter proportional to the effective charge on E. Following an enhancement of the electron-accepting properties of X, σ_n for the substituent X increases and so does the positive charge on the atom E.

According to theoretical ideas[11,12], the second cause of the discrepancy between $\Delta\nu_2$ and $\Delta\nu_{add}$ [i.e. the origin of the differences $\delta(\Delta\nu) = \Delta\nu_2 - \Delta\nu_{add}$; see Table 2] is a complex

but non-additive relation between the two- centre and group overlap integrals S. The group overlap integrals of EX_2 are related to two-centre integrals s of the E–X bonds by the expression $S = \sqrt{4/3}s$.[11] However, the values of $\Delta\nu_2$ for RX_2EH differ from the values of $\Delta\nu_{calc}$ calculated by the formula $\Delta\nu_{calc} = \sqrt{4/3}\Delta\nu_1$, where $\Delta\nu_1$ are the corresponding values for the compounds R_2XEH.

Table 2. The values of $\Delta\nu$ in the infrared spectra of the compounds $(C_2H_5)X_2SiH$.

X	$\Delta\nu_2$, cm^{-1}	ν_{add}, cm^{-1}	$\delta(\Delta\nu)$, cm^{-1}	$\Delta\nu_{calc}$, cm^{-1}	$\Delta(\Delta\nu)$, cm^{-1}	σ_n
C_6H_5	18	18	0	10	8	0.01
CH_2=CH	17	28	−11	16	1	−0.01
F	28	50	−22	29	−1	0.06
Cl	38	44	−6	25	13	0.22
Br	42	32	10	18	24	0.23
CH_3O	15	76	−61	44	−29	−0.27
CH_3S	26	44	18	25	1	−0.05

The differences $\Delta(\Delta\nu) = \Delta\nu_2 - \Delta\nu_{calc}$ are due to a single cause—the change in the effective charge on E as the substituents X are varied. The values of $\Delta(\Delta\nu)$ should therefore vary in parallel with the Hammett σ_n constants of the substituents X; experiment confirmed this. It follows from the relations

$$\Delta(\Delta\nu) = 92\,\sigma_n \quad (RX_2SiH), \tag{9}$$

$$\Delta(\Delta\nu) = 67\,\sigma_n \quad (RX_2GeH) \tag{10}$$

that an increase of the positive charge on the atom E (i.e. an increase of the values of σ_n) leads to an increase of $\Delta(\Delta\nu)$ and hence of $\Delta\nu_2$, i.e. to an enhancement of the π-acceptor properties of the atoms E. Such enhancement is more pronounced for silicon compounds[135,158].

These conclusions were confirmed by a theoretical estimate of the overlap integrals of the Si–X bonds (X = O, S, or Cl) in the SiX_n fragments (n = 1–4) and of the dependence of the overlap integrals on the effective charge on the silicon atom[135]. The dependence of the π-acceptor effects on the atomic charge of E is clearly manifested in the study of the stretching vibration frequencies of the Si–H bonds in the infrared spectra of arylsilanes[105] and of the intensity of the ν(E–H) bands in the spectra of silane and germane derivatives[41,42,50,165,166].

The electron-accepting nature of the group XC_6H_4 in arylsilanes $Alk_{3-n}(XC_6H_4)_nSiH$ becomes significantly more pronounced with enhancement of the electron-accepting properties of the *meta*- or *para*-substituents X. At the same time there is an increase of the positive charge on the silicon atom. The values of $\Delta\nu$ (examined in detail above), which characterise the π-acceptor effect of the silicon atom in relation to the aryl substituent, increase with enhancement of the electron-accepting properties of the aryl substituents, i.e. with increase of the positive charge on the silicon atom. Under these conditions, the following linear relation holds[105]:

$$\Delta\nu = 12\sum\sigma^* + 4, \tag{11}$$

since, according to the data of Fisera et al.,[167] the inductive constants σ^* of the aryl substituents are linearly related to their σ_n constants.

Systematic studies of the integral intensities of the bands associated with the highly characteristic vibrations of the Si–H [41,50] and Ge–H [42,165,166] bonds in the infrared spectra of silane and germane derivatives served as yet another source of information about the dependence of the π-acceptor properties of the atoms E on their charge. While analysis of the frequencies of the highly characteristic M–H vibrations (i.e. analysis of the force constants) yields information about the energies of the E–H bonds, the study of their intensities makes it possible to investigate the polarity (dipole moment) of the E–H bond and in particular the influence on polarity of the π-acceptor effects involving E.

The square roots $A^{1/2}$ of the ν(E–H) absorption band intensity in the infrared spectra are linearly related to the sums of the inductive Taft constants $\sum\sigma^*$ of the substituents, exhibiting only an inductive effect in trisubstituted silane and germane derivatives[166]:

$$A^{1/2}_{ind} = 1.20 - 0.21\sum\sigma^*(R_3SiH), \tag{12}$$

$$A^{1/2}_{ind} = 1.30 - 0.20\sum\sigma^*(R_3GeH). \tag{13}$$

The intensity ($A^{1/2}_{exp}$) of the ν(E–H) bands in compounds with substituents of the n- or π-donor type (X) is higher than the values calculated by Eqns.(12) and (13). The differences $\Delta A^{1/2}_{exp} = A^{1/2}_{ind} - [?]$ are characterised by the π-acceptor effect of the atom E and other conjugation effects. For compounds with E–X bonds in which the π-acceptor effect of the atom E is the dominant conjugation effect, the following linear relations hold[41,166]:

$$\Delta A^{1/2} = 1.47\Sigma\sigma_n + 0.12 \quad \text{(silane derivatives)}, \tag{14}$$

$$\Delta A^{1/2} = 1.09\Sigma\sigma_n + 0.36 \quad \text{(germane derivatives)}. \tag{15}$$

Thus it follows from the intensities of the infrared bands that the π-acceptor properties of the atoms E (characterised by the quantities $\Delta A^{1/2}$ and most pronounced for silicon compounds) increase with increase of the effective positive charge on E (characterised by the sums $\sum\sigma_n$ of the Hammett constants of the substituents linked to E).

Summarising the data presented in the third Section of this review, we may note that these conditions are regarded[3,10–15] as necessary and sufficient for the formation of d_π–p_π bonds. These were enumerated at the beginning of the Section and have been confirmed experimentally.

Thus the available experimental spectroscopic data for the π-acceptor effects of silicon subgroup elements do not require for their interpretation hypotheses other than that based on the d_π–p_π interaction and constitute an indirect confirmation of the widely held view that π-acceptor properties are a manifestation of the effect of the d_π–p_π interaction.

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Institute of Chemistry,
USSR Academy of Sciences,
Gorky