Translated from *Uspekhi Khimii*, 53, 772-801 (1984) U.D.C. 541.65 + 541.67 + 543.422 + 547.1'13

The Spectroscopy of Organic Compounds of Silicon Subgroup Elements and Hyperconjugation

A.N.Egorochkin

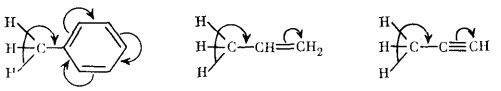
The general and theoretical aspects of the problem of hyperconjugation are examined. The factors determining the magnitude of the effect and its major role in organoelemental compounds compared with organic compounds are discussed. Various types of hyperconjugation (σ,π-, σ,σ-, and σ,p-conjugation) in the ground electronic state of organoelemental compounds of Group IV elements are considered.
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I. INTRODUCTION

The concept of hyperconjugation was introduced into organic chemistry in connection with the study of the reactivity of aromatic compounds, the influence of alkyl substituents of which cannot be described solely in terms of the inductive effect[1,2]. By analogy with π,π- and p,π-conjugation (the interaction of π or p electrons with the π-electron system), the σ,π-conjugation (hyperconjugation) of the σ electrons of the C–H bonds π-electron systems in the ground electronic state can be represented schematically as follows[3,4]:



(I) (II) (III)

In the system of Hammett–Taft equations the possibility of σ,π-conjugation is attributed to the presence in the alkyl group of a considerable resonance component having the same sign as the positive inductive effect. For example, the inductive (σ_I) and resonance (σ_R) constants for the CH_3 group are respectively -0.05 and −0.12.[3] For transition states in which a positive charge arises at the reaction centre (aromatic ring, multiple bond, or a substituent linked to them in the *para*-position relative to the alkyl group), the electron-donating properties of the alkyl groups are enhanced when the hyperconjugation effect is intensified[3,4].

The enhancement of the electron-donating properties as a consequence of the positive charge is reflected in the transition from the Hammett σ_n constants ($\sigma_n \approx \sigma_I + \sigma_R$) to the Brown-Okamoto σ_n^+ constants (see, for example, Exner[5]). For the CH_3, CH_3CH_2, $(CH_3)_2$, and $(CH_3)_3C$ groups, the constants σ_n and σ_n^+ (given in brackets) are respectively −0.17 (−0.31), −0.15 (−0.29), −0.15 (−0.28), and −0.20 (−0.26).[5]

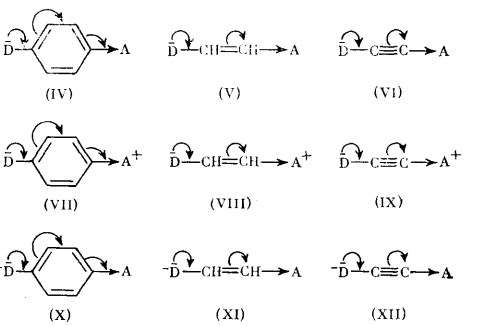
Thus the influence of alkyl groups can be twofold. The first case refers to the ground state and to transition states in which there is no direct resonance interaction between the alkyl substituent and the charged reaction centre. The influence of the substituents is then described by the Hammett σ_n constants, which vary irregularly on successive transition from CH_3 to $(CH_3)_3C$, reflecting the joint influence of the inductive effect and hyperconjugation. In this situation it is difficult to obtain information about hyperconjugation and there is a widely held view that this effect is absent in the ground state[3,6-8].

The second case refers to a transition state with a strong resonance interaction between the alkyl substituent and the positively charged reaction centre. Here the influence of the substituent is described by the σ_n^+ constants, which diminish in absolute magnitude on passing from CH_3 to $(CH_3)_3C$, i.e. vary in direct opposition to the inductive effects of these groups. This situation obtains in experiments where the concept of hyperconjugation has been resorted to in order to account for the results (see, for example, Refs.1,4, and 7–9).

The smallness of the σ,π-conjugation effect in organic compounds and the difficulty of isolating it from the set of other factors influencing the reactivity have led some investigators to doubt the reality of this effect[3,8]. At the same time there are also many arguments in support of the existence of hyperconjugation in organic compounds[4,6,9]. As regards hyperconjugation in organic compounds with participation of C–C σ-bonds, the data on this question are extremely contradictory.

Summarising the data examined[1-4,6,8,9], taking into account the work of Kreevoy and Taft[10,11], one can conclude, following Palm[7], that hyperconjugation is one of a variety of direct polar conjugation. This conclusion is extremely significant for the understanding of the characteristic features and the major role of hyperconjugation in organoelemental compounds.

The common features of the direct polar conjugation effects in organic compounds are known (see, for example, Johnson[12] and Minkin et al.[13]). The direct polar or "through" conjugation is a resonance interaction between the *para*-substituents of the donor (D) and acceptor (A) type in the ground state (or between the *para*-substituent and the charged reaction centre in the transition state) via the π-electron system:



(IV) (V) (VI)

(VII) (VIII) (IX)

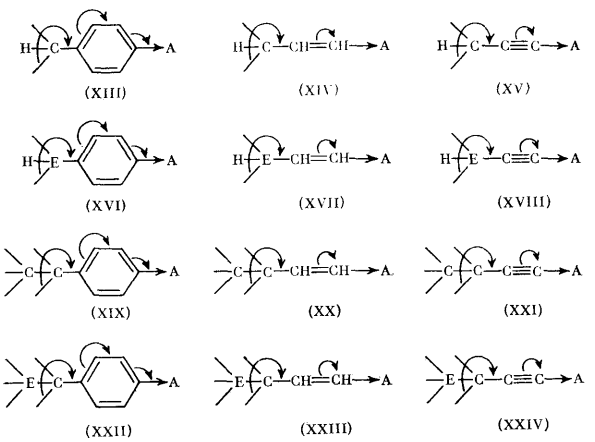
(X) (XI) (XII)

The magnitude of the "through" conjugation effect depends on the relative contributions of the donor–acceptor properties of the substituents D and A, increasing with enhancement of the electron-donating properties of D and the electron-accepting properties of A. The generation of a positive charge on A or a negative charge on D in the transition state [transition from compound (IV) to compounds (VII) and (X), from compound (V) to compounds (VIII) and (XI), and from compound (VI) to compounds (IX) and (XII)] enhances the effect considered.

When the substituent A(D) is kept constant and D(A) is varied, the magnitude of the direct polar conjugation effect varies linearly with the constants σ_R^+ of electron-donating substituents (or σ_R^- of electron-accepting substituents)[12,13].

It is also important that the polarisability of the π-electron system through which the D and A fragments interact is significant for polar conjugation[13,14]. These factors, characterising the direct polar conjugation and hence also hyperconjugation (σ,π-conjugation), which is a variety of the latter, should be especially important for organoelemental compounds for the following reasons. The electronegativities of all the central elements in organoelemental compounds are lower than the electronegativity of carbon[15]. Therefore fragments of the type EH_3 (where E are Group IV elements—silicon, germanium, tin, and lead) and EH_3CH_2, which are isostructural with respect to the methyl (CH_3) and ethyl (CH_3CH_2) groups respectively, should have more pronounced electron-donating properties than their carbon analogues as a result of the inductive mechanism. This has been frequently confirmed experimentally[5,16]. As regards the hyperconjugation mechanism, organoelemental fragments also manifest more pronounced electron-donating properties than the isostructural carbon groups[17–19].

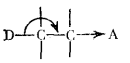
This is associated with the influence of a number of factors which are considered below, mainly with the greater polarisability of the bonds in the organoelemental compounds. By virtue of the higher polarisability of organoelemental fragments compared with the analogous carbon fragments, the effectiveness of the involvement of these fragments in the overall direct polar conjugation system is also improved. Thus the influence of the inductive effect and of the polarisability leads to an enhancement of the electron-donating properties of the substituents D in schemes (IV)–(XII), i.e. to an enhancement of the hyperconjugation in organoelemental compounds compared with their carbon analogues.



In view of the factors considered above, the influence of hyperconjugation should increase on passing from carbon compounds of types (XIII), (XIV), and (XV) to the corresponding organoelemental analogues (XVI), (XVII), and (XVIII) and also on passing from compounds (XIX), (XX), and (XXI) to compounds (XXII), (XXIII), and (XXIV).

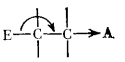
We may note that the effect of the $(p-d)\pi$ interaction between the electrons of the multiple bonds and the vacant *nd* orbitals of the E atoms is observed, together with hyperconjugation, in compounds (XVI)–(XVIII) containing the element E linked directly to a π-donor centre[20]. These effects operate in opposite directions, the $(p-d)\pi$ interaction exerting a dominant influence, as will become apparent below.

The idea of the greater role of hyperconjugation in organoelemental compounds compared with organic compounds was put forward for the first time and justified by Nesmeyanov[21] in a study of the characteristic features of the reactivities of organometallic compounds. A profound analogy is observed between the reactivities of classical test systems of the π,π- and *p*,π-types and σ,π- and σ,σ-conjugated systems (the concept of such systems was introduced by Nesmeyanov[21]). The idea of second-order hyperconjugation (σ,σ-conjugation) is indissolubly linked with the high polarity and polarisability of organoelemental compounds. The effect of the σ,σ-conjugation, expressed by scheme (XXV)



(XXV)

therefore plays a notable role only when there is a significant difference between the electronegativity of the D (donor) and A (acceptor) atoms and when the polarisability of the D–C bond is high; this can be ensured sufficiently only for organometallic compounds [as in a scheme of type (XXVI)]:



(XXVI)

where E is a silicon subgroup element or some other central atom of the organometallic compound.

The ideas concerning the effects of σ,π- and σ,σ-conjugation were initially developed in order to elucidate the characteristics of the reactivity of organoelemental compounds—its specific features compared with the properties of organic compounds. The results obtained refer to a transition state. Subsequent investigations of the effect by molecular spectroscopic and quantum-chemical methods confirmed the reality and importance of hyperconjugation in the ground and excited electronic states of organoelemental compounds and also the dependence of such conjugation on the electronic state of the molecule. In these studies the first steps were taken towards the investigation of the role of hyperconjugation on passing from a non-reacting to a reacting molecule, which is also significant for theoretical organoelemental chemistry. As a consequence of the low magnitude of hyperconjugation effects compared with other resonance effects and the complexity of the intramolecular interactions in organoelemental compounds, the experimental data for hyperconjugation are not reliable in all cases and their interpretation is not always unambiguous. Furthermore, data for hyperconjugation in organoelemental compounds are fragmentary and systematic studies in this field are only just beginning.

The main task of the present review is therefore a critical examination of data for hyperconjugation in organic compounds of mercury (as model and thoroughly investigated systems) and silicon subgroup elements, obtained by molecular spectroscopic and quantum-chemical methods.

It seems useful to characterise in a general form the criteria employed in theoretical and experimental studies in order to establish the existence of hyperconjugation and to

estimate the magnitude of the given effect. As stated above, the absence of fundamental differences between the classical conjugation effect and hyperconjugation was emphasised in the studies by Mulliken[2] and Nesmeyanov[21]; the hyperconjugation effect is merely smaller, but, on passing from organic to organoelemental compounds, the hyperconjugation becomes abruptly much more pronounced[21]. The influence of the organoelemental fragments of the molecules involved in hyperconjugation is comparable to the effect of the strongest organic donors, as will be demonstrated in detail below. Therefore the study of hyperconjugation, as a task for physical organic chemistry, consists primarily in the separation of the effects of substituents into the inductive and resonance components and, if the latter component consists of several contributions, in isolating the contribution associated with hyperconjugation. In relation to specific molecular spectroscopic methods, the solution of this problem presupposes the selection of spectroscopic parameters sensitive to the influence of electronic effects (especially conjugation effects), the correct isolation of the contributions due to hyperconjugation, and the determination of the relation between these contributions and the characteristics of the structure of the compounds studied.

As a task for quantum chemistry, the study of hyperconjugation does not reduce solely to the selection of the correct methods of study and the demonstration of the existence of this type of conjugation but consists mainly in a more profound consideration of the results of experimental studies. It is shown below that the experimental characteristics of hyperconjugation, such as the dependence on the donor–acceptor properties of the conjugated bonds and on the sign of the charge on the π-electron system, the nature of the central element in the organoelemental compounds, and stereoelectronic factors, have been justified theoretically in the quantum-chemical analysis of the total energy, the bond orders, the geometrical characteristics, and the conformations of the molecules.

II. THEORETICAL IDEAS ABOUT HYPERCONJUGATION

The work of Eaborn[22], Traylor and co-workers[23], Bock[24], and Pitt[25], which demonstrated experimentally the important role of σ,π-conjugation in systems with a positive charge in the highest occupied molecular orbital (HOMO) of the π-type in benzene derivatives, was a development of Nesmeyanov's classical ideas and stimulated a series of theoretical studies of the effect of hyperconjugation in derivatives of carbon and organometallic compounds by both non-empirical (*ab initio*) and semiempirical (different versions of the zero differential overlap procedures—CNDO and INDO) quantum-chemical methods. Strong resonance interaction between a substituted cyclopropane ring and groups of the type CH_3, $CH_2^{\cdot}$, and CH_2^+ bound to it was demonstrated by the INDO and CNDO/2 methods. For CH_2^+, such interaction is the strongest[26] and hyperconjugation is apparently partly responsible for it, although the separation of the contributions to the given interaction by the σ- and π-components is difficult[26]. (The questions concerning the electronic effects, including hyperconjugation, have been considered in relation to unsaturated cyclic compounds[27].) The possibility of resonance interactions of the type of hyperconjugation (intermediate in magnitude between the effects of saturated and unsaturated substituents) between the cyclopropane (or cyclobutane) ring and a double bond has been indicated by *ab initio* calculations[28]. The conformations and stabilities of the substituted ethyl, propyl, and butyl cations have been investigated by the same method[29].

Substituents stabilise cations to a greater extent compared with the corresponding hydrocarbons[29] and radicals[30]. The stabilising capacity of the substituent depends on the hyperconjugation and the inductive effect. The effect of hyperconjugation, which determines the preferred conformation of the cations, depends on the capacity of the bonds at a β-carbon atom for such conjugation. According to the results of Radom et al.,[29] the C–C bond has a capacity for hyperconjugation just as great as the C–H bond. The same conclusion was reached in a study of norbornylbenzenes, in which the C–C bonds involved in hyperconjugation have a marked *p* character[31]. The existence of preferred conformations of the cations $XCH_2CH_2^+$ or anions $XCH_2CH_2^-$ due to hyperconjugation follows from *ab initio* calculations[32]. Hyperconjugation determines the geometries of the given ions and the degree of conjugation depends on the nature of X.[32–34]

Within the framework of the molecular orbital theory, the stabilisation of vinyl, isopropyl, and butyl carbonium ions and of protonated toluene as a result of hyperconjugation is regarded as the interaction of the σ orbitals of strained C–H or C–C bonds (having a higher energy in the ions than in in the neutral compounds) and a suitable *p* orbital of the ion. The interaction lowers the energy of the bonding molecular orbitals of the ion[35]. These conclusions[35] can be extended also to organometallic systems having high-energy σ orbitals of the E–C bonds.

The state of the problem of the interaction of the methyl group with π-electron system has been most fully considered by Libit and Hoffmann[36]. Numerous quantum-chemical data summarised by the above workers[36] indicate a slight electron transfer from the CH_3 group to the double bond and the aromatic ring and an appreciable polarisation of the π-electron system. The polarisation involves the hyperconjugation of the σ orbital of the methyl group with the π-electron system of the double bond or the aromatic ring[36]. Some aspects of hyperconjugation have already been examined[37,38]. Thus it follows from calculations on siladispiroheptane by the extended Hückel method that, together with conjugation involving the *d* orbital of silicon, there is hyperconjugation involving the electron-accepting antibonding orbitals of the Si–H bond[38].

A series of theoretical estimates of the capacity of the E–C bonds for hyperconjugation, where E is an element other than carbon or hydrogen, have been made. Thus virtually identical capacities of the C–S and C–H bonds for hyperconjugation have been demonstrated[39,40]. According to quantum-chemical and photoelectron spectroscopic data the energy of the HOMO of the π-type in benzyl halides depends on the inductive and resonance (hyperconjugation) effects. After the separation of the effects, the energies of hyperconjugation involving the C–Hal bonds have been estimated as 0.16, 0.28, 0.33 and 0.44 eV for Hal = F, Cl, Br, or I respectively (the hyperconjugation of the C–H bonds with the benzene ring amounts to 0.12 eV)[41]. Similar estimation of the hyperconjugation energy between the C–Hal and C=C bonds yielded 0.22, 0.31, 0.45 0.63 eV for Hal = F, Cl, Br, or I respectively[42].

The hyperconjugation in organomercury compounds has been investigated by the extended Hückel method[43,44]. The calculations showed that benzylmercury bromide is most stable in the electronic ground state in the conformation which ensures the interaction of the polarisable Hg–C bond with the π-electron system of the ring (the Hg–C–C angle is 90°). As a result of the σ,π-conjugation, the $BrHgCH_2$ fragment is typically electron donating in proton exchange processes[43,45]. In conformity with Nesmeyanov's work[21], it follows from the calculations of the total energies and bond orders[43] that the replacement of the bromine atom in

$BrHgCH_2C_6H_5$ by the electron-donating CH_3 group enhances the σ,π-conjugation, while its replacement by the more electron-accepting chlorine atom weakens the effect. The effect of the σ,π-conjugation is benzylmercury bromide is much stronger than in benzyl bromide[43]. The Hg–C bond in allylmercury bromide is at right angles to the nodal plane of the olefinic π-electron system[44] and the degree of σ,π-conjugation increases in the transition state compared with the ground state. The hyperconjugation weakens on passing from allylmercury bromide to the cation $^+HgCH_2CH=CH_2$,[44] since the electron accepting properties of the mercury-containing fragments $^+HgCH_2$ in the cation are apparently enhanced.

Hyperconjugation in compounds of Group IV elements has been frequently confirmed by *ab initio* calculations and by the CNDO method. Although the non-empirical calculations[46,47] for propene and vinylsilane did not provide an unambiguous answer concerning the $(p-d)\pi$ interaction in vinylsilane (like the calculations by the CNDO/2 method[48]), they indicated definitely the existence of hyperconjugation in this compound. The latter has also been confirmed by calculations using the CNDO/2 method, which agree for allyl- and vinyltrimethyl-silanes with photoelectron spectroscopic data[49,50]. The σ,π-conjugation plays a significant role in allylsilane, which has been recently demonstrated[51] also by the MINDO/3 method. In vinyltrimethylsilane the effects of the $(p-d)\pi$ interaction and hyperconjugation act in opposite directions[49]. These conclusions for silicon-containing ethylene derivatives agree with other data[52–54] and with calculations by the extended Hückel method for the compound $(CH_3)_3ECH_2CH=CH_2$,[55] in which the significant role of the σ,π-conjugation on passing from E or C to silicon subgroup elements has been demonstrated.

The increase of the multiplicity of the bond between silicon and ethynyl groups is apparently ensured both by the σ,π-conjugation of the σ orbitals of the silicon atom with the π orbitals of the C≡C fragment[46] and by the $(p-d)\pi$ interaction of the π electrons of the multiple bond with the unoccupied 3*d* orbitals of the silicon atom[56]. It is striking that both experiment and calculations show that the inductive effect of the CH_3 group predominates over hyperconjugation in methylacetylene but at the same time they also show that hyperconjugation plays a greater role in silylacetylene than the inductive effect of the SiH_3 group[57]. Calculations for phenylsilane in terms of the CNDO/2 approximation[55] demonstrated the significance of three effects—the inductive effect, the $(p-d)\pi$ interaction, and σ,π-conjugation, which has also been confirmed by calculations using the MINDO/3 method[59] for related systems—trimethylphenyl- and trimethylbenzyl-silanes. The importance of all three effects for the former compound and the appreciable role of hyperconjugation for the latter[59] and also for benzyl derivatives of germanium and tin[54] was then established. The greater role of hyperconjugation in silylanilines compared with the carbon analogues has been demonstrated in calculations using the CNDO/2 method[60]. As in the carbon compounds[29,30,32–34], hyperconjugation has a significant influence on the conformation of ions of the type $H_3ECH_2CH_2^+$ (E = Si or Ge).[61] One cannot rule out the possibility that hyperconjugation obtains also in tetramethylsilane[62].

The familiar work by Pitt[17], in which the role of σ,π-conjugation was estimated by analysis of experimental data for compounds of Group IV elements combined with an application of molecular orbital perturbation theory and of calculations by the CNDO/2 method, has been a significant development of the problem of hyperconjugation in organoelemental compounds. The author, having developed the initial concept of, for example[63] the dominant role of hyperconjugation, emphasises the importance not only of hyperconjugation but also of the inductive effect and the $(p-d)\pi$ interaction for the interpretation of the properties of organoelemental compounds. The perturbation energy δE, arising as a result of δ,π-interaction (hyperconjugation), is defined by the expression

$$\delta E = \pm \frac{a^2(\pi)a^2(\sigma)P^2}{\Delta E},$$

where $\Delta E = E(\pi) - E(\sigma)$ is the difference between the energy of the unperturbed π and σ orbitals, $a^2(\pi)$ and $a^2(\sigma)$ are the electron densities in the *p* orbitals of the bonding atoms in the HOMO of the π- and σ-systems, and *P* is the perturbation integral, including the overlap of the *p* orbitals connecting the π- and σ-systems.

For a series of isostructural compounds with a variable central element E, for example for $(CH_3)_3ECH_2C_6H_5$, the quantities $a^2(\pi)$, $E(\pi)$, and *P* remain constant, while $E(\sigma)$ and $a^2(\sigma)$ vary, the principal contribution arising from $E(\sigma)$.[19,64,65] Since ΔE diminishes from Si to Pb, the degree of σ,π-conjugation involving the E–C bonds (characterised by the perturbation energy δE) increases as E is varied in the sequence Si < Ge < Sn < Pb,[19] which also agrees with the traditional ideas and, as will be shown below, with all the experimental data. For organoelemental compounds of the type $R_3EE'R_3$ and R_3EER_2X, there is a possibility of σ,σ- and σ,*p*-conjugation effects as a result of the pseudo-π-conjugation of the formally localised σ(ER) orbitals and, in the case of σ,*p*-conjugation, also accompanied by the involvement of the orbitals of the unshared electron pair of the atom X.[17]

The effects of the σ,σ- and σ,*p*-conjugation enhance the similarity of the molecular orbital energies, the increase of the perturbation integral *P*, and the bond polarity, which increases the electron density in the *p* orbitals of the bonding atoms. Pitt's calculations[17] confirm the increased stabilisation of the cationic centres by the R_3ECH_2 groups with increase of the atomic number of E and also the possibility of the manifestation of electron-accepting properties by the H_3SiCH_2 group relative to anionic centres.

The idea of more marked electron-donating properties of the R_3ECH_2 group compared with R_3E (although on the basis of the inductive effect alone for these groups, the opposite behaviour should have been observed—see, for example, Egorochkin et al.[66]) is very common in reviews of the properties of silicon-subgroup elements (E)[20,67–70]; this is usually attributed to the character of the σ,π-conjugation between R_3ECH_2 and the π-electron system.

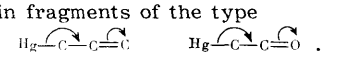
III. EXPERIMENTAL STUDIES OF HYPERCONJUGATION IN ORGANOELEMENTAL COMPOUNDS

1. Organomercury Compounds as Model Systems

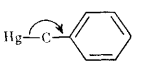
Organomercury compounds, which are widely used as model systems in organic and organoelemental chemistry, have also fulfilled this function in the study of σ,π-conjugation. These compounds were in fact the main objects of the study of the reactivity of which led Nesmeyanov and Lutsenko to the conclusion that the σ,π-conjugation plays an important role in organoelemental compounds[21,71].

In molecules containing the E–C–C=C or E–C–C=O fragments (E is a mercury or another metal atom), the σ,π-conjugation of the E–C σ-bond and the π-bond of the C=C or C=O group induces a series of specific properties. The

considerable difference between the electronegativities of mercury and carbon atoms (1.9 and 2.5 respectively) and the higher atomic number of mercury, which is in the VIth Period, are responsible for the polarity of the $Hg^{\delta+}-C^{\delta-}$ bond and its high polarisability. These factors favour the σ,π-conjugation in fragments of the type



Conjugation leads to the lability of the mercury–carbon bond and in many instances to the transfer of the reaction centre in reactions with electrophiles to the carbonyl group[71-73] and, for compounds with the fragments



to the aromatic ring[74].

The effect of σ,π-conjugation leads to the stabilisation of the transition state in the acid decomposition of allylmercury halides[44]. Hyperconjugation influences the properties of organomercury compounds not only in the transition state but also in the ground electronic state. This has been established in a series of experiments undertaken to demonstrate the very fact of the existence of σ,π-conjugation and to investigate the influence of molecular structure on the magnitude of this effect. Physicochemical experiments have confirmed the occurrence of the transfer of electron density via the conjugated system from the mercury atom to the electron-accepting molecular fragments (the multiple bond, the aromatic ring, the carbonyl group) and demonstrated the dependence of such transfer on the nature of the electron-accepting fragment and the decisive influence of the molecular geometry not only on the magnitude but also on the very possibility of the existence of the effect of σ,π-conjugation.

The data concerning the dependence of the energy of σ,π-conjugation on the molecular geometry are extremely clear. The greatest effect of σ,π-conjugation should be attained for the maximum overlap of the σ orbital of the Hg–C bond with the π orbital of the C=O (C=C, C_6H_5) group. Such overlap is ensured by the coplanar disposition of the Hg–C bond and the axis of the π orbital. When there is a marked deviation from such disposition of the interacting molecular fragments, there should be no σ,π-conjugation or it should be greatly weakened.

Experiment confirms this. Thus the closeness of the Hg–C–C angles to 90° in compounds with σ,π-conjugation was noted above[43,44]. Another characteristic example is provided by Raman spectroscopic data[75]. The intensity of the ν(C=O) bands in the Raman spectra of acyclic compounds having the Hg–C–C=O fragment and also in the spectrum of α-chloromercuricyclohexanone is appreciably higher than the intensity of the corresponding bands in the spectra of the non-conjugated ketones. On the other hand, the frequency of the ν(C=O) bands is lower in the spectra of organomercury compounds, which reflects the electron-donating properties of the mercury-containing molecular group relative to the C=O group in terms of the σ,π-conjugation mechanism and also apparently it reflects the higher polarity of the C=O bond owing to conjugation.

When the mercury-containing and carbonyl fragments are rigidly fixed in space, which rules out a resonance interaction between them, the spectroscopic characteristics of σ,π-conjugation disappear. Thus, judging from the positions and intensities of the ν(C=O) bands in the Raman spectra, α-chloromercuricamphenilone is a typical non-conjugated cyclic ketone[75].

The allyl derivatives of mercury containing the Hg–C–C=C fragment have, like the mercuriketones, Raman spectra with higher intensities of the ν(C=C) bands as a consequence of σ,π-conjugation[76,77]. However, the increase of the intensity of the ν(C=C) bands in the spectra of allyl derivatives of mercury is smaller by a factor of approximately two than the increase of the intensity of the ν(C=O) bands in mercuriketones due to σ,π-conjugation[76,77]. Thus, for unaltered electron-donating properties of the mercury-containing fragment, the intensity of the σ,π-conjugation increases with enhancement of the electron-accepting properties of the multiple bond. The latter properties are more pronounced for the C=O group (compared with the C=C group mainly owing to the greater electronegativity of the oxygen atom). The greater extent of hyperconjugation, approximately by a factor of two, in mercuriketones compared with the allyl derivatives[77] clearly illustrates Nesmeyanov's classical ideas (see Section I), according to which the hyperconjugation energy increases with the increase of the difference between the electron-accepting properties of the bonds involved in the conjugation.

Detailed study of the vibrational (infrared and Raman) spectra of organomercury compounds showed that the molecules of allyl- and benzyl-mercury halides in solutions have a non-planar configuration with the Hg–C bond located in a plane perpendicular to that of the double bond or the aromatic ring[78,79]. This constitutes yet another piece of evidence in support of the existence of σ,π-conjugation. Subsequent studies showed that a configuration favourable for σ,π-conjugation arises in the benzyl derivatives of mercury not only in solutions[33,78,80] but also in the crystalline[81] [for example, in the case of $C_6H_5CH_2HgSC(C_6H_5)_3$] and gaseous states[82] (benzylmercury chloride). The photoelectron spectroscopic data for benzylmercury chloride indicate the destabilisation of the HOMO of the π type as a result of the σ,π-conjugation and make it possible to estimate the interaction integral between the π and σ orbitals of the Hg–C type (0.99 eV). This quantity is extremely close to the value (0.98 eV) for allylmercury chloride, which, like the benzyl analogue, is a configuration necessary for σ,π-conjugation also in the gaseous phase[83].

Convincing data supporting the existence of σ,π-conjugation in organomercury compounds have been obtained by NMR spectroscopy[76,84-86]. The ^{199}Hg NMR data provide most information. The study of benzylmercury chloride and its derivatives showed that the introduction of methyl groups in the *ortho*- (but not in the *meta*- or *para*-) positions in the aromatic ring increases the fraction of conformers in which the Hg–C bond is not in the plane of the aromatic ring, favours the σ,π-conjugation, leads to an increase of the positive charge on the mercury atom (as a result of conjugation), and deshields the ^{199}Hg nucleus.

The stereochemistry of the σ,π-conjugation is also reflected in other parameters of the ^{199}Hg NMR[86] and ^{13}C NMR[76,84,86] spectra. According to chemical data, for example those of Nesmeyanov and Kritskaya[87], owing to the increase of the lability of the Hg–C bond as a consequence of σ,π-conjugation, polarographic reduction with dissociation of the bond takes place at much lower potentials for conjugated systems than for non-conjugated systems[75,76]. The electronic spectroscopic data for charge-transfer complexes (CTC) of benzyl derivatives of mercury with tetracyanoethylene are of fundamental importance[80,88]. This method makes it possible to investigate σ,π-conjugation under conditions where there is a positive charge in the π orbital of the aromatic ring. In this situation hyperconjugation constitutes a very powerful resonance effect with rigorous stereoelectronic requirements[25,80,88]—the breakdown of σ,π-conjugation (on passing to compounds where the Hg–C bond is located in the nodal plane of the π-electron system) diminishes the rates of certain electrophilic reactions by a factor of 10^8.[88]

An increase of the extent of σ,π-conjugation following the enhancement of the electron-donating properties of the substituents X has been established for systems with the cationic centre in the π-electron system (the compound $XHgCH_2C_6H_5$ under the experimental conditions according to electronic spectroscopic data for CTC)[80], which has been confirmed by ^{19}F NMR in the ground electronic state[89]. This constitutes convincing confirmation of Nesmeyanov's classical idea that the difference between the donor–acceptor properties of conjugated bonds has a significant influence on the hyperconjugation energy[21]. The negative ion mass spectra of σ,π-conjugated systems have a lower energy at the resonance maxima (destabilisation of the molecular orbitals due to conjugation) compared with the non-conjugated systems[76].

Thus Nesmeyanov's hypothesis[21,77] that the effect of σ,π-conjugation has a significant role in organoelemental compounds has been fully confirmed in a combined study of model derivatives of mercury[77].

We shall next consider data for hyperconjugation in compounds of silicon sub-group elements.

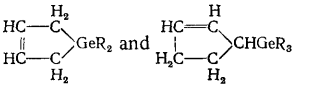
2. σ,π-Conjugation in Compounds of Silicon Subgroup Elements

The effect of σ,π-conjugation is clearly manifested in the study of compounds of silicon subgroup elements by vibrational spectroscopic methods[90–93]. An increase of the intensity of the bands corresponding to the vibration of the C=C bond and the vibration with a preferential extension of the $E-C_{all}$ bond as well as an increase of the degree of depolarisation of these bands have been observed in the Raman spectra of the compounds $(CH_3)_3ECH_2CH=CH_2$ (where E = C, Si, Ge, or Sn). On passing from silicon to tin, the exaltation of the molecular refraction in the allyl group increases. In the Raman spectra of the halogeno-derivatives Hal_3ECH_2. $CH=CH_2$ (E = Si or Ge), the intensity of the ν(C=C) line increases in the sequence F < Cl < Br and for fluoro-derivatives the line intensities are lower than for the methyl derivatives, which can be interpreted as a decrease of the extent of the σ,π-conjugation following the overall enhancement of the electron-accepting properties of the substituents R and the R_3ECH_2 fragment as a whole.

This conclusion as well as the conclusion that the σ,π-conjugation becomes more intense with increase of the atomic number of the element E on passing from Si to Ge and Sn evidently follows from the analysis of the highly characteristic out-of-plane vibrations of the $=CH_2$ group in the infrared spectra of the allyl derivatives[66,94] and has been confirmed by the study of the ^1H NMR spectra of the alkenyl derivatives of silicon and germanium[94]. Infrared spectroscopic study of a hydrogen bond of the type π...H–O– involving phenol indicates more pronounced π-donor properties of the allyl derivatives of silicon, germanium, and tin than for their carbon analogues. The differences between the electron-donating capacities cannot be accounted for by the differences between the electronegativities of the central atoms E. The increase of the electron density in the double bond with increase of the atomic number of E are a consequence of the increasing role of the σ,π-conjugation[95].

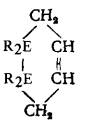
A method for the study of the electronic effects of the substituents at the π-donor centres (derivatives of ethylene, benzene, acetylene, etc.), which yields much information, is the electronic spectroscopy of charge-transfer complexes, for example, complexes of the π,π-type with tetracyanoethylene as the π-electron acceptor[96]. The principal spectroscopic parameter, the frequency of the charge-transfer band, contains information about the influence of the substituents not in the ground electronic state but in the charge-transfer state, where there is a positive charge in the π orbital of the donor. The presence of the charge can promote an increase of conjugation (including hyperconjugation) of typical electron-donating substituents of the +*M* type with the π-donor centre. Therefore in the state with charge transfer, modelling reaction systems with an ionic transition state [schemes of types (VII)–(IX)], the effect of σ,π-conjugation should be manifested most clearly[96]. This has been frequently confirmed experimentally for different compounds starting with the studies of Hanstein et al.,[23] Bock and Alt[24], and Pitt[25], and in particular for the allyl derivatives of silicon[97].

The fact that the electronic effects of the substituents R_3ECH_2 in $R_3ECH_2CH=CH_2$ are not limited to the inductive effect but include also a powerful σ,π-conjugation effect, which increases on passing from E = Si to E = Ge, is clearly manifested in the state with charge transfer[98]. A fairly strong σ,π-conjugation can occur only for a non-coplanar disposition of the E=C and C=C bonds, since this ensures a more effective overlapping of the electron clouds of the interacting bonds. Experimental confirmation of this fact has been obtained for allylsilane by infrared[99] and microwave[100] spectroscopic methods. In two compounds with the β-disposition of the germanium atom in relation to the C=C bond, i.e.



in the former (where the Ge–C and C=C bond are in the same plane) there is no hyperconjugation and in the latter (where the Ge–C bond deviates from the plane of the cyclopentene ring) the spectroscopic features of σ,π-conjugation are observed[101–103]. For the related silicon compounds, the stereospecificity of the σ,π-conjugation is shown just as clearly[104].

In contrast to sila- and germa-cyclopentenes having a planar ring structure, systems of the type



(E = Si or Ge) are non-planar and σ,π-conjugation in them has been established by vibrational and NMR spectroscopic methods[105]. In the electronic spectra of the trimethylallyl derivatives the absorption band near 55000 cm^{-1} (for E = C) undergoes a bathochromic shift and its intensity increases following a successive transition from carbon compounds to tin derivatives. According to the authors[106,107], these data indicate σ,π-conjugation in compounds of silicon subgroup elements, the extent of which increases with increasing atomic number not only in Group IV but also in the Periodic System as a whole. The cause of this phenomenon is apparently the more ready polarisability of the element with increase of its atomic number[107].

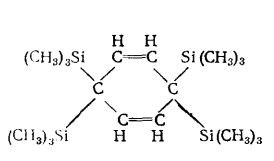
Important information about hyperconjugation has been obtained by photoelectron spectroscopy, which makes it possible to measure the vertical ionisation potentials[23], approximately equal to the energies of the corresponding molecular orbitals (with the sign reversed)[108]. In ethylene derivatives containing hydrocarbon substituents and their silicon-containing analogues, the highest occupied molecular orbital is of the π type[49,109]. The substituents $(CH_3)_3SiCH_2$ and H_3SiCH_2 increase the HOMO energy to a significant extent (the HOMO ionisation potentials are 9.0 and 9.49 eV)

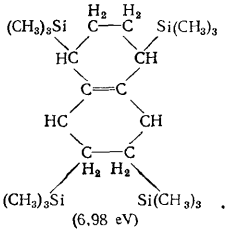
relative to the substituents $(CH_3)_3CCH_2$[49] and CH_3CH_2[110] (9.6 and 9.72 eV) as a consequence of the intense σ,π-conjugation in the silicon derivatives. The increase of the extent of σ,π-conjugation with increase of the atomic number of the Group IV element is accompanied by a further destabilisation of the π-type HOMO which is manifested by a decrease of the first ionisation potential[111,112] in trimethylallylgermane and trimethylallylstannane to ~ 8.8 and ~ 8.5 eV respectively (8.7 eV according to the data of Brown et al.[113]). The same conclusion concerning the influence of σ,π-conjugation on the ionisation potentials of HOMO have been reached using the mass-spectrometric method not only for trimethylallylsilane[114,115] but also for the disilyl derivatives of ethylene[116].

Thus the first vertical ionisation potentials, reflecting the influence of the substituents on the energy of the HOMO of the π type in the compounds *trans*-XHC=CHX when X is varied, are (in eV) 10.54 for H, 9.32 for $(CH_3)_3Si$, 8.99 for $(CH_3)_3C$, and 7.95 for $(CH_3)_3SiCH_2$.[116] The substituents X influence the HOMO energy via the inductive and conjugation mechanisms. Whereas the +*I* effect of the t-butyl group exerts the main influence on passing from X = H to $(CH_3)_3C$, when X changes from $(CH_3)_3C$ to $(CH_3)_3Si$, the $(p-d)\pi$ interaction (partial shift of the π electrons of the double bond to the unoccupied 3*d* orbitals of the silicon atom) has a dominant influence on the HOMO energy. This can be explained by the fact that the greater +*I* effect of the trimethylsilyl group compared with the t-butyl group (the inductive constants of these groups are respectively −0.9 and −0.3)[16] in the absence of the $(p-d)\pi$ interaction should have caused an increase of the ionisation potential in the disilyl derivative compared with its di-t-butyl analogue.

Judging from the ionisation potentials, the $(CH_3)_3SiCH_2$ group is the strongest donor although its σ* constant, amounting to −0.3,[66] is close to that of the t-butyl group and higher than the value for the trimethylsilyl group. The anomalously pronounced electron-donating properties of the substituents $(CH_3)_3SiCH_2$ are due to σ,π-conjugation. This effect increases regularly with increase of the number of substituents $(CH_3)_3SiCH_2$ at the double bond[117]. This is manifested experimentally by a decrease of the ionisation potentials, which are 7.7 eV for $CH_3[(CH_3)_3SiCH_2]C{=}C(CH_3).[CH_2Si(CH_3)_3]$ and 7.15 eV for $[(CH_3)_3SiCH_2]_2C{=}C[CH_2Si.(CH_3)_3]_2$, and also by an increase of the energy of the HOMO of the π type and the enhancement of the π-donor properties of the compounds[118]. The last compound does not form complexes with tetracyanoethylene of the usual type of olefins and the interaction involves the formation of radical-ion salts.

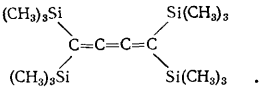
The following compounds have record low ionisation potentials[119]:


(7,00 eV)


(6,98 eV)

The large steric effects of the substituents at the multiple bonds make preferable the conformations of these molecules in which the Si–C bonds are arranged at right angles to the nodal plane of the olefin π-electron system, which ensures the most favourable conditions for σ,π conjugation. In the one-electron oxidation of a compound of this type, the products are radical-cations, which can be readily detected by EPR and which are stabilised as a result of σ,π-conjugation[118–120] (see also Bock and co-workers[121,122]).

An instructive example of the stabilisation of radical-ions by silicon-containing substituents is provided by butatriene derivatives:



The neutral silylbutatriene is unknown, but its radical-cation and radical-anion do exist[120]. Silylbutatriene formally contains π-electron systems of two types: the central ethylene bond and the butadiene system. The substituent $(CH_3)_3Si$ is a π-electron acceptor in relation to the butadiene system via the $(p-d)\pi$-interaction mechanism and therefore promotes the stabilisation of the radical-anions. The substituent $(CH_3)_3SiC\lesssim$ is an electron donor in relation to the ethylene bond via the σ,π-conjugation mechanism and stabilises the radical-cation[120]. The stabilisation of the radical-cation, sufficient for its detection by EPR at 220 K, confirms yet again the important role of σ,π-conjugation in systems with a positive charge in the π-electron system. The effective stabilisation of the radical-cations formed on electron transfer from allylsilanes via σ,π-conjugation with participation of an Si–C bond is an important factor in photochemical allylation reactions[123].

We shall now consider the σ,π-conjugation in the benzyl derivatives of silicon subgroup elements. It is known[22] that, as the substituent X in the ring, the $(CH_3)_3SiCH_2$ group exhibits anomalously pronounced electron-donating properties in electrophilic aromatic substitution reactions involving silicon derivatives of the type $(CH_3)_3SiC_6H_4X$. These properties cannot be accounted for by the inductive influence and they are related to the donation of electron density from $(CH_3)_3.SiCH_2$ to the ring via the σ,π-conjugation mechanism. With increase of the number of trimethylsilyl groups *n* in $[(CH_3)_3Si]_nCH_{3-n}Ar$ (where Ar = aryl), the degree of σ,π-conjugation also increases, which is indicated by the rates of cleavage of the Ar–Si bond in the compounds $[(CH_3)_3Si]_n.CH_{3-n}C_6H_4Si(CH_3)_3$ and the chemical shifts in the ^{19}F NMR spectra of the compounds p-$[(CH_3)_3Si]_nCH_{3-n}C_6H_4F$.[124] In the σ,π-conjugated systems in the transition state (and in its model consisting of a charge transfer state), there is a strong resonance interaction of substituents of the type R_3ECH_2 with the positively charged reaction centre. The constants σ^+, characterising the influence of the substituents in such a situation, indicate exceptionally marked electron-donating properties of R_3ECH_2, which become more pronounced with increase of the atomic number of E[23,96,125–128]. The accuracy of the determination of the constants σ^+ for organoelemental substituents depends on the quality of the initial correlation equations. The parameters of these equations differ somewhat when data for tens of compounds[125,126] and only a few compounds[23,127,128] are used. It has been suggested[128] that the accuracy of the initial equations and of the constants σ^+ increases when only a few compounds rather than tens of compounds are used. Although this view is not evident and requires special consideration, the order of magnitude of the quantities σ^+, established in a number of studies[23,125–128], makes it possible to place the substituents R_3ECH_2 in the same series with the strongest organic electron donors of the type of OAlk and $NAlk_2$.

Further investigation of the influence of σ,π-conjugation in the transition state[64,129,130] and comparison of the reactivities of benzyl derivatives of silicon subgroup elements with

the spectroscopic parameters of charge-transfer complexes of these compounds stimulated the study of the effects of organoelemental substituents in the ground electronic state of σ,π-conjugated systems. Thus the constants σ_R^0 (which characterise the conjugation of the substituent with the benzene ring) of the substituents R_3SiCH_2,[131] R_3GeCH_2,[126] and R_3SnCH_2,[131], calculated on the basis of infrared spectroscopic data, indicate marked electron-donating properties of these substituents in the ground electronic state due to the σ,π-conjugation.

The anomalously high intensity of the bands corresponding to the multiple bond vibration, the bathochromic shift of the ultraviolet bands, and exaltation of the molecular refraction have been observed in the vibrational spectra of benzyl derivatives of the type $R_3SiCH_2C_6H_5$ as well as allylsilanes[90]. Thus benzylsilanes exhibit the characteristic properties of σ,π-conjugated systems. This conclusion follows evidently also from the analysis of the ionisation potentials of wide series of benzene derivatives with silicon-containing substituents. The ionisation potentials and the approximate HOMO energies have been obtained by the mass-spectrometric method[114,115,132] from the frequencies of the charge-transfer bands in electronic absorption spectra of the complexes with tetracyanoethylene[17,24,25,80,115,133–136] and (the most accurate values) from photoelectron spectra[48,59,112,122,137,138].

The introduction of the $(CH_3)_3SiCH_2$ group into the benzene molecule entails a sharp decrease of the first ionisation potential (i.e. the destabilisation of the HOMO of the type) from 9.24 to 8.35 eV. The ionisation potentials of di- and tetra-substituted derivatives (in the 1- and 3- and 1-, 2-, 4-, and 5-positions) decrease further to 7.75 and 7.10 eV.[137] The ionisation potentials of the carbon analogues are significantly higher. For example, they are 8.25 and 7.75 eV for n-$(CH_3)_3CCH_2C_6H_4CH_2C(CH_3)_3$ and p-$(CH_3)_3SiCH_2C_6H_4CH_2Si.(CH_3)_3$.[122] Thus the large electron-donating effect of the trimethylsilylmethyl group increases as these groups accumulate in the molecule and hence there is an increase of the overall effect of σ,π-conjugation. This increase is not entirely additive, since the presence of several bulky $(CH_3)_3SiCH_2$ groups in the molecule prevents the establishment of the conformation most favourable for σ,π-conjugation. This is particularly marked for the *ortho*-disposition of the substituents and also for polysubstituted benzenes. Thus, on passing from the tetra- to the hexa-derivatives, there is no decrease but an actual increase of the ionisation potential from 7.10 to 7.40 eV.[137] The intense electron-donating properties of the trimethylsilylmethyl groups, comparable in their influence to the effects of the methoxy- or amino-substituents and increasing in the presence of a positive charge on the π-electron system, promotes the stabilisation of the radical-cations.

In the radical-cations formed from benzene derivatives containing substituents of the type $[(CH_3)_3Si]_nCH_{3-n}$ with ionisation potentials below 7.8 eV, the incorporation of one-electron oxidants can be readily detected by EPR[122,137–139]. Analysis of the parameters of the EPR spectra indicates (like the ionisation potentials of the initial compounds) the delocalisation of spin density over the substituting group and the existence of a preferred conformation of the radical-cations determined by steric factors and the degree of σ,π-conjugation[137–139].

It follows from the photoelectron spectra of the trimethylbenzyl derivatives of silicon, germanium, and tin that the ionisation potentials decrease steadily and the effect of σ,π-conjugation increases with increase of the atomic number of the silicon subgroup element[59,112]. Although it is difficult to estimate quantitatively the relative contributions of σ,π-conjugation and the +*I* effect to the overall electronic effect of the $(CH_3)_3ECH_2$ groups, there is no doubt (at least in systems with a positive charge in the π orbital) that σ,π-conjugation predominates[140], exerting a very marked influence on the rates of chemical reactions and stabilising effectively the carbonium ions.

A clear proof of the enhancement of the effect of σ,π-conjugation on benzyl derivatives has been obtained on comparing the π-donor properties of these compounds in the ground electronic state and in the charge-transfer state, i.e. in the presence of a positive charge in the aromatic ring[125,140–143]. The infrared spectroscopy of π...H–O hydrogen bonds between benzyl derivatives and phenol is used to investigate the π-donor properties in the ground state[144]. The parameter characterising the π-donor properties is the shift of the stretching vibration frequency of the bond involving phenol in the infrared spectrum ($\Delta\nu$) on formation of the hydrogen bond. As for the allyl derivatives of silicon subgroup elements, a steady enhancement of the π-donor properties is observed for the benzyl analogues with increase of the atomic number of E, which cannot be explained by the variation of the electronegativity of E and which reflects the enhancement of the σ,π-conjugation on passing from silicon to tin[125,144].

The same conclusion was also reached in the study of the electronic absorption spectra of charge-transfer complexes of benzyl derivatives with tetracyanoethylene[125,126,141,142] or iodine[143]. The charge-transfer frequency (ν_{CT}) characterises the π-donor properties of the given derivatives in the charge-transfer state, i.e. when, under the conditions of the electronic spectroscopic experiment, the electron from the HOMO, localised mainly in the aromatic ring, is almost fully transferred to an unoccupied orbital of tetracyanoethylene or iodine and a positive charge is formed in the HOMO of the π type. Analysis of the type of relation between $\Delta\nu$ and ν_{CT}[125,141] shows that the positive charge in the ring enhances the effects of the π,π–, *p*,π–, and σ,π-conjugations of the substituents with the ring.

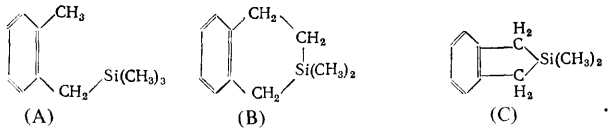
On transition to the state with charge transfer, a greater enhancement of the σ,π-conjugation is observed for the benzyl derivatives of germanium than for benzylsilanes[125,141].

Systematic studies of the ^{13}C and ^{19}F NMR spectra of compounds containing the $(CH_3)_3ECH_2$ and $(C_6H_5)_3ECH_2$ fragments (where E = Si, Ge, Sn, or Pb), linked to the benzene or naphthalene ring and the biphenyl group, showed[19,145–147] that in the ground electronic state these fragments possess electron-donating properties and influence the π-electron system mainly via the σ,π-conjugation mechanism. The conjugation is intensified with increase of the atomic number of E in the sequence Si < Ge < Sn < Pb. (The effect of σ,π-conjugation in the benzyl derivatives $R_3SiCH_2C_6H_5$ has also been established by ^{29}Si NMR.[148])

Yet another confirmation of the important role of hyperconjugation in organometallic compounds has been obtained by the joint application of the ^{13}C NMR and quantum-chemical methods[147]. A correlation has been established for derivatives containing the fragments $(CH_3)_3ECH_2$ (E = C or Sn) between the chemical shift difference in the ^{13}C NMR spectra of the tin and carbon compounds, on the one hand, and the change in the π-electron density, calculated by quantum-chemical methods, on passing from neutral to charged compounds modelling the intense conjugation of the substituent with the π-electron system, on the other. This correlation constitutes confirmation of the strong σ,π-conjugation of the $(CH_3)_3SnCH_2$ group with the benzene and naphthalene rings and the biphenyl group.

When the photoelectron spectroscopic data for benzyl derivatives were considered[137], the dependence of the degree of conjugation on stereoelectronic factors was noted above.

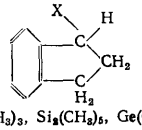
The influence of all these factors is clearly seen also from the Raman and NMR spectra. The characteristic features of σ,π-conjugation (high intensity of the band corresponding to the vibration of the multiple bond in the Raman spectra and exaltation of the molecular refraction) have been observed[149] for compounds (A) and (B) but not for compound (C).



(A) (B) (C)

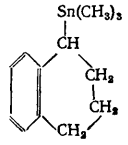
For the same compounds but with one fluorine indicator atom in the ring (instead of hydrogen), the above conclusion was confirmed by ^{13}C NMR[150] and ^{19}F NMR[151] methods. On passing to the bicyclic 2-silaindan (C), having a planar structure, from compound (A), the intense σ,π-conjugation in the latter breaks down owing to the disposition of the Si–C bond in the nodal plane of the π-electron system. In the conformationally non-rigid silatetralin (B), σ,π-conjugation becomes possible for certain conformations, but this effect is weaker than in compound (A).

The same conclusions were reached in the analysis of the ionisation potentials of these compounds and also of a number of organoelemental derivatives of indan[25]



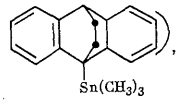
X=Si(CH3)3, Si2(CH3)5, Ge(CH3)3

and indene[152]. In these compounds the angle between the E–C σ-bond and the π-electron system is ~ 30°. The ionisation potential of the π-electron system therefore increases steadily with increase of the atomic number of E[152] owing to σ,π-conjugation. When X = $Sn(CH_3)_3$ and also for another conformationally labile compound



the conformation in which the maximum σ,π-conjugation obtains is preferred according to ^{13}C NMR data[89].

If the Sn–C bond is fixed in the nodal plane of the π-electron system (as in the model compound



then there is no σ,π-conjugation[89], as in the organomercury compound with a related structure[88].

One cannot rule out the possibility that hyperconjugation obtains in the substituent–aromatic ring system in derivatives of benzene, naphthalene, and anthracene containing substituents of the type ER_3 bound directly to the π-electron system. The possibility, in principle, of hyperconjugation follows from both general considerations, described in the introduction, and from the theoretical examination of the problem (for example, by Pitt[17]).

Considerable difficulties are encountered in the experimental study of hyperconjugation of this type. When E=C, the above effect is apparently extremely small and is possibly absent in the ground electronic state[3,6–8]. For silicon compounds, hyperconjugation of the type considered (consisting in the transfer of electron density from R_3Si to the aromatic ring) is masked by the influence of the stronger effect of the $(p–d)\pi$ interaction acting in the opposite direction[20,67–70], the traditional explanation of the mechanism of which consists in the concept of the transfer of π-electron density from the aromatic ring to the unoccupied 3*d* orbitals of the silicon atom.

On successive transition from E = Si to Ge, Sn, and Pb, the $(p–d)\pi$ interaction weakens[20] and hyperconjugation should be intensified according to all the available literature data. However, even under the most favourable conditions for the study of hyperconjugation in systems of the type $R_3E–Ar$ (i.e. for E = Sn or Pb), unambiguous experimental data supporting the occurrence of hyperconjugation have not been obtained. Thus detailed analysis of the parameters of the ^{13}C NMR spectra led the authors[153] to the conclusion merely that hyperconjugation is likely in the compounds $R_3E–Ar$, where E = Ge, Sn, or Pb. The conclusion that, of the two factors—hyperconjugation and $(p–d)\pi$ interaction—the former predominates in phenylsilane and trimethylphenylsilane, while the latter, discovered in the analysis of photoelectron spectra and by quantum-chemical calculations, predominates in trifluorophenylsilane[154], also appears ambiguous. Furthermore, numerous literature data, including those examined above as well as the results of a number of other studies[20,67–70], show that the SiR_3 fragments bound to the aromatic ring have electron accepting properties in relation to the groups CR_3, which is traditionally thought to be due to the $(p–d)\pi$ interaction.

Thus in compounds of the type R_3SiCH_2Ar the group R_3SiCH_2 (where R is an alkyl substituent) is a typical electron donor involving the σ,π-conjugation mechanism and also the inductive effect. The R_3Si fragment in the compounds R_3SiAr is a powerful electron donor operating via the inductive effect and is probably also a donor operating via the mechanism involving hyperconjugation with the ring, while, in terms of the mechanism involving the $(p–d)\pi$ interaction, this group is an electron acceptor.

The overall electronic effect of the R_3Si fragment is such that, compared with the isostructural carbon group R_3C, the silyl fragment is an electron acceptor in relation to the π-electron system. An unusual combination of the properties of the R_3SiCH_2 and R_3Si fragments is observed in the group R_3SiSiR_2 bound to the aromatic ring[143]. It is to be expected, firstly, that this group is as strong an electron donor as the R_3Si group in terms of the inductive effect. Secondly, like R_3Si, this group should exhibit electron-accepting properties in relation to the π-electron system of the aromatic ring in terms of the mechanism involving the $(p–d)\pi$ interaction. Thirdly, the R_3SiSiR_2 group, involved in σ,π-conjugation with the π-electron system, should exhibit electron-donating properties and the latter should be more marked than those of the R_3SiCH_2 group as a consequence of the higher polarisability of the Si–Si bond compared with Si–C. The overall electronic effect of the R_3SiSiR_2 group consists of the contributions listed above. It is therefore difficult to estimate *a priori* the resultant electronic effect of the R_3SiSiR_2 and R_3SiCH_2 groups relative to π-electron systems.

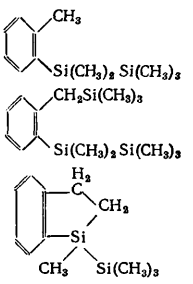
We shall now consider experimental data referring to systems of the type $R_3SiSiR_2–Ar$. Pentamethylphenyldisilane, its derivatives, and related compounds, as well as their complexes with tetracyanoethylene have been studied systematically by electronic spectroscopy (see Sakurai's review[155]). It was established that the Si–Si bond is involved in conjugation with the benzene ring and the multiple bond[155–161]. Whereas in the initial study the mechanism of the conjugation

was believed to involve the unoccupied 3*d* orbitals of the silicon atom[159], subsequently the important role of the σ,π-conjugation of the σ orbitals of the Si–Si bond with the π-electron system was established[155,162,163].

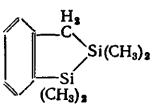
In relation to the benzene ring, the $Si(CH_3)_3Si(CH_3)_2$ group behaves as an electron donor in terms of the overall electronic effect, although its electron-donating properties are weaker than those of the $(CH_3)_3SiCH_2$ fragment[155]. This conclusion, reached in the analysis of the ultraviolet spectra, has been confirmed from σ^+ and σ^- constants for the group $Si(CH_3)_3Si(CH_3)_2$ determined by infrared and NMR spectroscopy[164,165]. These constants indicate a typical electron-donating character of the $Si(CH_3)_3Si(CH_3)_2$ group compared with $Si(CH_3)_3$ owing to σ,π-conjugation with participation of the Si–Si bond, although the numerical values of the constants require revision. The increase of the number of trimethylsilyl groups in the sequence $Si(CH_3)_2Si(CH_3)_3$ < $Si(CH_3)[Si(CH_3)_3]_2$ < $Si[Si(CH_3)_3]_3$ is accompanied by an enhancement of the electron-donating properties of the group characterised by the constant σ^+.[165] On the other hand, the trimethylsilyl and pentamethyldisilyl groups exhibit in the ground electronic state similar electron-accepting properties in relation to the ring[164].

The dual functions of the $Si(CH_3)_3Si(CH_3)_2$ group [electron-donating as a consequence of σ,π-conjugation and electron-accepting due to the $(p-d)\pi$ interaction] make it possible to understand[143] the regularities in the electronic absorption spectra of the charge-transfer complexes of π-donors containing this and similar groups[24,162,163,166-169] as well as the variation of the ionisation potentials of π-electron systems containing disilyl substituents[48,162,163,166]. The weaker electron-donating properties of the $Si(CH_3)_3Si(CH_3)_2$ fragment compared with $(CH_3)_3SiCH_2$ are not a result of the decrease of the effect of σ,π-conjugation with participation of the Si–Si bond (as was believed, for example, by Sakurai and Kira[163]) but are a consequence of the competition between two opposed conjugation effects [of the σ,π- and $(p-d)\pi$-types] in disilyl derivatives. If only the effect of σ,π-conjugation operated, then, owing to the greater polarisability of the Si–Si bond compared with Si–C, the disilyl fragment would have exhibited more pronounced electron-donating properties than the $(CH_3)_3SiCH_2$ fragment.

A test of the fulfillment of the stereoelectronic conditions for σ,π-conjugation by ultraviolet spectroscopy showed[169,170] that the compounds

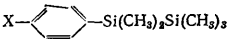


and a number of their analogues[169] have ultraviolet spectra characteristic of systems with σ,π-conjugation. On the other hand, in a compound of the type



the conjugation is weakened[169], while according to other data[170] it is altogether absent.

Important information about the characteristic features of σ,π-conjugation is provided by the analysis of the character of the HOMO of pentamethylphenyldisilane. The ionisation potential of the π electrons of the Si–Si bond (8.69 eV) in hexamethyldisilane[171] is lower than the ionisation potential of the π electrons of benzene (9.24 eV). The HOMO of pentamethylphenyldisilane, which is a linear combination of the symmetrical HOMO of benzene and the molecular orbital of the Si–Si σ-bond, contains a dominant contribution by the σ orbital of the Si–Si bond (72% according to quantum-chemical calculations[166]). As a result of this, the long-wavelength absorption bands in the electronic spectra of the charge-transfer complexes of phenyldisilanes[155,162,163,166] and vinyldisilanes[98] with tetracyanoethylene are assumed to involve intermolecular charge transfer from an orbital of the σ(Si–Si) type, like the bands in the spectra of complexes of methylpolysilanes[172,173]. The contribution of the σ(Si–Si) orbital to the HOMO of the compounds



depends on the nature of X and increases with enhancement of the electron-accepting properties of X.[166] From the standpoint of classical ideas about hyperconjugation, this can be interpreted as the intensification of the direct polar conjugation between the substituents $Si_2(CH_3)_5$ and X (or the intensification of the σ,π-conjugation of the Si–Si bond with the π-electron system) as the electron-accepting properties of the substituent X become more marked [Schemes (IV), (VII), and (X)].

Thus the effect of σ,π-conjugation has been studied in fair detail for derivatives of benzene and ethylene. The literature data on this effect involving other π-donor centres are limited but are consistent with the data for benzene and ethylene derivatives.

Thus the Si–Si fragments exhibits electron-donating properties via the σ,π-conjugation mechanism not only in relation to the benzene ring but also in relation to the double bond as well as the cyclopentadienyl ring, which follows from the EPR spectra of the cyclopentadienyl and silylcyclopentadienyl free radicals[174].

The effect of σ,π-conjugation in h^1-cyclopentadienyl derivatives $C_5H_5ER_3$ leads to a decrease of the ionisation potentials with increase of the atomic number of E on passing from silicon to tin[175], can influence the angles between the E–C bonds and the average planes of the rings[176,177] (although the structure of compounds of this type is still the subject of discussion[178]), and is also manifested in a series of other physicochemical properties[175].

The study of naphthalene derivatives by NMR[19,145,147], ultraviolet spectroscopy[162], the ultraviolet spectroscopy of charge-transfer complexes with tetracyanoethylene[160,162,163], and polarography[162] has shown that the substituent $(CH_3)_3SiCH_2$ is involved in σ,π-conjugation with the ring[19,145,147,160,162,163] and the overall electronic effect of the $Si(CH_3)_3$.$Si(CH_3)_2$ group is less electron-donating than the influence of the trimethylsilylmethyl group[162,163]. It has been shown[162,163] that the HOMO pentamethylnaphthyldisilane is a linear combination of the π-type HOMO of naphthalene and the molecular orbital of the Si–Si σ-bond. However, in contrast to the corresponding disilyl derivative of benzene[166], the HOMO in the naphthalene derivative has a preferential π character[162,163], since the ionisation potential of the π electrons of naphthalene (8.11 eV)[179] is lower than that of the π electrons of benzene (9.24 eV) and the σ electrons of the Si–Si bond (8.69 eV)[171]. The increase of the atomic number of E on passing from Si to Pb intensifies the σ,π-conjugation of the R_3ECH_2 fragment with the naphthalene

ring[19,145]. According to electronic spectroscopic data for complexes with tetracyanoethylene[180], the $(CH_3)_3SiCH_2$ fragment linked to the furan ring also exhibits anomalously pronounced electron-donating properties due to σ,π-conjugations which cannot be accounted for by the inductive effect.

Analysis of the positions and intensities of the absorption bands in the electronic spectra of 2-substituted pyridines[181] indicates the intensification of the σ,π-conjugation with increase of the atomic number of the element E in the $(CH_3)_3.ECH_2$ fragment and also on passing from substituents of the type $(CH_3)_3ECH_2$ to $[(CH_3)_3E]_2CH$. On the other hand, the diminution of the electron-donating properties of three substituents of the atom E, for example, on passing from $CH_2Si(CH_3)_3$ to the silatranyl derivative $CH_2Si(OCH_2CH_2)_3N$,[182]

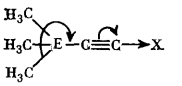
is accompanied by a weakening of σ,π-conjugation.

A significant role of effects of the type of π,π- and p,π-conjugation in acetylene derivatives has been noted in the literature[14]. According to Muller's estimates[9], hyperconjugation, treated as one of the conjugation effects, should be twice as intense on conjugation with a triple bond [Schemes (III), (VI), (IX), (XII), (XV), (XVIII), (XXI), and (XXIV)] as in conjugation with a double bond [Schemes (II), (V) (VIII), (XI), (XIV), (XVII), (XX), and (XXIII)]. This powerful influence of hyperconjugation on the properties of acetylenes is clearly manifested in organoelemental derivatives. Among all the π-donors investigated (derivatives of benzene[115], naphthalene[162,163], furan[180], thiophen[183], pyridine[181], ethylene[98,115], and buta-1,4-diene[115]), only acetylene derivatives exhibit anomalies in the character of the influence of substituents of the type $(CH_3)_3C$, $(CH_3)_3Si$, and $(CH_3)_3SiCH_2$.[115,184]

The substituents can usually be arranged in the sequence $(CH_3)_3Si < (CH_3)_3C < (CH_3)_3SiCH_2$ in terms of their electron donating properties in relation to the π-electron system. The diminution of electron-donating properties in $(CH_3)_3Si$ compared with $(CH_3)_3C$ in accordance with the above sequence is traditionally attributed to the influence of the electron-accepting (relative to the π-electron system) effect of the $(p-d)\pi$ interaction and the enhancement of the electron-donating properties of the $(CH_3)_3SiCH_2$ group relative to $(CH_3)_3C$ is due to σ,π-conjugation. If the possibility of effective hyperconjugation with a π-donor centre is ensured for the substituent $(CH_3)_3Si$ (this is apparently never attained for aromatic compounds and ethylene derivatives, as stated above), then the positions of the substituents $(CH_3)_3Si$ and $(CH_3)_3C$ in the series based on the electron-donating properties can change.

The inversion of the usually observed electron-donating order has been established as an experimental fact[115,184] for the acetylenes $HC\equiv CR$, where the electron-donating properties of the substituents R vary in the sequence $(CH_3)_3C < (CH_3)_3Si < (CH_3)_3SiCH_2$. On the other hand, judging from the charge-transfer frequency in the electronic spectra of the complexes of tetracyanoethylene[185], the usual sequence based on the electron-donating properties of the substituents is observed for the phenylacetylenes $C_6H_5C\equiv CR$. In the disubstituted derivatives $R-C\equiv C-R$ and $R-C\equiv C-C\equiv C-R$, the electron-donating properties of R also lead to the usual sequence $(CH_3)_3Si < (CH_3)_3C < (CH_3)_3SiCH_2$,[184] while the methyl group at the triple bond is a stronger donor than the silyl group[186].

The study of a wide range of silicon-, germanium-, and tin-containing acetylenes and their carbon analogues established the important role of hyperconjugation in organoelemental derivatives not only in the charge-transfer state (with a positive charge on the π-donor centre—electronic spectroscopy of the iodine complexes) but also in the ground state (infrared spectroscopy of the hydrogen bond with phenol)[187]. The hyperconjugation



is intensified with increase of the atomic number of E in the sequence Si < Ge < Sn and with enhancement of the electron-accepting properties of the substituents X. When the donor–acceptor properties of the substituents $(CH_3)_3E$ and X are equalised, the intensity of the hyperconjugation diminishes sharply but in compounds of the type $(CH_3)_3E-C\equiv C-E'(CH_3)_3$, i.e. when $X = E'(CH_3)_3$, it still remains fairly effective. Despite the similar donor–acceptor properties of the substituents $(CH_3)_3E$ and $(CH_3)_3E'$, the high polarisability of the atoms E' and E (silicon, germanium, and tin) and of the triple bond as well as the high sensitivity of the acetylenic π-electron system to the electronic effects of the substituents favour hyperconjugation in acetylene derivatives containing two silicon subgroup elements attached to the triple bond[187].

Thus, in compounds with the fragments $\rangle E-\overset{|}{C}-X$ or $\rangle E-\overset{|}{E}-X$ (E is a silicon subgroup element and X is an aromatic ring or a multiple bond), the interaction between the E—C and E—E bonds and the group X involves a σ,π-conjugation mechanism. The effect operates in the direction from the element E to the group X. If the substituent X is an atom with unshared electron pairs, then the mechanism of the interaction between E and X changes fundamentally[69] and involves the transfer of electron density in the direction from X to E (see the relevant reviews[188,189]). The traditional treatment of the interaction between X and E involves in this instance the concept of intramolecular coordination with participation of the unshared electron pairs of X and the unoccupied *nd* orbitals of the atom E,[190] but there exist also alternative approaches[191].

Apparently in certain systems there is a possibility of both types of interaction. This probably cannot be ruled out for silyl ketones where the presence of the C=O double bond and of the unshared electron pair of the oxygen atom is responsible for the complexity of the intramolecular interactions and the ambiguity of the conclusions concerning hyperconjugation[160,192,193]. Both intramolecular coordination and hyperconjugation apparently occur in cyclic silyl- and germyl-ketones[194].

3. The σ,σ- and σ,*p*-Conjugation in Compounds of Silicon Subgroup Elements

The effect of σ,σ-conjugation is a specific feature of organometallic compounds to an even greater extent than that of σ,π-conjugation. Systematic studies of the effect of σ,σ-conjugation have not been published and the few data available on this question can be consistently interpreted mainly in those cases where σ,σ-conjugation influences the reactivity of organometallic compounds in the transition state. Many clear examples of such influence have been quoted by Nesmeyanov[21,71], who established, in particular, a fairly profound analogy between the properties of the conjugated systems (π,π-, *p*,π-, σ,*p*-, σ,π-, and σ,σ-) which makes it possible to treat them from the same general standpoint[9]. It follows from the last conclusion that the absence of fundamental discrepancies with the rules established for

other conjugated systems constitutes an indirect confirmation of the validity of the conclusions reached in the study of σ,σ-conjugation in the ground electronic state.

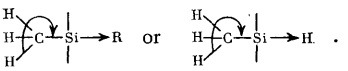
On the basis of the proton chemical shifts in the methyl groups in the ^{1}H NMR spectra of the tetramethyl derivatives $(CH_3)_4E$, Allred and Rochow[15] proposed an electronegativity scale for Group IV elements: C(2.60) > Pb(2.45) > Ge(2.00) > Sn(1.93) > Si(1.90). It was then postulated that there is a possibility of hyperconjugation in the tetramethyl derivatives $\rangle E^- = CH_2H^+$, but the authors assumed that this effect should be equally important for all the compounds of silicon subgroup elements. (In Section II it was noted that the occurrence of hyperconjugation in tetramethylsilane follows from quantum-chemical calculations[62].) According to Allred and Rochow[15], hyperconjugation should therefore make a constant contribution to the electronegativities.

Criticism of the Allred–Rochow electronegativity scale by Egorov[195] was based on the fact that this scale is not only a measure of the inductive effect but also includes the so called *C* effect and hyperconjugation. However, we believe that the *C* effect and hyperconjugation are synonymous terms. Indeed, analysis of the vibrational spectra established that an electron-accepting *C* effect is characteristic of the E atoms, increasing monotonically on passing from silicon to germanium and tin[195]. The presence of this effect has been demonstrated sufficiently rigorously only for methyl derivatives and the nature of the *C* effect has not been elucidated. Bearing in mind that hyperconjugation in methyl derivatives (like σ,π-conjugation in benzyl derivatives) does not constitute a constant contribution but increases in the sequence Si < Ge < Sn < Pb with increasing polarisability of the elements E, the conclusion that the terms "*C* effect" and "hyperconjugation" describe the same electronic σ,σ-conjugation effect becomes evident.

The concept of hyperconjugation has been used in the interpretation of the infrared and ^{1}H NMR spectra of silane[196] and stannane[197] derivatives. In the absence of extreme steric effects of the substituents[198], the frequency ν of the highly characteristic stretching vibration of the Si–H bond in the vibrational spectra of R_3SiH depends almost exclusively on the electronic effect of the substituents R.[199] If there are no resonance effects, then the frequency depends only on the inductive effect of R. However, the equation relating ν and the inductive constants σ* of the substituents R has an insufficiently high correlation coefficient. The frequency ν decreases when R is varied in the sequence CH_3 > iso-C_4H_9 > H = C_3H_7 ≅ n-C_4H_9 ≅ C_2H_5 > iso-C_3H_7; this series deviates from the σ* constant scale apparently owing to σ,σ-conjugation[196]. Shielding of the hydrogen atom in the Si–H group increases in the following sequence according to ^{1}H NMR spectra: CH_3 ≅ iso-C_4H_9 < n-C_4H_9 < C_2H_5 < iso-C_3H_7. The explanation[196] of the discrepancy between this sequence and the variation of the constants σ* by σ,σ*-conjugation is not quite so unambiguous in the given instance (as in the case of the frequencies ν), since the shielding revealed by ^{1}H NMR spectra can involve contributions due to magnetic anisotropy, which mask the donor–acceptor effects of the substituents.

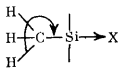
According to the ^{1}H NMR spectra of the stannane derivatives R_3SnH, R_2SnH_2, and $RSnH_3$, hydrogen atom shielding in the Sn–H group increases in the sequence iso-C_3H_7 < n-C_4H_9 ≅ n-C_3H_7 ≅ C_2H_5 < CH_3 and the frequencies of the stretching vibrations of the Sn–H bond in the infrared spectra of the methyl derivatives are anomalously high and are close to those for the phenyl derivatives. This also indicates the presence of hyperconjugation, which is particularly pronounced for the methyl derivatives[197]. An anomalously high frequency ν(Ge–H) is also observed in the infrared spectrum of trimethylgermane compared with other trialkylgermanes[200]. The greater role of σ,σ-conjugation in organogermanium compounds compared with organosilicon compounds is apparently the main cause of the higher intensity of the ν(Ge–H) bands compared with ν(Si–H) in the infrared spectra of compounds of the type R_3EH having an analogous structure (where E = Si or Ge)[201].

A semiquantitative estimate of the effects of σ,σ-conjugation has been made for the methyl derivatives of silicon. As mentioned above, the frequencies ν(Si–H) in the infrared spectra of the compounds R_3SiH depend mainly on the inductive effect of the substituents R. If R is not involved in strong conjugation with the silicon atom [of the type of $(p-d)\pi$ interaction], then the equation $\nu_{ind} = 23.1\Sigma\sigma^* + 2112$ holds[199]. Although the frequency ν is in fact influenced by σ,σ-conjugation, the inductive effect makes a dominant contribution to ν. The low contributions of σ,σ-conjugation are due to the fact that the substituents R, which exert only an inductive effect, have as a rule small inductive constants and the difference between the donor–acceptor properties of the conjugated bonds in compounds with such substituents R is therefore small and the extent of hyperconjugation is likewise slight:



Nevertheless the dipole moment of the Si–C bond in methylsilane has the direction $H_3C \rightarrow SiH_3$.[202]

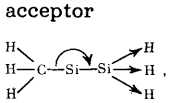
The introduction into the molecule of the substituents X forming $(p-d)\pi$ bonds with the silicon atom (and exerting a powerful inductive $-I$ effect) reduces the experimental values of ν_{exp} compared with ν_{ind}. The difference $\Delta\nu = \nu_{ind} - \nu_{exp}$ characterises the conjugation effects and for the methyl derivatives is smaller than for the ethyl derivatives. The effect of σ,σ-conjugation



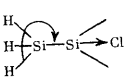
operates in opposition to the $(p-d)\pi$ interaction and the decrease of Δν for the methyl derivatives is a result of the stronger σ,σ-conjugation than for the ethyl derivatives[203–207].

Careful analysis taking into account the magnetic anisotropy of chemical bonds shows that, in terms of the ^{1}H NMR spectra, hyperconjugation decreases the shielding of the methyl protons compared with the CH_2 protons in the ethyl group[203]. The high polarisability and low ionisation potential of the silicon–silicon bond lead to extremely specific properties of polysilanes[208], which has been noted, in particular, in the study of σ,π-conjugation involving the pentamethyldisilyl group[143]. σ,σ-Conjugation is also manifested to an appreciable extent in polysilanes[209].

Depending on the nature of R in R_3SiSiH_3, the inductive constants σ* of the groups SiH_3, calculated on the assumption that only the inductive effect operates in disilanes, assume unrealistic values in the range from +1.5 to −1.5. As a partner in σ,σ-conjugation, the substituent R_3Si regulates the donor–acceptor properties of the silyl group which can function both as an acceptor

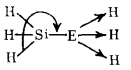


and as a donor



in hyperconjugation[209].

Thus, as for acetylene derivatives containing two organoelemental substituents[187], the variable contributions from σ,σ-conjugation impose fundamental limitations on the possibility of calculating the inductive constants of organoelemental substituents from infrared spectroscopic data for polysilanes. This applies equally to compounds of the type

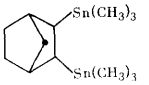


where σ,σ-conjugation becomes more intense on passing from E = Ge to E = Sn.[209]

The study of the ionisation potentials of cyclopropylmethyl-(trimethyl)stannane, allyltrimethylstannane, and a series of related compounds by photoelectron spectroscopy established[113] low values of the potentials in the first compound as a result of the σ,σ-conjugation of the C–Sn bond with the cyclopropane ring and in the second compound as a consequence of σ,π-conjugation. The similar energies of the σ,σ-interaction (1.6 eV) and the σ,π-interaction (2.2 eV) are consistent with the results of a study of silicon-containing derivatives of benzene, ethylene, and cyclopropane by the electronic spectroscopy of their iodine complexes[210]. This observation has been checked in order to compare the characteristics of σ,π- and σ,σ-conjugations.

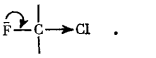
The presence of a positive charge on the cyclopropane and benzene rings as well as the double bond in the charge-transfer state leads to a qualitative indistinguishability of the characteristic features of the conjugation in all three systems[210]. We may note that in small strained cyclic systems of the type of bisbicyclobutane hyperconjugation plays an appreciable role also in the absence of organoelemental substituents[211].

Theoretical study[17] and experiments on photoelectron spectroscopy[212] indicate the interaction of the E–C σ-bonds via the σ,σ-conjugation mechanism in compounds of the type $(CH_3)_3ECH_2CH_2E(CH_3)_3$, where E = Si or Sn. The ionisation potentials of these compounds are appreciably lower than those of the related compounds where there is no hyperconjugation and the example of the compound



with rigidly fixed C–Sn bonds emphasises the importance of the stereoelectronic factors not only for σ,π-conjugation but also for σ,σ-conjugation[212].

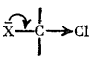
Systematic studies of the effect of σ,*p*-conjugation have not been made and most of the existing data have been obtained by the NQR method for chloro-derivatives of carbon and silicon subgroup elements. It is known, for example[213], that the frequencies in the ^{35}Cl NQR spectra of compounds of the type Cl–X increase with increasing electronegativity of X. The frequency therefore increases with increase of *n* in compounds of the type CCl_nH_{4-n}. As a consequence of the greater electronegativity of fluorine compared with chlorine, the increase of *n* in CF_nCl_{4-n} should also increase the frequency of the ^{35}Cl NQR signal, but the frequency is in fact somewhat reduced[213]. In order to account for this anomaly, which cannot be interpreted in terms of the inductive effect (electronegativity), the author[214] resorted to the concept of σ,*p*-conjugation:



As a result of the conjugation, the electron-accepting properties of the fluorine atom are diminished and the frequency of the ^{35}Cl NQR signal decreases compared with the value anticipated if only the inductive effect of the fluorine atom operated. Subsequently it was established[215] that hyperconjugation intensifies when fluorine atoms accumulate in the molecule. These problems were examined in greater detail by Semin et al.[213]

The initial data concerning σ,*p*-conjugation were developed significantly and generalised in the analysis of the ^{35}Cl NQR spectra of the compounds $R'R''R'''CCl$.[213,216–218] The compounds were combined in two groups. The first group included compounds whose substituents R did not contain unshared electron pairs. The NQR frequencies of these derivatives are linearly related to the sum of the inductive constants of the three substituents R: $\nu = 33.9 + 10.64\Sigma\sigma_I$. The compounds of the second group have R with unshared electron pairs (F, Cl, Br, I, or O) and their NQR frequencies deviate from the linear relation towards lower values. The deviation Δ is linked by the relation $\Delta = 13.32\Sigma\sigma_R$ with the sum of the constants σ_R characterising the capacity of R for conjugation.

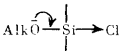
The two-parameter equation $\nu = 33.9 + 10.64\Sigma\sigma_I + 13.32\Sigma\sigma_R$ indicates an important role of the effects of σ,*p*-conjugation



in carbon compounds[213,219,220]. According to classical ideas concerning hyperconjugation, when the electron-accepting properties of the chlorine atom remain unchanged, the σ,*p*-conjugation intensifies (Δ increases) as the electron-donating properties of the atom with unshared electron pairs are enhanced (the constants σ_R increase).

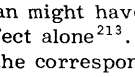
Systematic study of the dependence of the ^{35}Cl NQR frequencies on the electronic effects of the substituents in chlorosilanes[217] and chlorogermanes[220] showed that the inductive effect of the substituents is not the only cause of the changes in the frequencies[213,218,221,222]. Statistical treatment of the literature data on the frequencies of the ^{35}Cl signal in the spectra of $(R_1)_3E–Cl$[223] established the significance of the resonance effects.

At the same time the interpretation of the resonance effects within the framework of σ,*p*-conjugation was not found to be quite as evident as for the carbon compounds. Thus the extent of σ,*p*-conjugation in organosilicon compounds



and probably also the direction of this effect[221] depend greatly on the nature of the two other substituents at the silicon atom. The effect of σ,*p*-conjugation is observed for compounds in which the substituents exert the maximum influence on the central silicon atom via the $(p–d)\pi$ conjugation and inductive mechanisms. Significant changes in the positive charge on the silicon atom and of the bond polarities apparently influence greatly the extent of σ,*p*-conjugation, but this problem has not so far been studied. It is believed that such studies permit a deeper understanding of the relative contributions of σ,*p*-conjugation and electrostatic interaction, the latter being sometimes put forward as an alternative to the former[222].

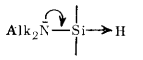
The ^{35}Cl NQR frequencies in the spectra of alkoxychlorogermanes are lower[222] than might have been expected on the basis of the inductive effect alone[213]. As in the case of alkoxychlorosilanes and the corresponding carbon derivatives, we believe that this is caused by σ,*p*-conjugation:



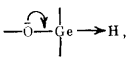
In the infrared spectroscopic study of compounds where the existence of σ,p-conjugation can be postulated[204,224-226], the possibility of interpreting the experimental data within the framework of the inductive effect and the $(p-d)\pi$ interaction alone was demonstrated. This conclusion was also reached in the analysis of the dependence of the frequencies and intensities of the highly characteristic stretching vibrations of the Si–H and Ge–H bonds in the infrared spectra on the electronic effects of the three substituents at the atoms E. The frequencies ν(Si–H) confirmed the presence of σ,p-conjugation in alkoxychlorosilanes[204] and chlorodimethylaminosilanes[224]



and also in silanes of the type Alk_2NSiH_3 and $(Alk_2N)Alk_2$.SiH.[224] The effect of σ,p-conjugation in compounds of the latter type



is possible in view of the exceptionally high capacity of dialkylamino-groups for conjugation, including hyperconjugation. The polarity of the Si–H bond in dialkylaminosilanes increases as a consequence of σ,p-conjugation, which is clearly manifested in the intensities of the Si–H bands in the infrared spectra[225]. The anomalous increase of the intensities of the stretching vibration bands of the Ge–H bond as a result of σ,p-conjugation in compounds containing the fragments



has been established[226].

Thus the studies of hyperconjugation in organic derivatives of silicon subgroup elements by spectroscopic methods resulted in the accumulation of fairly extensive experimental data concerning mainly σ,π-conjugation. The principal characteristics of σ,π-conjugation, confirmed by quantum-chemical methods (the sharp intensification of the effect on passing from carbon compounds to silicon derivatives and its further intensification with increase of the atomic number of silicon subgroup element; the dependence on the stereoelectronic factors which in the limiting cases determine the very possibility of hyperconjugation; the significant dependence of the magnitude of the effect on the difference between the donor–acceptor properties of the conjugated bonds and the possibility of regulating these properties by varying the substituents at the donor and acceptor fragments of the molecule; the intensification of the effect in the presence of a positive charge on the π-electron system) are not only features of the ground electronic state but also the most important factors which determine the reactivity of σ,π-conjugated compounds.

The effects of σ,σ- and σ,p-conjugation have been so far inadequately investigated. However it is of fundamental importance that the same features which are characteristic of σ,π-conjugated compounds are observed in σ,σ- and σ,p-conjugated systems. The hypothesis of a major role of hyperconjugation in organoelemental compounds and of a profound analogy between the conjugation effects in general, which was put forward 35 years ago[21,71], is thereby fully confirmed.

In future studies of hyperconjugation in organoelemental compounds, derivatives of Group IV elements and mercury will probably play the role of model systems. The characteristics of the hyperconjugation in these model systems are important both for the solution of the overall problem of the relation between the structure and reactivity of organoelemental compounds and for the investigation of many specific problems, for example of the role of σ,p-conjugation and other resonance effects in organoelemental compounds, the characteristics of the influence of σ,σ-conjugation in the ground and excited electronic states, and the role of hyperconjugation in compounds with a chain of metal atoms and highly polarisable chemical bonds.

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Institute of Chemistry,
USSR Academy of Sciences,
Gorky