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Conjunction in organic compounds of silicon-subgroup elements

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ABSTRACT. The existing theoretical ideas concerning the intramolecular interactions in organic compounds of silicon-subgroup elements are examined in relation to the results of experimental studies. It is shown that the overall resonance effect of organoelement substituents includes acceptor (joint influence of unoccupied *nd* and antibonding σ* orbitals) and donor (σ,π conjugation, σ,π* conjugation, and σ,*n* conjugation) components. The relative contributions of these components to the resonance effect are analysed as a function of the type of central element, the organic groups linked to it, and the reaction centre.

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I. Introduction

The problem of intramolecular interactions is of key importance in theoretical and applied organoelemental chemistry. A steady trend in recent years has involved the appearance of new ideas and improvement of the methods of study of this still inadequately elucidated problem (see, for example, Refs. 1–10). The aim of the present review is to analyse the experimental data and the existing theoretical ideas about the intermolecular interactions and especially about the effects of conjugation in silicon-subgroup compounds.

Group IVB organoelemental compounds constitute unusual model systems in the chemistry of non-transition [main Group] elements.[3,11,12] Typical difficulties, arising in the solution of the problem of intramolecular interactions where alternative but inadequately supported views are put forward about a number of its important aspects, are manifested clearly for the given compounds. Under the conditions of a growing stream of information, which requires the development of a general theoretical standpoint for its consideration, one has to adopt a critical attitude to extreme views claiming universality—not only to attractively simple ideas but also to hypotheses seemingly disproving them which are applicable in reality only to a limited number of facts. The overall concept must, firstly, include these polar ideas as special limiting cases and, secondly, must be based on large sets of correct experimental data, must explain them without contradictions, and must possess predictive power, at least in principle.

Unfortunately this entirely evident methodology has been frequently infringed in the study of conjugation in compounds of silicon-subgroup elements despite the availability in the literature of a constructive basis for the avoidance of such errors.[13] Since the available data on the subject of the review are contradictory, the reivew has been constructed in accordance with the following scheme to elucidate the causes of the contradictions and to seek ways for their elimination: the choice of a general theoretical concept most consistent with the available set of experimental data and intramolecular interactions: the elucidation on its basis of "score" points in the literature data; comparison of the possibilities of the concept employed and of alternative ideas for the explanation of experimental facts; establishment of the limits of applicability of the chosen concept.

In the present review, preference is given to the consideration of (1) studies of fundamental importance for the elucidation of the given subject and (2) the most thoroughly investigated compound of tetracoordinate silicon-subgroup elements. The review does not deal with data, which are of specialised interest, concerning the relationship between intramolecular interactions and reactivity (see, for example, Refs. 2, 11, 12 and 14) and also compounds of pentacoordinate elments.[12,15–19]

II. Theoretical ideas concerning conjugation

1. Separation of the inductive, resonance and steric effects

In the first place, it is necessary to make a series of general remarks which will explain the approaches used in the review to the analysis of literature data. The absolute majority of publications on the subject of the review presuppose the use in an explicit or implicit form of two important principles of physical organic chemistry: the linear relation between free energy changes (LFE) and the independence and additivity of the influences of the inductive, resonance, and steric effects on the free energy change. An enormous number of studies have been devoted to the verification of these semiempirical principles (see, for example, Refs. 6, 20, and 21), which indicate a high degree of their generality. At the same time, a number of difficulties arise in the theoretical justification and practical use of these principles. These have been analysed in greater detail in a number of other communications.[6,20,21] We shall consider briefly the essential features of the above principles.

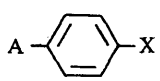
The most concise formulation of the LFE principle is the familiar Hammett equation $\lg K - \lg K_0 = \rho\sigma$,[22] which relates the rate or equilibrium constants K (a spectroscopic or other physical parameter having the significance of the Gibbs free energy can also be used as $\lg K$ [20,23]) for substituted and unsubstituted compounds to σ constants characterising the substituent. The reaction constant ρ characterises the sensitivity of the reaction centre (for chemical

reactions) or the indicator centre (for physical parameters) to the electronic effects of the substituents. The quantity σ is a constant only for constant properties of the medium (temperature, solvent, etc.).[6,22] For compounds of the type $A-B-ER_3$, the value of σ for an organoelement substitutent ER_3 (here and henceforth E is a silicon subgroup element, i.e. Si, Ge, Sn, or Pb) can generally speaking depend on the nature of the conducting fragment B of the molecule and on the type of the reaction (indicator) centre A.[6,24,25] The latter factor necessitates, on the one hand, a cautious approach to the use of σ constants as universal characteristics of the electronic effects of organoelement substituents, but, on the other hand, it can be used in the study of the dependence of intramolecular substituent–reaction centre and substituent–conducting fragment interactions on the nature of the varied A and B.[6,24,25]

In practice, when the LFE principle is used it is necessary in the majority of cases to take into account yet another principle, whose essential feature consists in the possibility of representing the Gibbs free energy change ΔG (in chemical processes or in the correlation of physical properties) by the sum of independent and additive components, i.e. $\Delta G = \Delta G_I + \Delta G_R + \Delta G_S$, determined by the influence of the inductive, resonance, and steric effects. The LFE principle must then be applied not to the overall quantity ΔG but to each of the three components separately.[20,22] The development of the LFE principle on this basis leads to three new σ constants: σ_I, σ_R, and E_S (there are also other designations), characterising the above effects. We shall mention briefly the problems arising in attempts at a theoretical justification of the principle of independence and additivity and of its practical application.[20–22]

Among the three components of ΔG, only the inductive component can be characterised with an adequate degree of approximation by a set of universal constants σ_I of the substituents.[20] The nature of the inductive effect (the field and/or bond polarisation effect) remains controversial.[26–28] Both factors are apparently significant for substituents EX_3 with electronegative groups X.[6] In highly excited electronic states, where there is appreciable charge separation under the influence of the inductive effect, the universality of the constants σ_I may break down.[29]

The constants σ_R of organic and organoelement substituents are used to characterise the change in ΔG under the influence of the resonance effect. The values of σ_R depend on the type of reaction centre.[6,20,21] Thus the constants σ_R^+ *and* σ_R^- have been widely used[6,22] as a quantitative measure of the resonance effect of substituents X (organic and organoelement) in the systems



in the presence of positive and negative charges on the reaction centre A respectively.

The resonance effects of two substitutents are not in general additive, which follows from theoretical analysis,[20,30,31] quantum-chemical calculations,[32] and experiment (for example, a wide variety of spectroscopic studies).[5,25,33,34] It has been established[5,20,25,30–34] that the non-additivity makes an appreciable contribution only when there is a large difference between the donor– acceptor properties of the two substituents or when both substituents are typical resonance electron donors.

The problem of isolating the component ΔG_R due to the influence of conjugation effects is unduly complex only at first sight. Experiment shows that the successive application of methods of correlation analysis with adequately representative selections of objects makes it possible to convert the above complications into their opposite, i.e. into an instrument for the study of fine details of resonance interactions in organoelement compounds. In particular, the important role of hyperconjugation effects in organoelement compounds was established in this way. It will be considered in greater detail below.

The isolation of the steric component ΔG_S constitutes a complex problem, since the influence of steric effects cannot be characterised by a standard set of universal constants invariant in relation to the system investigated. Steric constants of the type E_S, v, and their derivatives[35] are of limited applicability, especially in the study of intermolecular and intramolecular interactions with participation of Group IVB organoelement compounds.[36] Furthermore, the electronic and steric aspects of intramolecular interactions are interrelated in many instances (the stereoelectronic effect—see, for example, Egorochkin[3,36]). Generally speaking, a dual approach to the elucidation of the presence or absence of a dependence of ΔG_S on the nature of the varied substituents is possible. Firstly, there are several versions of computational schemes estimating with different degrees of approximation the shielding of the reaction (indicator) centre by substituents.[37–40] Secondly, the role of the component ΔG_S can be estimated by carrying out a correlation analysis of representative sets of experimental data of the kind mentioned above for ΔG_R. The significance of steric factors then becomes evident if the impossibility of explaining the influence of substituents (at least bulky ones) by electronic effects alone is observed explicitly.

An independent and extremely important approach to the study of intramolelcular interactions, one which has as yet been inadequately developed for organoelement compounds, is based on quantum-chemical methods. The principal results will be examined below.

Thus fairly stable ideas have arisen in the literature concerning the possibilities and limitations of the experimental methods for the study of intramolecular interactions in organic and organoelement compounds. The principle of maximum consistency with these ideas has been the main criterion for the selection of correct literature data on intramolecular interactions in Group IVB organoelement compounds.

We shall now consider the problem of the selection of a general theoretical concept satisfying the experimental data to the greatest extent.

2. Characteristic features of conjugation in organoelement Group IVB compounds

The long trial and error procedure followed in the study of intramolecular interactions in compounds of the silicon-subgroup elements has still not reached completion. The evolution of views on conjugation, frequently reflected in review communications,[6,13,41–46] is especially contradictory. We shall consider briefly the main stages of this evolution.

The first stage was based on the idea that unoccupied $3d$ orbitals of the silicon atom may participate in the formation of multiple bonds ($d_\pi-p_\pi$ conjugation).[47] This idea was invoked to account for the small length of the silicon–oxygen and silicon–halogen bonds.[48] A series of symbols are used to designate the conjugation of the atoms E with π- and n-electron substituents, among which the most concise are d,π and d,n respectively.

The hypothesis of unoccupied nd orbitals was subsequently applied to the interpretation of an enormous number of experimental facts obtained in the study of virtually all types of organoelement Group IVB compounds with the aid of chemical and physical methods (see the relevant reviews[41,42,49–51]). This hypothesis proved

to be extremely effective for the explanation of a most important difference between compounds of the elements E and carbon—the existence of π-acceptor properties in the atoms of E. It was established that these properties weaken with increase in the atomic number of E and that there is a close analogy between them and the conjugation effects in organic chemistry.[42]

Although the *nd*-orbital hypothesis agrees qualitatively with general quantum-chemical ideas, numerous attempts to obtain quantitative information about the involvement of *d*,π orbitals by means of approximate semiempirical methods were always open to criticism, since they did not lead to unambiguous, correct conclusions.[42,46,52] Such dual role of the approximate quantum-chemical methods left a strong imprint on the second stage of the evolution of ideas about conjugation in silicon-subgroup compounds.

The second stage was prepared for by the vigorous development with the aid of various chemical and physical methods[3,10,54–56] of the initial idea of Nesmeyanov and co-workers[53] concerning the more important role of hyperconjugation in organoelemental compounds than in organic compounds. A study by Pitt,[57] in which the author concluded without adequate justification that only hyperconjugatin occurs in silylacetylenes and that there is no need to resort to the idea of *d*,π conjugation, can apparently be regarded as the start of the second stage. Although subsequently Pitt corrected his ideas signifcantly,[13] his initial study[57] actually stimulated a series of publications (see, for example, Ponec and Chvalovsky[58,59]), whose authors considered hyperconjugation as an alternative to *d*,π conjugation in α,β-unsaturated compounds of the elements E. Despite the erroneous nature of the initial postulate, these studies have also played a constructive role, because they promoted the recognition of the complexity of the overall effect of conjugation in organoelemental Group IVB compounds.

The next stage of the evolution of views on conjugation, which arose almost simultaneously with the second, was the attempt to explain the electron-accepting properties of the atoms E not by the presence in them of *nd* orbitals but by the involvement of the antibonding σ* orbitals of the E–X bond in hyperconjugation.[7,9,60–65] Different versions of hyperconjugation interactions were proposed as alternatives to the *d*-orbital hypothesis (and sometimes as an addition to it—see, for example, West and Wadsworth[66,67]): (1) the interaction of σ*(E–C) orbitals with the π-electrons of the substituents Y in the C–E–Y fragments, where Y = aryl,[68] ethenyl,[69] ethynyl,[69] furyl, or thienyl;[70] (2) the interaction of the σ*(Si–C) and σ*(Si–H) orbitals with the lone pairs (LP) of Y in the (H)C–Si–Y fragments, where Y = NR_2, OR, SR, SeR, or F (R = organic and organosilicon groups);[7,64,65,71] (3) the interaction of the σ*(Si–H) orbitals with the carbanionic centre in $H_3SiCH_2^-$.[61,72] The qualitative aspects of the hyperconjugation interactions involving the antibonding orbitals of the bonds formed by elements of the Second and Third Periods were examined in the study of the anomeric effect[7,9,64] and other stereoelectronic effects.[9,73–75] The general approach to the problem of the involvement of antibonding orbitals will be examined below. Here we may note the possibility of invoking the concept of antibonding orbitals in the study of hypervalent bonds[15] in atranes (see, for example, Arshinova[9]) and in certain other compounds,[76,77] especially SiH_5^-.[78]

It is noteworthy that none of the three systems of views on conjugation presented above contains rigorous evidence for the erroneous nature of alternative ideas. In the search for such evidence, fundamental difficulties apparently arise inevitably owing to the complexity of the conjugation effects in organoelemental Group IVB compounds. Therefore views constituting the basis of the general theoretical concept which satisfies best the experimental facts must not exclude but supplement one another.

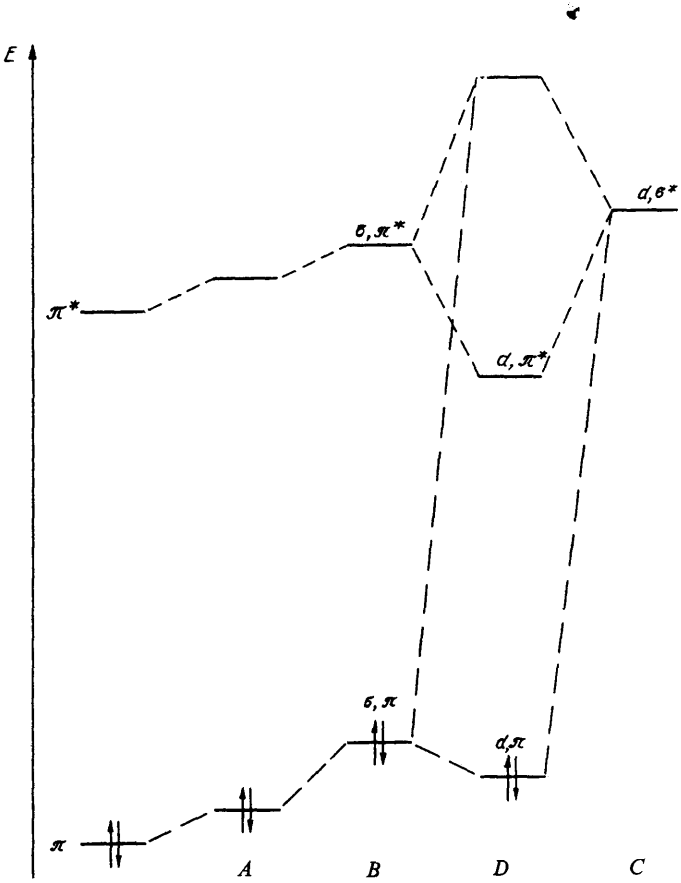


Figure 1. The influence of the substituents $E(CH_3)_3$ on the energies of the frontier orbitals π and π* of unsaturated hydrocarbons (according to Pitt's data[13]). Stage A—inductive +*I* effect of $E(CH_3)_3$; Stage B—σ,π and σ,π* conjugation; Stage C—mixing of σ*(E–C) orbitals of the substituent $E(CH_3)_3$ with the *nd* orbitals of the E atoms (a mixed *d*,σ* orbital with a lower energy is illustrated); Stage D—mixing of the *d*,σ* orbitals with σ,π* and σ,π; the formation of HOMO (*d*,π) and LUMO (*d*,π*) in the molecule.

Such a unifying concept was proposed by Pitt[13] in the fourth stage of the evolution of views on conjugation. Following Pitt, we shall consider this concept in relation to the change in the energy levels of frontier π and π* orbitals of substituted unsaturated hydrocarbons under the influence of the substituents $E(CH_3)_3$ (Fig. 1), i.e. as a result of the intramolecular interactions in compounds of the type $YE(CH_3)_3$, where Y = C_6H_5, $CH_2=CH$, etc. To facilitate the treatment, we shall represent arbitrarily the overall electronic effects of the substituents $E(CH_3)_3$ by several components.[13] In conformity with the ideas described in the first

part of Section II, the differentiation of the inductive and resonance components of the influence of the $E(CH_3)_3$ group then becomes entirely evident. As regards further subdivision of the overall resonance effect of $E(CH_3)_3$ into components, this problem is close in its significance to that solved in physical organic chemistry in estimations of the contributions of the hyperconjugation component to the overall conjugation effect of organic substituents.[20,22]

Stage A. The inductive effect. The inductive donor–acceptor properties of the substituents EX_3 depend on the nature of the groups X. The substituents $E(CH_3)_3$ have a positive inductive $+I$ effect (inductive electron donors), so that their influence results in an increase in the energy (destabilisation) of the orbitals π and π^*. On the other hand, if X are electronegative groups, then the substituent EX_3 is an inductive electron acceptor ($-I$ effect).

Stage B. Hyperconjugation of the σ,π and σ,π^* type [mixing of the $\sigma(E-C)$ orbitals of the substituent $E(CH_3)_3$ with the π and π^* orbitals of the fragment Y after taking into account the change in the energies of the initial orbtials under the influence of the inductive effect in stage A]. We may note certain key postulates and conclusions in Pitt's study.[13] From the linear combination of three $\sigma(E-C)$ orbitals, it is possible to obtain three wave functions, one of which, namely $\psi(\sigma)$, has π-type symmetry and can therefore interact with the $p_z(\pi)$ wave functions of the $Y-\psi(\pi)$ fragment. According to the perturbation molecular orbital theory,[13,30] the energy of the initial orbitals $E(\sigma)$ and $E(\pi)$ changes by the following amount after σ,π mixing:

$$\delta E(\sigma) = -\delta E(\pi) = \pm\sum[(4P^2(\pi\sigma) + \Delta E^2)^{1/2} - \Delta E] / 2, \quad (1)$$

where $P(\pi,\sigma)$ is the $\psi(\pi)P\psi(\sigma)d\tau$ perturbation operator and $\Delta E = E(\pi) - E(\sigma)$. If $\Delta E = 0$, then $\delta E = P(\pi\sigma)$ and if $\Delta E \gg P(\pi\sigma)$ (the case most often encountered), then Eqn. (1) becomes

$$\delta E = \pm P^2(\pi\sigma) / \Delta E. \quad (2)$$

Since $P(\pi\sigma) = a(\pi)a(\sigma)P$, where $a(\pi)$ and $a(\sigma)$ are respectively the p_z orbital coefficients of the carbon atom of the fragment Y and of the E atom in the σ orbital of the E–C bond while P is the perturbation integral of the $C(p_z)-E(p_z)$ bond, Eqn. (2) can be written in the form

$$\delta E = \pm a^2(\pi)a^2(\sigma)P^2 / \Delta E. \quad (3)$$

The perturbation integral in Eqn. (3) is related to the overlap integral $S(\sigma\pi)$ by the expression

$$P = -KS(\sigma\pi)[I(\sigma) + I(\pi)] / 2,$$

where I is the ionisation potential of the σ and π orbitals.

In hyperconjugation of the σ,π and σ,π^* types, the substituents $E(CH_3)_3$ behave as resonance electron donors in relation to the π system of the fragment Y, which results in further (in relation to that induced by the inductive effect) increase in the energy of the frontier orbitals, the latter acquiring a mixed character. It is significant that the degree of mixing of the σ,π^* type is smaller than that of the σ,π type owing to the smaller value of the overlap integral $S(\sigma, \pi^*)$ and the larger value of $\Delta E = E(\pi^*) - E(\sigma)$ compared with $\Delta E = E(\pi) - E(\sigma)$. Therefore conjugation of the type considered results in a greater destabilisation of the highest occupied molecular orbital (HOMO) compared with the lowest unoccupied molecular orbital (LUMO).

The ideas described above in connection with the consideration of stages A and B are sufficient, after slight modification, for the complete description of the electronic effects of the substituents in the benzyl derivatives $C_6H_5CH_2E(CH_3)_3$ and allyl derivatives $CH_2=CHCH_2E(CH_3)_3$, but are fundamentally inadequate for further analysis of compounds of the type $C_6H_5E(CH_3)_3$ and $CH_2=CHE(CH_3)_3$, since the electron-accepting properties of the substituents $E(CH_3)_3$ in relation to the π system cannot be explained on their basis. A constructive basis for the understanding of the causes of the above electron-accepting properties is the concept combining the hypotheses of the *nd* orbitals and antibonding σ^* orbitals. Using this concept as a guide, we shall consider stages C and D.

Stage C. The mixing of the $\sigma^*(E-C)$ orbitals of the substituent $E(CH_3)_3$ with the *nd* orbitals of the atom E. Although this stage was taken into account in the qualitative schemes for the consideration of the electron-accepting properties of $E(CH_3)_3$ as early as 20 years ago,[13,79] the authors of certain publications (see, for example, Giordan and Moore[68,69]) devoted to it unjustifiably little attention or actually neglected it. On the other hand, a number of considerations support the involvement of *nd* orbitals in conjugation. Thus it follows from Eqns. (1)–(3) that, in the absence of symmetry prohibition, the mixing of orbitals is greater, other conditions being equal, the smaller the difference between their energies. On the basis of this principle, Giordan and Moore[69] explained the electron-accepting properties of the substituents $E(CH_3)_3$ exclusively by the hyperconjugation interaction of the $\sigma^*(E-C)$ orbtials with the π^* orbitals of benzene, ethylene, and acetylene, whereas for thiophene and furan derivatives[70] the mixing of the $\sigma^*(E-C)$ and *nd* orbitals was not ruled out. Nevertheless, on the basis of the above principle, a real possibility of the mixing of the $\sigma^*(E-C)$ orbitals not only with the π^* orbitals of the fragment Y but also with the atomic *nd* orbitals of E for all the π systems enumerated follows from a simple consideration of the orbital energies.

Fig. 2 presents the experimental energies of the $\sigma^*(E-C)$ [68] and π^* [69,70] orbitals in the compounds YEX_3 determined by electronic transmittance spectroscopy. The energy of the unoccupied *nd* orbitals of the atom E (for the silicon atom as an example) was estimated by two procedures. Calcualtions by the Hartree–Fock self-consistent field method yield about –2 eV for the energy of the 3*d* orbitals of the silicon atom.[80–82] According to approximate estimates using a series of spectroscopic data for unsaturated compounds containing the $Si(CH_3)_3$ substituents, the 3*d* orbitals of silicon have a higher energy than the π^* orbitals of the fragment Y;[83] this view gained fairly wide currency (see, for example, Refs. 41, 50, and 79). Thus the orbitals $\sigma^*(E-C)$, *nd*, and π^* were found to have comparatively similar energies. There exists therefore a real possibility of the mixing of the $\sigma^*(E-C)$ orbitals with both π^* and *nd* orbitals. Following Pitt,[13] we shall arbitrarily select the mixing of $\sigma^*(E-C)$ and *nd* orbitals as the initial stage of the interaction between the three orbtials. This results in the formation of two mixed orbitals—with greater and smaller (presented in Fig. 1 and designated by *d*, σ^*) energies. Thus an unoccupied orbital arises in stage C with a lower energy than those of the $\sigma^*(E-C)$ and *nd* orbitals of the atoms E.

Certain comments must be made concerning the mixing of the orbitals in stage C. Fig. 2 presents only approximate energies of the orbitals $\sigma^*(E-C)$ and π^*. The exact energies of the initial orbitals

σ*(E–C) and π* could be obtained only after taking into account the influence of the inductive effect. Thus, for the calculation of the energy $E(\sigma^*)$, it is necessary to know the form of the dependence of $E(\sigma^*)$ for the fragment $E(CH_3)_3$ on the inductive effect of the substituent Y in $(CH_3)_3EY$ (Y = C_6H_5, $CH_2=CH$, etc.) while for the calculation of $E(\pi^*)$ account must be taken of the inductive effect of of $E(CH_3)_3$ and Y. Such calculations are so far lacking in the literature.

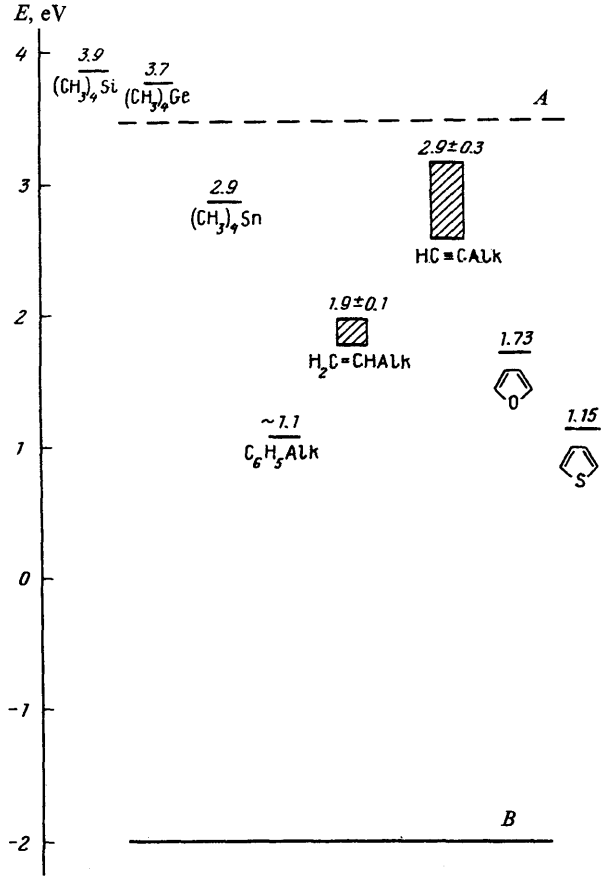


Figure 2. The energies of the σ*(E–C) orbitals in $E(CH_3)_4$,[68] the π* orbitals in certain unsaturated compounds,[69,70] and the unoccupied 3*d* orbtials of the silicon atom [(*A*) approximate estimate;[83] (*B*) calculated values[80–82]].

The problem of the exact energies of the *nd* orbitals *E*(*d*) is even more complex. This problem, as well as a number of others arising in the study of conjugation involving *nd* orbitals (their energy in isolated atoms E and molecules, the size and amplitude of *nd* orbtials, the charge on the atom E and the population, polarisation corrections in quantum-chemical calculations or real involvement of *nd* orbitals in bond formation) have been examined in a number of reviews.[41,42,46,49,51,84] Here we shall merely note yet again the absence of fundamental prohibition of the involvement of the *nd* orbitals of the atoms E in conjugation from the standpoint of quantum chemistry, but the results of even non-empirical calculations depend greatly on the choice of the basis set (see, for example, Res. 46, 85–88). Therefore, in estimating the correctness of such results, it is essential to exercise reasonable scepticism and caution.

One should also note that the π-bonds, formed with participation of the *nd* orbitals of the atoms E, are not analogous to those existing in unsaturated organic compounds.[84] As frequently mentioned in reviews,[3,6,36,42] the involvement of *nd* orbitals is only partial. Under these conditions, one cannot as yet estimate reliably the contributions of the atomic *nd* orbitals to the molecular orbitals. The self-evident nature of this assertion can be seen if only from the consideration of stage C above and the discussion of the data presented in Fig. 2.

Stage D. The mixing of the orbitals *d*,σ* and σ,π* formed in stages C and B, involving the formation of two new orbitals—with greater and lower (presented in Fig. 1 and designated by *d*,π*) energies. Similarly, on mixing of the *d*,π* and σ,π* orbitals, two orbitals are also produced [the orbital with a smaller energy (HOMO) is presented in Fig. 1 and is designated by *d*,π]. The orbital *d*,π* is stabilised i.e. its energy is reduced compared with the energy $E(\sigma,\pi^*)$ to a much greater extent than for the orbital *d*,π; this is caused by the sharp difference between the energies of the π* and π orbitals (10–15 eV [8,68–70]).

It follows from the foregoing that the orbtials σ*(E–C), *nd*, and π* are comparatively close to one another although they are not rigorously defined as regards energy. Therefore, the differentiation of stages C and D in the mixing of these three orbitals is purely arbitrary.

It follows from the consideration of stages C and D that attempts at an *a priori* quantum-chemical estimation of the relative role of each of them can at best claim to yield merely qualitative conclusions. At the same time, as quantum-chemical methods have improved, data have accumulated for the simplest organoelemental compounds, which can, on the one hand, be interpreted, at least in principle, on the basis of the scheme presented above and, on the other, they can serve as a justification of the individual stages (especially B) of this scheme. These data will be invoked in the third Section of the review together with the consideration of experimental studies in stages A–D and on conjugation as a whole.

III. Comparison of theoretical ideas with experiment

The consideration of the relevant data in this review is based predominantly on the methodology involving the separation of electronic effects adopted in physical organic chemistry, whose principles have been described in Section II. The separate stages of the intramolecular interactions with the substituents EX_3 and CH_2EX_3 as well as groups with a more complex structure having centres of not only π type but also *n* type are analysed. The arbitrary nature of the separation of the overall electronic effect of the above substituent into individual stages was considered in Section II.

1. The inductive effect

The differentiation of the inductive component ΔG_I from the overall electronic effect ΔG of organoelemental substituents constitutes, generally speaking, a standard procedure. Taking into

account certain limitations (see Section II as well as literature data[6,10]), the constants σ_I and their derivatives, tabulated, for example, by Egorochkin and Razuvaev[6] and Hansch et al.,[21] serve as a universal characteristic of the $\pm I$ effect. The possibile presence of a variable hyperconjugation component (σ,σ conjugation) constitutes in this connection a still inadequately elucidated problem. Although the contribution of this component is as a rule insignificant (except in special cases, for example, in compounds with chains of highly polarisable atoms E [3]), it can nevertheless depend on the type of centre to which the substituent is linked.[6]

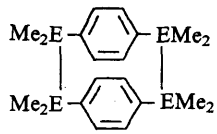
2. Hyperconjugation of the σ,π and σ,π^* type

This type of hyperconjugation has been studied in especially great detail (with the aid of physical and chemical methods) in the compounds YCH_2EX_3, where Y = phenyl, vinyl, ethynyl, furyl, thienyl, etc. In a number of reviews[3,6,10,55,89,90] and subsequent communications,[25,91–96] it was established that the substituents $CH_2E(CH_3)_3$ always behave as resonance electron donors in relation to the π systems of the fragment Y. This is indicated, in particular, by the negative values of their resonance constants σ_R^0, σ_R, and σ_R^+ as quantitative characteristics of conjugation respectively in the electronic ground state (NMR, IR spectroscopy), under the conditions of direct polar conjugation (IR spectroscopy of the hydrogen bond),[24] and in the presence of a positive charge on the π system (UV spectroscopy of charge-transfer complexes). The frontier orbitals formed on interaction of CH_2EX_3 with the π system of Y are of the σ,π and σ,π^* type. The HOMO energy increases (according to quantum-chemical calculations and photoelectron spectroscopic data) under the influence of the substituents $CH_2E(CH_3)_3$, while the LUMO energy is less sensitive to the effect of substituent.

With an increase in the atomic number of E (other conditions being equal), an enhancement of the σ,π conjugation is observed. Hyperconjugation also increases following the appearance of a positive charge on the π system. Thus the negative values of the resonance constants of the substituent $CH_2E(CH_3)_3$ increase in the sequence $\sigma_R^0 < \sigma_R < \sigma_R^+$. The magnitude of the effect of the σ,π conjugation depends on the nature of the groups X in CH_2EX_3 and on the substituent Z bound to the π system. The enhancement of the electron-accepting properties of X in CH_2EX_3 is accompanied by a weakening of the σ,π conjugation, whereas under conditions favouring direct polar conjugation between the substituents $CH_2E(CH_3)_3$ and Z via the π system [for example in the case of $(CH_3)_3SnCH_2C{\equiv}CSi(CH_3)_3$ [97]], σ,π conjugation intensifies with enhancement of the electron-accepting properties of Z.

In organotin and organolead compounds, especially in the presence of a positive charge on the π system, σ,π conjugation is a powerful resonance electron-donating effect, which exerts a strong influence on the reactivity of these compounds.[2,54]

Hyperconjugation of the σ,π and σ,π^* type depends significantly on stereoelectronic effects. The maximum σ,π conjugation therefore occurs only under favourable steric conditions, which has been considered in detail in a number of studies.[3,10,36,55,89,95] In σ,π conjugation with the π systems of a double bond, a triple bond, and benzene and naphthalene rings, substituents containing the E–E′ groups also participate. Here E and E′ represent different combinations of identical or different elements (Si, Ge, Sn).[3,55,98–101] Thus, as a consequence of the parallel disposition of the E–E bridges and the p_π ring orbitals, the σ,π conjugation in cyclophanes of the type



(E = Si, Ge)

is stronger than in the corresponding acylclic compounds.[102] On the other hand, the σ,π conjugation with participation of the groups $-Si-Si(CH_3)_3$ constitutes an appreciably weaker resonance electron-donating effect than the conjugation involving the substituent $CH_2Si(CH_3)_3$.[3] This finding can be explained by the existence in the disilyl substituent of two opposite resonance effects — the electron-donating effect [σ,π conjugation is apparently stronger than in the substituent $CH_2Si(CH_3)_3$ because of the greater polarisability of the Si–Si bond compared with Si–C [93]] and the electron-accepting effect [d,π conjugation, which is absent in the $CH_3Si(CH_3)_3$ group].[3]

According to the results obtained by different methods,[6,41,42,50,51] the substituents SiX_3 containing any organic groups X exert an overall resonance electron-accepting effect in relation to the π system, which follows, for example, from the positive resonance constants σ_R.[6,21] An alternative interpretation of the resonance effects of the substituents SiX_3 is formally permissible: either (a) these substituents manifest only electron-accepting properties or (b) the overall effect includes a weaker electron-donating component (σ,π conjugation) and a stronger electron-accepting component. Evidence in support of the second view, obtained in a general theoretical study (see Section II as well as the literature[103–105]) until recently had not received convincing experimental confirmation. Unambiguous proof of the presence of an electron-donating component (σ,π conjugation) in the overall resonance effect of the substituents EX_3 (E = Si, Ge, Sn, Pb) and $E'X_n$ (E′ = Hg, B, P, As, Sb, Bi) was obtained in the joint analysis of the constants σ_p abd σ_p^+ of phenyl derivatives with the above substituents and the benzyl derivatives $C_6H_5CH_{3-n}[E(CH_3)_3]_n$.[93] The principal factor determining the enhancement of the σ,π conjugation following the appearance of a positive charge on the aromatic ring in both phenyl and benzyl series is the polarisability of the chemical bonds of the substituent.[93] Under these conditions, the hyperconjugation is enhanced more the greater the atomic number of E in EX_3 and $CH_{3-n}[E(CH_3)_3]_n$.[93]

Yet another feature of the σ,π conjugation is its dependence on the type of the π system to which the organoelement fragment is linked. Thus systematic studies by different methods of benzene and acetylene derivatives with different substituents $EAlk_3$ [6,24,25,57,89,97,106] established, in particular, that the enhancement of the σ,π conjugation on passing from substituted benzenes to acetylenes is greater the higher the atomic number of the element E in the substituent $EAlk_3$ attached to the π system.[24] The idea that the σ,π conjugation between $E(CH_3)_3$ and π systems intensifies with increase in the atomic number E was also confirmed in other studies.[107–109]

Semiempirical quantum-chemical methods are used in the vast majority of cases in studies on σ,π conjugation, so that the conclusions reached with their aid are only qualitative. The existence of both electron-donating (σ,π conjugation) and electron-accepting effects in the substituents EX_3 and of only hyperconjugation in CH_2EX_3 has been established for benzene,[13,103,104,110] ethylene,[10,52,88,95,111,112] acetylene,[13,52,89,113,114] and furan[105,115]

derivatives and also for π systems of more complex structure.[116,117] Non-empirical calculations for vinylsilanes and their radical-cations,[118,119] silylacetylenes,[120,121] stannylacetylenes,[122] as well as the cyclopentadienyl[123] and naphthyl[101] derivatives of silicon provide better evidence. The joint application of modern quantum chemistry and photoelectron spectroscopy proved especially effective.[8,89]

3. Hyperconjugation of the σ,*n* type

The development of ideas about the dual nature of the overall resonance effect of substituents EX_3 in relation to π systems, which includes electron-donating (σ,π conjugation enhanced as E varies in the sequence Si < Ge < Sn) and electron-accepting components, was accompanied by the accumulation of facts concerning the effects of these substituents in relation to the groups Y comprising atoms with lone pairs in the α-position relative to the E atom. Pauling's initial concept,[48] according to which the substituents EX_3 exhibit exclusively an electron-accepting resonance effect in relation to Y ($d_\pi-p_\pi$ conjugation) was subsequently given a deeper content. This was based on numerous data obtained by various physical and chemical methods, which, although to a large extent indirect, nevertheless generated a consistent system of views concerning the presence of not only electron-accepting but also of electron-donating properties in the substituents $E(CH_3)_{3-n}X_n$ linked to Y.[3,124-128]

Initially (see, for exmaple, Egorochkin and co-workers[3,129]) the electron-donating properties of the substituents in the H−C−E−Y fragments were interpreted as the σ,σ conjugation of the H−C and E−Y bonds (like the conjugation of the E−C bonds in compounds with E−C−C−E atomic groups[130]). However, such interpretation is doubtful bearing in mind the weaker hyperconjugation in the H_3C-Si fragments than in H_3C-C.[131] On the basis of orbital approaches, the treatment of the resonance electron-donating properties of $E(CH_3)_3$ relative to Y as the σ,*n* mixing of the initial unperturbed σ orbitals of E−C with the *n* orbitals of the lone pairs of Y, which have a higher energy, appears more adequate.

The same procedures of the perturbation theory are applicable to the consideration of the σ,*n* conjugation as for σ,π conjugation. The rigorous allowance for the influence of the inductive effect on the energies of the initial orbitals gives rise to an appreciable complication under these conditions (see, for example, Baidin et al.[132]). Only qualitative estimates of the σ, *n* conjugation in the compounds $(CH_3)_3EX$ (X = OAlk, SAlk, Cl, Br) and $[(CH_3)_3E]_2X$ (X = O, S) are therefore available at the present time.[133-135] The effect of σ,*n* conjugation intensifies as E and X are varied in the sequences Si < Ge < Sn < Pb, S < O, and Br < Cl. On passing from the compounds $(CH_3)_3EX$ to $[(CH_3)_3E]_2X$, the σ,*n* conjugation is enhanced for X = O and is weakened for X = S, which is due to stereoelectronic factors determining the directions assumed in space by the interacting orbitals.[134]

Thus the effects of the σ,π and σ,*n* conjugation of the substituents $E(CH_3)_3$ linked to π or *n* systems intensify with increase in the atomic number of the E atom and depend on the type of each of the systems indicated. The effect of the σ,*n* conjugation in $(CH_3)_3EY$ intensifies as the atomic nubmer of the atoms with the lone pair in the α-position relative to the E atom diminishes. Within the framework of the phyiscal-organic chemical concept of the separation of the effects of substituents, adopted in this review, these facts have provided in recent years much evidence in support of the idea of the resonance effects of the groups $E(CH_3)_3$ as effects combining electron-donating and electron-accepting properties.

After the rigorous allowance for the inductive effects of the groups $E(CH_3)_3$, it was shown that the resonance electron-accepting effect of these groups is not enhanced but is actually weakened with increase in the atomic number of the E atoms, in contrast to σ,π and σ,*n* conjugation. On the other hand, both σ,*n* conjugation and the resonance electron-accepting effect weaken with increase in the atomic number of the Group VI or VII elements linked to E.[6,42,133,135] Thus the overall resonance effect of the groups $E(CH_3)_3$ relative to centres of the π and *n* type, representing the result of the combination of two opposed components, is a typical electron-accepting effect for organosilicon compound and a weak electron-accepting effect (and sometimes an electron-donating effect) for organotin compounds. In the case of organogermanium compounds and also in systems with weak resonance interactions, situations frequently arise which are difficult to predict. Therefore in the analysis of experimental data in early reviews[41,49-51] the interpretation of the overall resonance effect (traditionally given the term $d_\pi-p_\pi$ conjugation) on the assumption that $E(CH_3)_3$ has electron-accepting properties only encountered a number of difficulties. It is essential to note also the significantly different sensitivities of the research methods and indicator centres to the influence of resonance effects to which special attention has been drawn recently.[10]

The idea of dual donor−acceptor resonance properties of the substituent $E(CH_3)_3$ examined above was confirmed by non-empirical quantum-chemical calculations for the compounds $(CH_3)_{4-n}SnCl_n$ (n = 1, 2, 3), $[Sn(CH_3)_3]_2X$ and $[(CH_3)_2SnX]_3$ (X = S, Se).[136,137] The fragments $CH_3-\overset{|}{\underset{|}{Sn}}-$ exhibit in relation to chlorine atoms both resonance electron-accepting properties (the involvement of 5*d* orbitals of Sn in bonding) and electron-donating properties [σ,*n* mixing of the σ(Sn−C) orbitals and *n* orbitals of the lone pair of chlorine]. σ,*n* conjugation apparently predominates in the reonance interaction between the $Sn(CH_3)_3$ group and the sulphur (selenium) atom, which agrees, in particular, with the present author's experimental data.[133,134] The same type of conjugation is evidently responsible for the low values of the first ionisation potentials of compounds with the Si−C−S groups.[138,139]

Thus experimental data and non-empirical quantum-chemical calculations indicate, in conformity with the theoretical ideas described in Section II, a dual nature of the resonance interactions of substituents of the $E(CH_3)_3$ type with π and *n* systems. The electron-donating properties of these substituents are caused by their involvement in σ,π conjugation, σ,π* conjugation, and σ,*n* conjugation and possibly also in other versions of hyperconjugation, which have so far been scarcely investigated.

We shall now analyse the question to what extent experimental studies on the resonance electron-accepting properties of $E(CH_3)_3$ agree with the general approach to this problem (stages C and D in Section II of the review).

4. Resonance electron-accepting properties of the substituents $E(CH_3)_3$

We shall consider the simplest case, that of the compound $(CH_3)_3EY$, where only one group Y, having π electrons or a lone pair in the α-position relative to E, is linked to the E atom. In this situation, the overall electron-accepting effect of E in relation to Y diminishes with increase in the atomic number of the elements E

(i.e. from Si to Ge and Sn) and Y (in the sequences N > P, O > S > Se, and F > Cl > Br > I). The relative capacity of the substituents Y for conjugation with silicon or germanium atoms (i.e. the overall electron-donating effect of the conjugation of Y with E) is correlated with the resonance constants σ_R of the groups Y. These conclusions were reached from data obtained by NMR and IR spectroscopy.[6,42]

Here one should note that the energies of the initial orbitals E(E−C), $E(\pi)$, and $E(n)$, which are extremely significant for σ,π and σ,n conjugation [see Eqns. (1)−(3)] are not explicitly decisive for the resonance electron-accepting effect (designated as $d,\bar{\pi}$ or d,n conjugation in Section II).[134] The effects of the σ,n and d,n conjugation (as well as σ,π and d,π conjugation) can depend in different ways on the type of substituents X in X_3EY.

The influence of X on d,n conjugation for E = Si and Ge has been studied in fair detail.[42] The enhancement of electron-accepting properties increases the effective positive charge on E,[41,49,84,140] which induces, according to a widely held hypothesis,[41,42,51] the contraction of the diffuse unoccupied *nd* orbitals of E and hence improves the conditions for d,π or d,n conjugation in the molecule. Linear relations are known between experimental quantities characterising the charge on the E atom and the resonance electron-accepting effect of EX_3 (i.e. d,π or d,n conjugation under conditions where it clearly predominates over σ,π or σ,n conjugation): variation of the charge on E ensures the variation of the resonance electron-accepting properties of ER_3 within wide limits.[42]

On the other hand, the dependence of σ,π or σ,n conjugation on the nature of X in X_3EY is extremely complex. The enhancement of the electron-accepting properties of X (i.e. an increase in the charge on E) should increase the absolute energies E(E−C), $E(\pi)$, and $E(n)$. However, there are no grounds for the expectation that the form of the dependences of E(E−C), $E(\pi)$, and $E(n)$ on the charge on E is the same. Therefore, the relation between the charge on E and the values of ΔE [Eqns. (1)−(3)] as well as other quantities characterising the σ,π and σ,n conjugation is virtually unpredictable.[134]

The effects of σ,π and σ,n conjugation are determined by the interaction of the orbitals with the energies $E(\pi)$, $E(n)$, and E(E−C) leading to the formation of the HOMO. Therefore the methods based on the analysis of the orbital characteristics (photoelectron spectroscopy, UV spectroscopy of charge-transfer complexes[3,6]) are most effective for the study of hypoconjugation. The effects of d,π and d,n conjugation are maximum for E = Si and depend greatly on the charge on E; the π- or n-donor properties relative to $E(CH_3)_3$ (E = Si, Ge) are determined by the σ_R constants of Y.[6,42] Therefore the effective and sensitive methods for the study of d,π and d,n conjugation are based on the analysis of charge characteristics, for example, the intensities of the E−H (E = Si, Ge) bands in the IR spectra of Alk_2HEY (the effects of σ,π and σ,n conjugation are then comparatively small, i.e. the electron-donating component of the overall resonance effect of Alk_2HE relative to Y in Alk_2HEY is small). It must be emphasised that d,π and d,n conjugation undoubtedly affects the energy of HOMO and other orbitals (see, Section II and Fig. 1), but such dependence is complex, since the antibonding σ^* orbitals of E−C also participate in conjugation of this type together with *nd* and π (or n) orbitals [this was taken into account more than 20 years ago (see, for example, Pitt et al.[79])]. As regards the *nd* orbitals of the E atoms, they are stabilised under the influence of the electronegative substituents linked to E, i.e. their energy diminishes.[41,49,81,84] This last finding justifies the assumption that the *nd* orbitals are located between the π and π^* orbitals, i.e. their energy approaches that of the n orbitals; ultimately this should enhance d,π and d,n conjugation.

Thus all the foregoing considerations concerning the complexity of the resonance electron-accepting properties of the groups $E(CH_3)_3$ cast doubt on the legitimacy of the simplified view on these properties. Such a simplified approach can be encountered in many studies during the last decade (typical examples can be found in Refs. 65, 68−71, and 141 and in reviews[2,11,12,56]). In these studies, sometimes regarded as an alternative to the *nd* orbital hypothesis, the resonance electron-accepting properties of $E(CH_3)_3$ relative to Y are explained exclusively by the mixing of the antibonding σ^*(E−C) orbitals with π or n orbitals of Y. The only argument in support of this choice is the smallness of the *nd* orbital contributions according to the results of certain non-empirical quantum-chemical calculations.[60−63,65,72,141,142]

However, this argument is open to objection. Firstly, there have been non-empirical calculations[136,143−145] in which the involvement of the *nd* orbitals was found to be significant not only in silicon but also in tin derivatives. Secondly, in quantum-chemical studies[63,72,87,142] involving a rigorous approach to the problem of conjugation the necessity for further investigations for a correct assessment of the role of *nd* orbitals has been pointed out. The importance of these studies has been noted in a review.[46] Thirdly, even in non-empirical calculations for resonance interactions between systems and organic substituents not containing the atoms of Third Period elements, the results depend on the choice of the basis sets.[106] The current interest of this problem increases greatly on passing from organic[88] to organoelement[46,77,86,87] compounds. In non-empirical calculations for the latter, the authors of many investigations have noted an improvement of the agreement between the calculated and experimental data when *d* functions are included in the basis set.

For the reasons indicated, there are at present no well-founded grounds for the simplification of the idea, examined in Section II of the present review, that the resonance electron-accepting effects of the substituents $E(CH_3)_3$ relative to centres of the π or n type are complex. Therefore, in particular the overall resonance effect of the substituents $E(CH_3)_3$ on the HOMO and LUMO energies in benzene, ethylene, acetylene, thiophene, and furan derivatives[68−70] and on the HOMO energy in silyl ethers and siloxanes[141−146] as well as the effect of SiH_3 on the ionisation potentials of the lone pairs in $Y(SiH_3)_n$ (Y = N, O, S, and Se) [71] can be interpreted with greater justification not on the basis of hyperconjugation interactions with participation of the σ^*(E−C) and σ^*(Si−H) orbitals but as a result of the simultaneous operation of the electron-donating effect of the σ,π (or σ,π^*) as well as σ,n conjugation and the electron-accepting effect of the d,π (or d,π^*) as well as d,n conjugation. The large Si−O−C bond angles in compounds of the type $(CH_3)_3Si-O-Aryl$ and $(CH_3)_2ClSi-O-Aryl$ (where the oxygen atom has long been known[42] to participate in resonance interactions with both substituents) also cannot be accounted for within the framework of the concept of the electron-accepting properties of the Si−C and Si−Cl σ^* orbitals,[147] which casts doubt on the application of this concept by Reed et al.[65] to compounds with a related structure.

5. Electronic effects of the substituents $E(CH_3)_{3-n}X_n$

It was shown above that the substituents $E(CH_3)_3$ in the simple compounds $(CH_3)_3EY$ exhibit, together with the electron-donating inductive $+I$ effect in relation to π or n systems, also resonance electron-donating (σ,π or σ,n conjugation intensifies in the sequence Si < Ge < Sn < Pb) and electron-accepting (d,π and d,n conjugation weakens in the sequence Si > Ge > Sn) properties. We shall now consider the more complex systems $(CH_3)_{3-n}X_nEY$, where two or three groups X and Y having π electrons or lone pairs in the α-position relative to E, are linked to the latter.

The enhancement of the electron-accepting properties of X and/or the increase in the number of groups X is accompanied by a change in the sign and increase in magnitude of the I effect of $E(CH_3)_{3-n}X_n$ compared with $E(CH_3)_3$. Thus, for any element E, the groups EHal are typical $-I$ inductive σ-acceptors.[6,21]

The resonance interactions between $E(CH_3)_{3-n}X_n$ and Y are distinguished by a greater variety [compared with those in $(CH_3)_3EY$], since they depend not only on the nature of E and Y but also on the type and number of the groups X. Only the simplest versions of these interactions have been investigated hitherto. We shall now consider the main ideas formulated in this field.

1. Judging from the values of the constants σ_R, the overall resonance effect of the substituents $(CH_3)_{3-n}X_nE$ in benzene, ethylene, and acetylene derivatives intensifies with enhancement of the electron-accepting properties of the groups X and their number.[6] In the study of silane and germane derivatives $(CH_3)_{3-n}X_nEH$ by IR spectroscopy, where the situation at the indicator centre (E–H bonds) is determined predominantly by the charge characteristics (see Section III. 4), it was shown that the overall resonance interactions in the EX_n fragments are regulated by the effective charge on the silicon or germanium atom, which depends in its turn on the inductive and mesomeric effects of X.[42,148,149] In the analysis of the integral intensities of the E–H bands in the IR spectra, which was especially sensitive to the effect of conjugation, linear relations were established between the overall resonance effect in the EX_n fragments and the positive charge on the E atom (Si or Ge).[42,150]

2. The groups $E(CH_3)_{3-n}X_n$ for any X possess not only an electron-accepting component (which decreases in the sequence Si > Ge > Sn) but also an electron-donating component of the overall resonance effect. Unambiguous proof of the existence of the electron-donating component has been obtained both for the substituents $E(CH_3)_3$ (see Section III. 2) and for $E(CH_3)_{3-n}X_n$ in the analysis of the constants σ_p and σ_p^+ characterising the overall electronic effect (inductive and resonance) respectively in the absence and presence of a positive charge on the benzene ring to which these substituents are linked.[93]

The difference between the constants σ_p and σ_p^+ is caused by the enhancement of the electron-donating component (i.e. σ,π conjugation) of the overall resonance effect when a charge appears on the ring. Such enhancement is determined by the polarisability of the E–C and E–X bonds in $E(CH_3)_{3-n}X_n$. Thus the SiF_3 acceptor ($\sigma_p = +0.66$), which is strongest among silicon-containing acceptors, does not lose its electron-accepting properties appreciably in the presence of a positive charge on the ring in $C_6H_5SiF_3$ because of the low polarisability of the Si–F bonds. However, the electron-accepting properties of the substituent $GeCl_3$ ($\sigma_p = +0.79$) diminish sharply ($\sigma_p^+ = +0.33$) owing to the high polarisability of the Ge–Cl bonds.

Other features of the σ,π conjugation with participation of the groups $E(CH_3)_{3-n}X_n$, for example the enhancement of the effect, other conditions being equal, in the sequence Si < Ge < Sn, have been examined in detail.[6,93] Although the ratio of the resonance electron-donating and electron-accepting properties of these substituents, bound to the benzene ring, varies within wide limits as a function of the type and number of the groups X in $E(CH_3)_{3-n}X_n$ (the values of σ_p and σ_p^+ can differ not only in magnitude but also in sign), the electron-accepting resonance effect predominates in the groups $EHal_3$.[6,21,104] This predominance evidently persists also in those cases where the groups $EHal_3$ are linked to other reaction centres, for example to a double bond.[151] The strong resonance electron-accepting properties of the $SiCl_3$ group at the iron atom in $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiCl_3$ are caused, according to the authors,[152] by both the antibonding σ^*(Si–Cl) orbitals and the d orbitals of silicon.

The electronic effects of the substituents $E(CH_3)_{3-n}X_n$ with groups X of the same type were examined above. If the atoms X or X and Y, having lone pairs in the α-position relative to E, are of different types in $(CH_3)_{3-n}X_nEY$, then an additional conjugation channel arises in the molecule. In compounds with the O–E–Cl and N–E–Cl fragments, the occurrence of additional resonance interactions can be observed by NQR [3,153–155] and IR spectroscopic[3,51,156] methods.

Initially, such interactions were established in carbon compounds with F–C–Cl [157] and X–C–Cl (X has a lone pair in the α-position relative to C)[158] groups and were explained by σ,p conjugation.[157] A modern interpretation of this effect, close in its significance to that of Lucken,[157] in the X–A–Y (A = Be, Mg, B, Al, C, N, P, O, S) or X–O–Y systems is based on the idea of the n,σ^* interaction (negative hyperconjugation) of the lone pair of the atom X with electron-accepting σ^*(A–Y) [7,9,64,65] or σ^*(E–Y) orbitals.[7,64,65]

The significant role of n,σ^* conjugation is indicated by quantum-chemical[7,9,64,65] and experimental studies using indicator centres sensitive to charge[3] and especially orbital interactions.[7,9,64,77,159] In view of the appreciable influence of the n,σ^* interaction in silicon, phosphorus, and sulphur compounds and the less definite situation involving nd orbitals, the contributions of the latter to conjugation have been altogether denied in certain quantum-chemical studies[64,65,160] or are believed to be relatively insignificant. However, this view appears to be insufficiently supported by arguments, in view of the simplification of the complex pattern of electronic effects, for the following reasons.

Firstly, the effect of n,σ^* conjugation cannot serve as an alternative to the nd orbital hypothesis, since it occurs, for example, in carbon and nitrogen compounds,[7,9] while the contribution of the nd orbitals can be neglected *a priori*. Secondly, the ambiguity of the quantum-chemical conclusions concerning the involvement of nd orbitals has already been examined above (see Section III. 4). Nevertheless, we may note that non-empirical calculations for hypervalent compounds indicate an appreciable role of the nd orbitals of phosphorus, sulphur, and chlorine.[77] Thirdly, application of the standard procedure[20,22,31,158] adopted in the interpretation of experimental data[3,153,155,156,161] by the methods of correlation analysis to the separation of electronic effects indicates a significant difference between the resonance interactions in compounds containing X–E–Y fragments with groups X and Y of the same or different types. For X and Y of the same type, the above interactions include the inductive effect as well as d,n and σ,n conjugation. For X and Y of different types, the interpretation

of the experimental data becomes impossible without invoking the idea of the additional effect of n,σ^* conjugation.

IV. Conclusion

The analysis in this review of the available theoretical ideas in the literature concerning conjugation in organic compounds of the silicon-subgroup elements and their comparison with experiment permits a series of general conclusions.

None of the existing theoretical concepts (Pauling's *d*-orbital hypothesis, hyperconjugation as an alternative to this hypothesis, the involvement of the antibonding σ^* orbitals of the E–C or E–X bonds in conjugation), invoked to account for the nature of the resonance π-acceptor properties of the substituents $E(CH_3)_{3-n}X_nE$, where E = Si, Ge, or Sn, withstands criticism both from the standpoint of demonstrating the inadequacy of alternative systems of views and as regards the possibility of an exhaustive interpretation on their basis of the entire set of experimental data accumulated hitherto. The general theoretical concept in which the resonance electron-accepting properties of the groups $E(CH_3)_{3-n}X_n$ are treated from the standpoint of the joint involvement in conjugation of the *nd* orbitals of E and also of the antibonding orbitals $\sigma^*(E-C)$ and/or $\sigma^*(E-X)$ is consistent with experimental data most completely and with least contradiction. The ratio of these two contributions to the overall electron-accepting effect remains, however, obscure and reliable quantum-chemical approaches to its estimation are so far lacking. It has apparently been finally demonstrated merely that the transition of the E atoms to the sp^3d or sp^3d^2 hybridised state does not occur and the involvement of *nd* orbitals constitutes a special case.

Systematic comparative studies on the resonance electron-accepting properties of the groups $E(CH_3)_{3-n}X_n$ in the electronic ground and excited states have not so far been carried out.

Together with electron-accepting properties, the substituents $E(CH_3)_{3-n}X_n$ possess also resonance electron-donating properties in relation to π systems (σ,π conjugation) and groups containing an atom with lone pairs in the α-position relative to E (σ,n conjugation). Whereas the resonance electron-accepting effect is diminished as E is varied in the sequence Si > Ge > Sn, the σ,π- and σ,n-conjugation effects are actually enhanced with increase in the atomic number of E.

The resonance electron-donating and electron-accepting properties of the substituents $E(CH_3)_{3-n}X_n$ are responsible for the significant dependence of the relative contributions of these properties on the type of reaction centre. Therefore the variation of the nature of the latter (for example, the appearance of a positive charge) can lead not only to a change in the overall resonance effect of the substituents but also to a change in its sign. Such inversion of the donor–acceptor properties of the substituents $E(CH_3)_{3-n}X_n$ is of fundamental importance in the study of the reactivities of systems with these groups. It appears that accumulation and systematic treatment of facts and a deeper consideration of the characteristic features of the changes in the donor–acceptor properties of $E(CH_3)_{3-n}X_n$ compared with the behaviour of the substituents $(CH_3)_{3-n}X_nECH_2$, which do not have resonance electron-accepting properties, will make it possible in the future to avoid speculative constructions in the analysis of reactivity. Instead experimentally tested elements of the theory being created will be invoked.

It is essential to note also the fruitfulness of the orbital ideas, which are being used to an increasing extent in the organoelement chemistry of Group IVB elements. A complex organoelement molecule contains as a rule several indicator centres sensitive in different experiments, the application of physical research methods to charge and/or orbital interactions. The accumulation and analysis of such data together with non-empirical quantum-chemical calculations is important for the development of concepts concerning the charge and orbital control of reactions with participation of organoelement compounds and for the more active incorporation of the principle of hard and soft acids and bases in its modern interpretation. In its turn, progress on these lines will promote the improvement of our knowledge about conjugation effects in organic compounds of silicon-subgroup elements.

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