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Spectroscopic Study of the Steric Effects in Organic Compounds of Silicon Subgroup Elements

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The principal theoretical and experimental approaches to the study of the influence of the steric effects of substituents on the properties of organic and organoelemental compounds are examined. The role of these effects in complex formation with participation of organic compounds of silicon subgroup elements and the influence of steric effects on the conjugation in these compounds are analysed.
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I. INTRODUCTION

The idea of a significant role of steric effects in chemistry, apparently put forward for the first time by Mayer,[1] has now undergone an extensive development not only in stereochemistry[2,3] but also in all other branches of chemistry.[4-10] Thus in the study of reactivity the possibility of the approach of the reacting molecules in space is considered to be an important factor determining the barrier to the reaction, i.e. the activation energy.[11,12]

The role of steric effects does not reduce solely to the alteration of the reactivity of the compound by regulating the degree of shielding of the reaction centre on varying the bulk of the substituents adjoining the centre. Another factor is the steric inhibition of resonance, i.e. partial or complete breakdown of the conjugation in the molecule (and hence also a change in its reactivity) after the introduction of bulky substituents into the molecule. Such substituents prevent the steric disposition of atomic fragments necessary for their conjugation with one another. Both the first[2,3,4,7 13,14] and second[15,16] factors have been examined in fair detail for organic compounds. For organoelemental compounds, the existing factual data are not so extensive and have been surveyed to a lesser extent, although there are reviews on the chemistry of phosphorus[17,18] and silicon[19-22] derivatives. At the same time, in organoelemental chemistry steric effects play a more varied role compared with carbon compounds. We shall differentiate three aspects of the influence of steric effects: on the reactivity, on the complex-forming capacity, and on conjugation in organoelemental compounds.

1. The Influence of Steric Effects on Reactivity

Organoelemental and particularly organopolyelemental compounds, containing chains of heteroatoms, possess polar and highly polarisable chemical bonds. Although such compounds are entirely stable thermodynamically, they are distinguished by an enhanced (compared with organic compounds) reactivity. The reactivity of organoelemental compounds varies within very wide limits not only under the influence of the inductive and resonance effects but also (sometimes predominantly) owing to the steric blocking of the reaction centres by bulky substituents. In the literature, including the review literature[6,8,10,19,20,22,23] there exist numerous clear examples of the inter-relation between the reactivity of organoelemental compounds and the steric effects of the substituents. The present review presents only isolated data concerning the influence of steric effects on reactivity and deals particularly with studies designed specifically to reduce the reactivity of organoelemental compounds.

For example, the thermal stability of the compounds $(R_3Sn)_2Hg$ increases significantly on passing from lower alkyl to phenyl substituents and to an even greater extent the trimethylsilylmethyl[24] substituent, which exhibits pronounced steric effects. Similarly, when CH_3 is replaced by C_6H_5 and C_6F_5 in the compounds $(R_3Ge)_2Hg$, which is accompanied by an increased shielding of the mercury atom, their reactivity diminishes and their thermal stability increases.[25] A sharp increase in thermal stability occurs on passing from $[(C_6H_5)_3.Ge]_2M$ (M = Hg or Cd) to $(C_6H_5)_3Ge-M[Ge(C_6H_5)_3]Ni(\eta^5-C_5H_5)-M-[Ge(C_6H_5)_3]Ni(\eta^5-C_5H_5)-M-Ge(C_6H_5)_3$, in which the atoms M are fully shielded by the ligands.[25,26] Yet another example of the influence of steric effects, this time not on the reactivity but on the very possibility of the existence of compounds, is provided by the synthesis of the derivatives $Mes_2Si=SiMes_2$, where Mes = mesityl,[27,28] and $[(CH_3)_3Si=C[OSi(CH_3)_3]R$, where R = $CAlk_3$ or 1-adamantyl,[29,30] with double bonds at the silicon atom. Despite the lack of theoretical prohibition of their existence, compounds of this type had not been isolated under normal conditions as stable species until the investigations of West and Fink[27,28] and Brook and co-workers,[29,30] and were merely detected in low-temperature matrices by means of physical methods or their formation was assumed as intermediates in reactions (see, for example, Gusel'nikov and Nametkin[31]). There is no doubt that, together with the electronic effects of substituents, the steric effects of bulky mesityl, adamantyl, t-butyl, and other substituents are important for the stabilisation of the double bond at the silicon atom.

2. The Influence of Steric Effects on the Complex-Forming Capacity

On passing from organic to organoelemental compounds, the possibilities for the formation of complexes of the donor-acceptor type (DA complexes) is greatly enhanced. Whereas the carbon derivatives R_3C-X (X is an unsaturated group of the type of aryl, alkenyl, naphthyl, etc.) are formed predominantly in complexes with electron acceptors by virtue of the electron-donating properties of the fragments X,[32,33]

two further types of DA complexes are extremely characteristic of organoelemental compounds.[34-37] These are complexes with an increased coordination number of the central element as well as DA complexes in which element–carbon bonds with low ionisation potentials play the role of carriers of the electron-donating properties.

Analysis of the characteristic features of the formation of these three types of DA complexes has shown that in many cases the steric effects play a major role in complex formation. In the general case the steric accessibility of the atom E in organoelemental compounds of the type R_nE (R is an alkyl group or a carbo-functional substituent and n is the oxidation state of the central element E) is determined not only by the size of R but also by the size of E and the length of the E–R bond, i.e. by the distance from the bulky group R to the reaction centre E. Similarly, when an organoelemental compound $R_{n-1}E-C\diagup\diagdown$ participates as an electron donor, by virtue of the fragment $E-C\diagup\diagdown$, in complex formation with an acceptor, then in this instance one must take into account both the dimensions of the given fragment and the steric effects of the substituents R and the atom E in the formation of the DA complex. Finally, in compounds of the silicon subgroup elements R_3C-X for $n = 4$, the steric effects of the R_3E and R_3C substituents apparently do not influence the formation of the DA complexes between the unsaturated groups X and the acceptor molecules (tetracyanoethylene, iodine, etc.).[38,39]

For compounds with several bulky organoelemental substituents at the unsaturated group X (for example, in the benzene ring or at the double bond), the influence of the steric effects of the substituents becomes comparable or even greater than their inductive and resonance influences.[40-42] A characteristic feature of DA complexes, which follows both from a theoretical study by quantum-chemical methods and from experimental data (see the relevant reviews[13,32-34]), is the mutual approach of the donor and acceptor centres of the interacting molecules in the complex to a distance optimal for the DA interaction, which depends on the nature of the given centres. The introduction of bulky substituents into the molecules constituting the DA complex can prevent such approach for purely steric reasons. This steric "inhibition" of the DA interaction is reflected in the spectroscopic and thermodynamic characteristics of the complex.[10,43]

It must be emphasised that the steric effect of substituents in the donor or acceptor molecules in complex formation are to some extent conventional in character. Indeed, with increase of the steric accessibility of the interacting centre in the donor (acceptor) molecule, the steric hindrance to the formation of a DA complex with the acceptor (donor) molecule diminishes even if the latter contains several bulky substituents.

As an example, one may quote the stannylacetylenes $(CH_3)_{3-n}R_nSnC\equiv CR$ with bulky substituents R (t-butyl, etc.), which can hinder the formation of DA complexes via the triple bond.[44] Steric effects are distinctly manifested in the formation of complexes with molecular iodine and become enhanced when the groups R accumulate in the molecule. In contrast to this, the substituents R do not in any way hinder the formation of a hydrogen bond with phenol, i.e. in DA complexes of this type stannylacetylenes do not exhibit the features of sterically hindered systems. The above example emphasises the difficulty of interpreting the experimental data in order to elucidate the characteristics of the influence of steric effects, since the latter are manifested in many instances as a property not of the donor acceptor separately but of the DA complex as a whole.

Generally speaking steric hindrance to the formation of complexes is pre-determined by the structure of the initial donor and acceptor molecules. For this reason, even if the donor (acceptor) centre is sterically blocked by bulky substituents and the acceptor (donor) centre is distinguished by a considerable steric accessibility, then the properties of the DA complex as a whole may be the same as in a system where there is no steric hindrance to complex formation.

Another factor closely related to the complication of the interpretation of steric effects already examined is the possibility of a change in the donor or acceptor properties of the initial components of the DA complexes owing to the steric effects of the variable substituents in their molecules. It is known, especially in organic chemistry,[2,4,7,13,15,45] that the introduction of bulky substituents can entail a weakening of the electronic intermolecular interactions in the molecules of the other species constituting the complex. If the donor or acceptor centre of a component of the DA complex is involved, then, together with the steric hindrance to the mutual approach of the centres, there is a possibility of secondary complications, which exert their influence via the steric effects in the initial components and the donor–acceptor properties of such interacting centres. From the above brief list of the complications introduced by steric effects into the complex-formation process, it already follows that the study of these effects in organoelemental compounds constitutes as a whole an extremely large and varied problem. It is useful to examine initially the influence of steric effects for a narrower range of model systems. There are organic compounds of silicon subgroup elements which have served for a long time as models for the solution of the most important problems in organoelemental chemistry.[42,46,47] The important role of steric effects and conjugation effects in organoelemental chemistry has been demonstrated in the literature in relation to these systems.

3. The Influence of Steric Effects in Conjugation

The problem of the inter-relation of the steric and resonance effects in organoelemental compounds is of independent importance. Indeed, conjugation effects in organoelemental chemistry are distinguished by a greater variety than in the chemistry of carbon. Together with the resonance effects characteristic of organic compounds, the role of hyperconjugation (σ,π-, σ,σ-, and σ,p-conjugation) is sharply enhanced in organoelemental compounds[42] and a conjugation effect arises which is in principle impossible for carbon compounds, namely the so-called $(p-d)\pi$ interaction which is traditionally attributed to the presence of unoccupied *nd* orbitals in the central elements E.[46,47]

It was shown a comparatively long time ago[48,49] and has been subsequently frequently confirmed by means of various methods, including spectroscopic methods (in particular for compounds of the silicon subgroup elements[42,46]), that there is a profound analogy between various conjugation effects. Therefore the magnitude of the effect both in the resonance interactions of the type of π,π- and p,π-conjugation, which are common in organic chemistry, and in the hyper-conjugation effects, which are more specific to organoelemental compounds, depends on the steric disposition of the interacting orbitals.[42] For example, the degree of the σ,π-conjugation (the variety of hyperconjugation which has been most thoroughly investigated) can be regulated within wide limits by varying the stereoelectronic state of the molecule.[23,42,50,51] The presence or absence of a strong resonance effect of the σ,π-conjugation, comparable in magnitude to that of the typical p,π-conjugation in organic compounds, in many instances alters radically the reactivity.[48,49,52]

Without analysing the role of steric effects, it is impossible to study the characteristics of another resonance effect specific to organoelemental compounds of Group IVB elements, namely that of the $(p-d)\pi$ interaction. The steric effects in such interactions are examined in greater detail below. Here we shall mention that the $(p-d)\pi$ interaction is less sensitive to steric effects, by virtue of the characteristic features of the geometry of the *d* orbitals,[47,53,54] than the σ,π-conjugation. Nevertheless, when there are several substituents X (with unshared *p*-electron pairs) at the central atom E (with unoccupied *nd* orbitals), the overall effect of the $(p-d)\pi$ interaction in the molecule due to pure steric effects, which specify the conditions governing the overlap of the interacting p_π and d_π orbitals, is significantly smaller than might have been expected on the assumption that the contributions by each E–X bond are additive.[47,53-55]

Thus there is a close inter-relation between the steric structure of organoelemental compounds, the steric effects of the substituents in their molecules, and the resonance intramolecular interactions. Determination of the characteristic features of this interaction for model compounds of silicon subgroup elements is the second aim of the present review.

Extensive data obtained in studies of the dependence of both the capacity for complex formation of organic compounds of silicon subgroup elements and the conjugation effects in these compounds on steric effects have accumulated in the literature. Despite this, both aims of the review are of current importance, since the available data have been subjected to an inadequate systematic treatment and conclusions reached in many studies are frequently ambiguous and their evidential value is low. The important question of the reliability of given studies devoted to the analysis of the extent to which the electron-donating properties of organic compounds of Group IVB elements are weakened owing to the steric effects of the substituents is fairly complex. Particular attention was therefore devoted in this review to the elucidation of the validity and soundness of the literature data.

II. GENERAL IDEAS CONCERNING STERIC EFFECTS

The aim of this Section of the review is to formulate the general ideas concerning the steric effects of substituents which follow from the existing reviews[3-5,7,8,13,15-17,43,56-59] and other publications of fundamental importance.

It has been emphasised[7] that one of the key postulates is that the set of phenomena combined by the term "steric effects of substituents" must be regarded as a special case of a more general problem, which is the object of conformational analysis.[60] A quantitative theoretical approach to the study of steric effects must therefore be based on the advances in the theory of conformational analysis, i.e. on quantum-chemical calculations of the total energy of the molecule as a function of the angles of rotation, which makes it possible to establish the most stable conformation.

Conformational analysis has led to the accumulation and systematic treatment of experimental data for the potential barriers to internal rotation and for the differences between the free energies of the conformers. Historical surveys of these studies have been published[16,56,58] and reviews of modern data for several thousands of compounds also exist.[3,16,58,59] In many cases the relations between the barriers to rotation and the electronic and steric effects are manifested extremely clearly. Thus the barriers to internal rotation in ethane derivatives (3–20 kcal mol^{-1}) are higher than for ethane itself (3 kcal mol^{-1}) and exhibit a tendency to increase with increase in the bulk of the substituents at the carbon atom.

The spatial removal to a greater distance of the groups involved in free rotation with increase in the length of the chemical bond connecting them lowers the barrier to internal rotation, which follows, for example, from a comparison of the barriers for Cl_3CCCl_3, Cl_3CSiCl_3, and $Cl_3SiSiCl_3$ (respectively ~11, 4.5, and ~1 kcal mol^{-1}); this is also indicated by the fact that the free energy of activation for internal rotation is significantly smaller in $[(CH_3)_3C]_2HSiSiH[C(CH_3)_3]_2$ (13.7 kcal mol^{-1} [61]) than in $[(CH_3)_3C]_2HCCH[C(CH_3)_3]_2$ (23 kcal mol^{-1} [62]) and also by the ratio of the molecular dipole moments of ethane and disilane derivatives.[63]

In compounds of Group IVB elements the type of $E(CH_3)_4$ an increase in the bulk of the atom E in the sequence C, Si, Ge, Sn lowers the barrier to internal rotation from ~4.5 to 2, 1.5, and <1 kcal mol^{-1} respectively.[61]

Important data have been obtained in the study of the barriers to internal rotation in benzene derivatives. The barrier to the internal rotation of the methyl group in toluene, which is almost zero, increases significantly on passing to $C_6H_5SiH_3$, which indicates an increase in the multiplicity of the silicon–phenyl bond due to the $(p-d)\pi$ interaction.[64] In the Ar–X–Ar (X = O, CO, etc.) systems and also in *ortho*-disubstituted biphenyls, structures with the "propeller" rotation of the aromatic rings are produced for steric reasons despite the fact that a planar molecule would have been most favourable for conjugation. It is striking that, with increase in the size of the *ortho*-substituents in halogeno-biphenyls, the dihedral angle steadily increases.

The review literature (see, for example, Refs.3, 16, 58, and 59) presents compilations of data for barriers to internal rotation also in other types of organic compounds. For example, it has been established for esters $R-C(=O)-OR'$ that the difference between the energies of the *cis*- and *trans*-isomers, arising as a result of rotation about the C–O bond, increases with increasing size of the substituents R and R'. At the same time, it follows from literature data that it is frequently impossible to observe a very clear and evident relation between the potential barriers to internal rotation and the conformer energy difference, on the one hand, and the characteristics of the molecular structure and especially the steric influence of the substituents, on the other. Together with experimental studies, computational empirical as well as semiempirical and non-empirical quantum-chemical methods are being developed in conformational analysis.

In the empirical methods the molecule is regarded as a system of interacting atoms.[58] Here five different contributions to the potential energy of the molecule, taking into account the energy of the non-bonding interactions between the atoms as well as the influence of the deformations of the angles and bonds and the electrostatic contribution to such interactions, are distinguished. Although the empirical methods do in fact make it possible to obtain practically important estimates of the potential barriers to internal rotation without resorting to extremely complex calculations, they do not provide a clear understanding of the nature of the barrier.[65]

An improved reliability of the calculations of the barriers to rotation and of the energy differences between the conformers can be achieved by employing semiempirical quantum-mechanical methods. The possibilities of the semi empirical methods have been assessed in two investigations.[58,65] It was found that, despite the importance of the information obtained (for example, for the estimation of the barriers to rotation in a series of compounds with related structures), these methods have limited applicability, because they include a series of empirically determined parameters. The dependence of the result on the suitability of the selected parameters lowers the

objectivity of the semiempirical methods. Non-empirical *ab initio* quantum-chemical methods have therefore been developed to an increasing extent recently for calculations of the potential barriers to internal rotation and of the total energy of the molecule as a function of the angles of rotation.[65] The theoretical principles of conformational analysis should apparently be developed in the course of systematic studies of the principle classes of compounds by non-empirical methods. However, so far this problem is extremely far from solution, in particular because of the high cost of such calculations even for molecules of medium size, the inadequate effectiveness of the computer programmes, and the necessity to employ faster computers for calculations on fairly complex molecules.[65] The application of *ab initio* methods has not so far led to a complete understanding of the nature of the barriers to internal rotation, but it has been shown in many instances that, for the most stable conformation of the molecule, the bond around which internal rotation takes place is characterised by the highest electron density, i.e. exhibits the maximum stability.[65–67]

We shall consider certain calculated quantum-chemical data for organosilicon molecules. Non-empirical calculations carried out in terms of different basis sets, established a significantly lower barrier to inversion at the nitrogen atom in the H_3SiNH_2 molecule than in the ammonia molecule and an increased multiplicity of the silicon–nitrogen bond due to the $(p-d)\pi$ interaction;[68] they confirmed the covalent character of the silicon–oxygen bond under conditions where the Si–O–Si angle in the disiloxane fragment is varied within wide limits;[69] they revealed a preference for a non-planar structure in 5-silylcyclopentadiene (apparently as a consequence of hyperconjugation), in contrast to its carbon analogue.[70]

Semi-empirical calculations have been used more widely for organosilicon compounds in conjunction with several variants of the zero differential overlap—the CNDO and INDO methods. As already mentioned above, the quality of the semiempirical calculations depends on the soundness (or success) of the selection of the computational parameters. A typical example is provided by the attempts to reproduce by the calculations the experimentally established planar structure of trisilylamine $(H_3Si)_3N$. According to Sadimenko et al.,[69] agreement between calculation and experiment has been achieved in only one[71] of the several variants of the calculation. The barrier to rotation in trisilylamine obtained from the calculated data of Rank et al.[72] is too high. The necessity for a critical approach to the results of semiempirical calculations follows, in particular, from the fact that one of the most important features of organosilicon compounds, namely the degree of their $(p-d)\pi$ interaction (for example, in the silicon–nitrogen bond) depends on the molecular geometry.[71,73] Inaccurate information about the geometry obtained from the calculations can therefore lead to incorrect conclusions about the importance of such interaction.

It follows from semiempirical calculations that a change in the conformation of the $H_3SiOSiH_3$ molecule, accompanied by the variation of the Si–O–Si angle, induces not only a change in the energy of the highest occupied molecular orbital but also the inversion of the sequence of orbitals.[74]

It has been established by the CNDO/2 method that the non-bonding Hal...Hal interactions are sharply weakened on passing from CF_4 to CCl_4 and their silicon analogues[75] and also to other fluoro- and chloro-silanes.[76,77] For the more complex molecules of methylsilanes and fluoromethylsilanes, semiempirical calculations[78–80] yield conformations which agree with experiment, but they are relatively unsuitable for the estimation of their barriers to rotation.

A wide variety of the conformations of the polysilanes Si_nH_{2n+2}, which has been confirmed indirectly by experiment, follows from calculations by the CNDO method.[81] The calculations also indicate an explicit preference for the geometry of benzyltrimethylsilane which is most favourable for hyperconjugation.[82] According to the calculated data of Drews et al.,[83] the minimum in the total energy of the trimethylsilylaniline molecule is attained for the geometry in which one methyl group is located in the plane of the aromatic ring.

Thus, while taking into account the above remarks about the applicability and accuracy of the quantum-chemical methods, one should note their important role in the establishment of the theory of conformational analysis, i.e. ultimately also in the solution of the problem of the influence of steric effects on chemical properties. At the same time, the limited amount of literature data precludes at present sufficiently unambiguous conclusions concerning the role of steric effects in organic chemistry; the data obtained for organoelemental compounds are clearly insufficient.

Together with the methods for the investigation of the role of steric effects examined above, a completely different approach proposed by Ingold and Taft,[7,9,14] has developed independently. It is based on the assumption (supported subsequently by theoretical considerations[7]) that it is possible to represent the Gibbs free energy ΔG of reaction or activation by the sum of independent components, i.e. $\Delta G = \Delta G_I + \Delta G_R + \Delta G_S$, which reflects the influence of the inductive (I), resonance (R), and steric (S) effects. This linear free energy principle holds for enormous numbers of chemical processes (and also in the correlation of many physical properties[84]) and among them it is possible to select those in which the influence of one of the effects on ΔG predominates. The process in which the steric effects exert a dominant influence ($\Delta G = \Delta G_S$) is in particular the acid hydrolysis of the esters XCH_2COOR. The logarithms of the hydrolysis rate constants, which are proportional to ΔG, depend on the steric constants E_S of the variable substituents X:[14]

$$\lg\left(\frac{k}{k_0}\right) = \delta E_S ,$$

where k and k_0 are respectively the rate constants for the acid hydrolysis of the substituted (XCH_2COOR) and unsubstituted (CH_3COOR) esters and δ is a constant which depends on the type of reaction series (the nature of R). Assuming that for hydrogen $E_S = 0$, the steric parameters E_S for a large number of substituents have been obtained.[14,84] Although theoretical evidence supporting the view that the constants E_S characterise only the steric effect has been presented in the literature,[85] the initial fundamental publication[14] was followed by a series of studies whose authors analysed, on the one hand, the possibility of the presence of a hyperconjugation component in E_S[7,45,86,87] and, on the other hand, examined the physical significance of E_S and estimated the validity of the experimental methods for each determination.[45,88,89] Ultimately no unambiguous conclusions were reached concerning the role of hyperconjugation, whose contribution to E_S depends on the type of compounds investigated[45] and in many instances is apparently extremely low.[87]

Analysis of the most thoroughly determined values of E_S (for 107 substituents) has shown[45] that the E_S for simple symmetrical

groups X are linearly related to the quantity $\nu_x = r_X - r_H$ [89] which represents the differences between the van der Waals radii of the atom X and the hydrogen atom. However, for bulky asymmetric groups and a complex steric configuration of the type of CR'R"R"' with different substituents, there is no simple correlation between the experimental E_S and the ν_x. The quantity ν_x for such groups may not have just one value but at least two, the minimum and maximum values,[88] and in neither case is a correspondence observed[45] between the calculated and experimental E_S. Even greater difficulties arise on passing from aliphatic to aromatic compounds, in which the *ortho*-effect of the substituents cannot be explained[90] solely by steric factors. Thus it has not been possible to use the parameter E_S to characterise the steric effects in cyclohexane derivatives.[91]

On passing to organoelemental compounds, the non-universality of the parameter E_S, which characterises in general (taking into account the above remarks concerning very complex substituents) the size of the substituent, becomes still more evident. Indeed, in these compounds it is necessary to take into account in the first place no longer simply the size of the substituent, i.e. the parameter ν_x or E_S (although even they are unknown for many organoelemental substituents), but the distance of the substituent from the reaction centre. Furthermore, the distance between a bulky substituent and the reaction centre can vary within wide limits both owing to the changes in the length of the chemical bond between them when the central element is varied and as a consequence of the possible mutual approach in space of the substituent and the reaction centre even when they are separated by several bonds. The size of the substituent alone does not then generally determine the steric situation and it can be characterised by the parameters of the type E_S and ν_x only in exceptional cases.

Two methods have been proposed for the estimation of steric effects in similar complex instances. In the method of cone angles,[17,92] developed in relation to compounds of the type of $Ni(PR_3)_4$, account is taken of the change in the size of the bulky ligand PR_3 as a function of the type of R. This change is characterised by the angle in the plane and the distance from PR_3 to the reaction centre (the nickel atom) is assumed to be unchanged. In the more sophisticated method of solid angles,[25,26,93] the steric shielding of the central element E in ER_n is estimated in terms of the sum of n solid angles (with the vertex at the atom E) occupied by the substituents R. The method of solid angles can also be used to estimate the shielding of atomic fragments, for example by an individual chemical bond or the remainder of the molecule.[25,26,93] This method has been used, in particular, to estimate the steric accessibility of a donor centre localised predominantly at a tungsten atom with formation of molecular complexes with derivatives of dicyclopentadienyltungsten dihalides.[94] A steric model, close in its physical significance to the method of solid angles, has been proposed by Galkin and Cherkasov.[95]

Thus it is impossible to propose a set of universal constants characterising steric effects. Among the methods for the estimation of the role of steric effects in the molecule and especially in a series of compounds with consistently varied substituents, that of solid angles appears to be the most promising. Its use, however, requires the application of computers and data (sometimes exact) for the molecular geometry.

As a problem in physical organoelemental chemistry, that of steric effects can be formulated by isolating from the overall Gibbs free energy the component due to the influence of steric factors. Despite the limitations and difficulties arising under these conditions, this approach is in fact used in most investigations.

III. EXPERIMENTAL STUDIES OF THE STERIC EFFECTS IN COMPOUNDS OF SILICON SUBGROUP ELEMENTS

1. Steric Effects in Complex Formation

The data presented in this Section are classified in terms of the fragments E–X (E is a silicon subgroup element and X is a substituent).

(a) Compounds with E–Group V Element Fragments

Steric effects have a marked influence on the properties of the carbon analogues of these compounds, namely amines.[2,5,13,58] For example, tertiary alkylamines have an anomalously low basicity due to the steric effects of the substituents at the nitrogen atom.[96] A linear relation between the inductive constants σ^* of the substituents and the basicity has been observed for primary, secondary, and tertiary amines.[96] The points corresponding to compounds with bulky substituents show consistent deviations from these straight lines. Another characteristic example is that of the sharp increase of the basicity of aromatic amines with increasing bulk of two alkyl groups at the nigrogen atom. The basicity of the nitrogen atom increases owing to the steric inhibition of the p,π conjugation between the aromatic π-system and the substituent NR_2, which does not occupy the position most favourable for conjugation, since this position is prohibited owing to the intimate steric contacts between R and the *ortho*-hydrogen atoms of the aromatic ring.[97]

Steric effects exert a significant influence also on the properties of compounds with a silicon–nitrogen bond. Its length (1.71–1.76 Å)[98] is less than the sum (1.80 Å) of the covalent radii of the silicon and nitrogen atoms corrected for the amount of ionic character of the bond.[99] The shortening of the Si–N bond can be attributed to the influence of the $(p-d)\pi$ interaction,[46] which increases the multiplicity of this bond. However, steric factors also make a definite contribution, which follows from the increase of the length of the silicon–nitrogen bond when the methyl group is replaced by the bulkier silyl group in the series (the Si–N bond lengths are given in brackets in Å) $N(CH_3)_2SiH_3$ (1.715), $N(CH_3).(SiH_3)_2$ (1.726), and $N(SiH_3)_3$ (1.734), on replacement of the silyl group by the trimethylsilyl group in the series $NH(SiH_3)_2$ (1.725), $NH[Si(CH_3)_3]_2$ (1.738), $N(SiH_3)_3$ (1.734), and $N[Si(CH_3)_3]_3$ (1.760), and on replacement of a hydrogen atom in the organoelemental substituent X on passing from $NH[Si(CH_3)_3]_2$ to $NX[Si(CH_3)_3]_2$.[98] At the same time the barrier to the internal rotation of the SiH_3 groups in $N(CH_3).(SiH_3)_2$ (3.3 kcal mol^{-1}) is higher than in $N(CH_3)_2SiH_3$ (1.5 kcal mol^{-1}), which is believed[100] to demonstrate (together with steric factors) a greater contribution of the $(p-d)\pi$ interaction to the Si–N bond in the first of these compounds. The steric effects of the bulky trimethylsilyl groups leads to the appearance of a fairly high barrier to the rotation about the N–N bond in the radical-cation $[(CH_3)_3Si]_2N \overset{+}{-} N[Si.(CH_3)_3]_2$.[101]

The possibility of the approach of the silicon and nitrogen atoms in space with formation of a donor–acceptor bond between them, as in silatranes, is regulated not only by the electronic but also by the steric effects of the substituents R and R' at these atoms in compounds of the type $R_2Si(OCH_2.CH_2)_2NR'$.[102–104] Bulky substituents increase the length (i.e. weaken) of the donor–acceptor bond. Thus, on passing from R' = H to CH_3 and $C(CH_3)_3$, the Si–N distance increases from 2.30 to 2.68 and 3.16 Å respectively.

Analysis of the factors determining the steric structure of the germatranes $RGe(OCH_2CH_2)_3N$ also led Tandura et al.[105] to the conclusion that the degree of transannular interaction between the nitrogen and germanium atoms depends not only on the electronic but also on the steric effects of the substituents R.

Ideas concerning the intramolecular coordination interactions between the E and X atoms (here X has an unshared electron pair), similar to those observed in silatranes and related derivatives, have been invoked also to account for the physical properties of compounds with a simpler structure, for example, those with fragments of the type $Si(CH_2)_nX$.[106] Together with the electronic effects of the substituents at the E and X atoms, the intramolecular coordination [which apparently takes place via a mechanism involving the $(p-d)\sigma$ interaction[106]] is also regulated by steric factors, as shown[107] for X = N (this will be discussed below for other X).

The influence of steric effects in the formation of intermolecular complexes involving compounds with E–N fragments is just as evident. Steric effects play a significant role both in the reactions of vinylsilanes with amines[108] and in the formation of complexes with $SnCl_4$ as acceptor.[109] The enthalpy of complex formation with $SnCl_4$ is determined not only by the electronic effects of the substituents in the Si–N fragments but also by steric factors, which is indicated by the decrease of ΔH in the presence of bulky substituents at the nitrogen atom. The absence of appreciable steric effects in the protonation of the same compounds, i.e. under conditions where there is a sharp decrease of the possible steric hindrance originating from the acceptor in the donor–acceptor complex, is striking.

Systematic investigations of the electron-donating capacity in the formation of hydrogen bonds involving compounds with the Si–N,[110–114] Ge–N,[110,112,114,115] and Sn–N [110,116,117] groups, starting with the first studies by Abel et al.[110] and Pacl et al.,[111] revealed the possible influence not only of electronic but also of steric effects of the substituents attached to these groups. In the study of a hydrogen bond of the type $\geq E-N\cdots H-N\leq$ or $\geq E-N\cdots D-C\leq$ with pyrrole or deuteriochloroform by infrared spectroscopy, the parameter $\Delta\nu$, namely the shift of the stretching vibration frequency of the unassociated pyrrole or deuteriochloroform on formation of a hydrogen bond, was used as a quantitative measure of the electron-donating capacity. This parameter is proportional to ΔH and ΔG for hydrogen bond formation at least in series of isotypical compounds.[118]

The steric shielding of the donor centre (the nitrogen atom) by three substituents should be accompanied by a decrease of $\Delta\nu$ and ΔH and hence of the electron-donating capacity of the compounds. In order to obtain information about the donor–acceptor properties of the substituents R_3E (E = C, Si, Ge, or Sn) in the compounds $(R_3E)_nNR'_{3-n}$ (this was one of the main tasks in the investigations quoted above[110–117]), it is therefore necessary to have information about the influence of the steric effects on $\Delta\nu$.

For certain compounds with E–N fragments, such information has been obtained by correlation analysis in a study,[117] where, together with organoelemental amines, a wide range of organic amines were also considered. Among the latter, there are compounds for which the parameters $\Delta\nu$ [the shift of the ν(C–D) frequency in the infrared spectrum of deuteriochloroform on formation of the $\geq N\cdots D-C\leq$ hydrogen bond] vary linearly with the sum of the inductive constant σ^* of the three substituents at the nitrogen atom, which indicates the virtual absence of steric effects in the formation of the hydrogen bonded complex. The steric effects are insignificant both for the compounds $AlkN(CH_3)_2$ and for $(CH_3)_3EN(CH_3)_2$ (E = Si, Ge, or Sn). However, on passing to compounds with the $N(C_2H_5)_2$ and $N[Sn(CH_3)_3]_2$ fragments, the steric hindrance generated by the substituents at the nitrogen atom prevents the formation of a hydrogen-bonded complex and is responsible for the decrease of $\Delta\nu$.[117] The increased role of steric effects following the accumulation of substituents of the type $(CH_3)_3E$ (E = C, Si, and Sn) at the Group V element is also indicated by NMR data for the compounds $(C_2H_5)_{3-n}\cdot P[E(CH_3)_3]_n$.[119] It follows from these data that the anomalies (from the standpoint of the donor–acceptor properties of the substituents) in the changes in the chemical shift increase with increasing n.

(b) Compounds with E–Group VI Element Fragments

The Si–O–C and Si–O–Si valence angles are known for many organosilicon compounds (see, for example, a number of reviews[120–122]). If it is assumed that these angles are determined by the influence of only the electronic factors of the substituents at the silicon and carbon atoms and that steric effects do not play an appreciable role, a number of contradictions arise. Thus, on passing from $(CH_3)_2O$ (the C–O–C angle is 111°43′ [123]) to Alk_3SiOCH_3 [120] (Alk = CH_3, C_2H_5, or n-C_3H_7) and H_3SiOCH_3,[124] the Si–O–C angle increases to 117–123°, while in the case of $Alk_3SiOC(CH_3)_3$ it amounts to 127° ± 3°.[120] Similarly the angle increases from 121° to 140° on passing from $CH_3OC_6H_5$ to $Alk_3SiOC_6H_5$.[120]

There is no doubt that the main cause of the larger changes in the Si–O–C angles compared with the C–O–C angles is the electronic effects of the silyl substituents, i.e. the electron-accepting properties of the $SiAlk_3$ group compared with the electron-donating properties of the substituents CH_3 or $CAlk_3$. However, steric effects are also significant,[120] which is manifested particularly clearly in the disiloxanes $R_3SiOSiR_3$. The successive transition from R = CH_3 to H, Cl, and F is accompanied by some shortening of the Si–O distance (1.63, 1.63, 1.59, and 1.58 Å respectively) and a significant increase of the Si–O–Si valence angle from 130° ± 10°[125] to 144°,[126] 146°,[127] and 156°,[128] in conformity with the enhancement of the electron-accepting properties of R in this series.

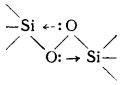
Contrary to the expectation based on the comparatively similar electronegativities of the hydrogen atom and the phenyl and vinyl groups, the Si–O–Si angles in hexaphenyldisiloxane,[129,130] hexavinyldisiloxane[131] and also in $(H_2C{=}CH)_3\cdot SiOSi(C_6H_5)_3$ [131] are 180°. Apparently the main cause of the linear structure of the disiloxane fragment is the large bulk of the substituents, while the packing effects do not exert a decisive influence,[130] although, according to Vlasenko,[131] they do contribute to an increase of the Si–O–Si angle.

A number of instances of the influence of steric effects on the structure of organocyclosiloxanes have been quoted in a review of X-ray diffraction data.[122] The steric effects of two bulky $(CH_3)_3SiO$ substituents in *ortho*-positions in the benzene ring hinder the free rotation about the $O-C_{ar}$ bond, revealed by a change in both the dipole moments[132] and the NMR spectra.[133] Intramolecular coordination interactions between the E and O atoms not linked by direct chemical bonds are well known for organoelemental compounds.

However, it follows from the review of early studies[106,134] that data for intramolecular coordination in silicon compounds are contradictory. It is known[46,55] that, with increase of the effective positive charge on E and also on passing from E = Si to E = Ge and Sn, the energy of the coordinate bonds increases. Therefore there is no doubt about the occurrence of intramolecular interactions in compounds with fragments of

the type SiF_3, $SiF_2(CH_3)$, and $SiF(CH_3)_2$ [135,136] and also for germanium and, even more so, tin[105,106,137] derivatives.

Analysis of the literature data has shown that the coordination interactions between the E and O atoms are influenced (like the intramolecular coordination between E and N) by the steric effects of the substituents linked to the donor and acceptor centres in the molecule. This is shown very clearly for organosilicon peroxides with the fragment



in which intramolecular coordination leads to a decrease of the electron-donating capacity of the oxygen atoms owing to their involvement not only in $(p-d)\pi$ interaction with the neighbouring silicon atom but also in an intramolecular interaction with the more remote silicon atom. With alkyl substitution at silicon, intramolecular coordination is disturbed and the electron-donating capacity of the oxygen atoms increases. This is manifested particularly by a sharp increase of $\Delta\nu$(O–H) on formation of the hydrogen-bonded complexes (>O...HO) with phenol.[138]

The length of the Ge–O intramolecular coordinate bond in compounds with the O=C–C–C–$GeCl_3$ fragments varies from ~2.1 to 3.2 Å.[105] Together with intermolecular interactions, whose influence on the length of the coordinate bond has been considered by Tandura et al.,[105] the energy of this bond is apparently determined also by the influence of the substituents on the geometry of the five-membered rings formed, i.e. by the steric factors. Study of the thermodynamic and kinetic parameters of an intramolecular metallotropic rearrangement (the 1,5-shift of the R_3Ge group between two oxygen atoms in $R_3GeOC(CH_3)=CHC(CH_3=O]$ has shown that formation of a coordinate bond between the germanium atom and the oxygen atom of the CO group is influenced by the steric effects of the substituent R.[139]

The steric effects of the substituents are shown very clearly in the formation of intermolecular complexes with a siloxane or disiloxane group.[121] Thus a decrease of the heat of complex formation with increasing length of the alkyl substituent R and with the degree of its branching was established a comparatively long time ago[140] in studies by the dipole moment, infrared spectroscopic, calorimetric, and cryoscopic methods of the complexes of $SnCl_4$ with the alkoxysilanes $Si(OR)_4$ and $R'Si(OR)_3$. The complex forming capacity also decreases with intensification of the steric effects of the substituents at the silicon atom, which follows from the data obtained in a study of the complexes of $SnCl_4$ with $(R_3SiO)_3PO$.[141]

Whereas compounds containing siloxane linkages show little tendency towards self-association,[121] the formation of intermolecular associated species is an extremely characteristic feature of the related tin and lead compounds and the influence of the steric effects of the substituents is then strikingly revealed. Thus, according to NMR data for tin nuclei, compounds of the type $(C_4H_9)_3SnOAlk$ are monomeric at room temperature and have a tetrahedral tin atom,[142] while the derivatives $(C_4H_9)_2Sn(OAlk)_2$ are monomeric only for Alk = s-C_4H_9 or t-C_4H_9, which prevent dimerisation by virtue of steric factors. The replacement of the butyl group in the OC_4H_9 fragment of the monomeric complex $C_4H_9Sn(OC_4H_9)_3$ by lower alkyl groups leads to a decrease of steric hindrance, the compounds undergo association, and the tin atom becomes hexacoordinate.[142] The bulky substituents R and R' prevent the association of the tin carboxylates $R_3SnOCOR'$ [143] and, when R = $C_6H_5C(CH_3)_2CH_2$, the compounds are monomeric also for R' = H or CH_3.[144,145] The lead derivatives R_3PbX (where X has unshared electron pairs) are highly associated, but in the presence of bulky substituents the compound [for example, $(C_6H_5)_3PbOSi(C_6H_5)_3$ [146]] exists in the monomeric form.

The most systematic information about the influence of electronic and steric effects of substituents at the E–O bond, referring mainly to silicon compounds, has been obtained in the study of the hydrogen bonds with various electron acceptors by infrared spectroscopy and ^1H NMR[121] (although the information about the steric effects has also been obtained by analysing the infrared spectra of individual siloxanes[147]).

Individual correlation lines of the type $\Delta\nu = \Delta\nu_0 + a\Sigma\sigma^*$, representing the correlation between $\Delta\nu$ [the shift of the ν(O–H) frequency of phenol in the formation of hydrogen bonds with the test compounds] and the sum of the inductive constants σ^* of the substituents at the silicon atom have been observed also for the compounds $R_3SiOC_2H_5$, $RSi(OC_2H_5)_3$, $RSi(OCH_3)_3$, and $(R_3Si)_2O$.[148,149] However, a more careful analysis of the parameters $\Delta\nu$ [150,151] as well as the data of Voss et al.[152] and the conclusions reached by Voronkov et al.[121] demonstrated the influence on the electron-donating properties of compounds with the Si–O bond not only by the inductive effect but also by the steric effect of the substituents linked to the silicon and oxygen atoms. For example, on passing from the compounds $X(CH_3)_2SiOC_2H_5$ to $X(CH_3)_2SiOC(CH_3)_3$ (X represents various organic substituents), the electron-donating capacity does not increase (as might have been expected on the basis of the inductive effect) but actually falls.[151,152]

The accumulation of bulky substituents at the atoms of the Si–O or Ge–O fragment results in a dependence of the steric accessibility of the silicon atom in these fragments, as an electron donor centre for the formation of the hydrogen bond, on the size and geometry of the other species involved in the hydrogen-bonded complex. By varying the hydrogen bond acceptor (phenol, pyrrole, deuteriochloroform), it is therefore possible to discover the electron donors which entail steric hindrance in complex formation with the acceptors. Such difficulties are observed, in particular, on formation of hydrogen-bonded complexes with pyrrole by compounds of the type $(CH_3)_3EOE(CH_3)_3$, where E = C or Si,[151] and also $Ge(OC_6H_5)_4$ and $CH_3Ge(OC_6H_5)_3$.[153]

When an even more pronounced steric hindrance is generated at the oxygen atom, for example, on passing to compounds of the type $(C_6H_5)_3SiOSi(C_6H_5)_3$, hydrogen-bonded complexes with the phenol coordinated to the oxygen atom of the Si–O–Si fragment cannot be detected from the infrared spectra,[154] despite the seemingly extremely favourable configuration of this fragment (the angle between the heavy atoms is 180°).[129,130]

Although the steric hindrance in the formation of hydrogen-bonded complexes between alkoxysilanes and deuteriochloroform is apparently weaker than in the case of pyrrole,[151,153] steric effects have also been detected by ^1H NMR in the complexes with chloroform.[121,155,156] The change in the chemical shift in the ^1H NMR spectrum of chloroform on formation of a hydrogen bond with $(CH_3)_3SiOAlk$ depends both on the inductive and steric (E_S) constants of the alkyl substituents and the steric hindrance increases with increasing n in $(CH_3)_{4-n}Si(OC_2H_5)_n$.[156] The comparatively high electron-donating capacity of the cyclotrisiloxanes $(R_2SiO)_3$ compared with compounds having a linear structure or containing larger rings can serve as yet another clear example of the manifestation of steric effects on formation of hydrogen-bonded complexes with phenol. In strained cyclic trisiloxanes, the electron-donating capacity at the oxygen atom increases both as a result of the

improved steric accessibility of these atoms for the formation of the hydrogen bond and the weaker $(p-d)\pi$ interaction in the silicon–oxygen bonds.[157] Bulky substituents at the silicon atom reduce the capacity of silanols with the Si–O–H fragments for the formation of intermolecular hydrogen bonds.[158]

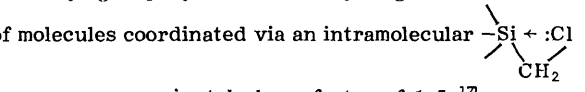
The high efficiency of the NMR method in the study of steric effects [for example in compounds of the type $(CH_3)_3$. .SiOAlk [159]] was recently demonstrated yet again in the systematic investigation of alkoxysilanes by ^{13}C, ^{29}Si, and ^{17}O NMR.[160–162] It was established that the chemical shifts of the signals in the NMR spectra of mono-, di-, tri-, and tetraalkoxysilanes are determined by the joint influence of the inductive and steric effects of the substituents. The role of the steric effect increases with increasing number of alkoxy-groups at the silicon atom, in conformity with the results obtained by the other research techniques examined above. Steric effects can influence also the chemical shifts in the NMR spectra of alkoxygermanes.[161,163] According to NMR data,[164] in compounds with the $(CH_3)_3Si–O–C=C$ fragments, the conformations in which conjugation between the oxygen atom and the double bond is reduced are preferred owing to the steric effects of the trimethylsilyl group.

(c) Compounds with the E–Group VII Element Fragments

There is limited information in the literature about the influence of steric effects on the complex-forming capacity and physical properties of compounds with such fragments. An infrared spectroscopic study of hydrogen bonding with phenol in compounds of the type $R_3E–Cl...H–O–C_6H_5$ and $R_3ECH_2Cl...H–O–C_6H_5$ failed to reveal[165] anomalies which could not be accounted for by the electronic effects of the substituents at the chlorine atoms and would require allowance for steric effects. However, it does not follow from this that steric effects are completely absent from compounds of the type considered, since careful analysis of the ^1H NMR spectra of derivatives of the type $(n-C_3H_7)_3ECl$, where E = Si, Ge, or Sn, indicates the presence of steric hindrance to free rotation about the C–E bonds, which increases in the sequence Sn < Ge < Si.[166]

The free rotation about the Si–C bond is hindered also in $[(CH_3)_3C]_3SiX$, the barrier increasing from 6 to 8.5 kcal mol^{-1} with increase in the size of X in the sequence H < Cl < Br < I.[167] There are indications of a dependence of the complex-forming capacity of the compunds R_nSiCl_{4-n} (R = CH_3 or C_2H_5, n = 0–4) in relation to acetone on the bulk of the substituents at the silicon atom.[168]

Steric effects exert an appreciable influence on the intramolecular coordination between the silicon and chlorine atoms not linked by a direct chemical bond in compounds containing the $SiCH_2Cl$ fragments.[106] Such intramolecular interactions, which have already been partly examined above, are intensified with increase of the atomic number of the element E and with increase of its effective positive charge. Under conditions close to the most favourable ones, for example, in the case of $Cl_3SnCH_2CH_2CH_2Cl$,[169] the presence of a coordinate bond was therefore demonstrated by direct experiments. In silicon compounds this kind of bond is fairly strong only in the presence of three acceptors—the fluorine atoms at the silicon atom,[135] the enthalpy of formation of the coordinate bond diminishing after the replacement of the fluorine atoms by methyl groups,[135] and in $(CH_3)_2(ClCH_2)SiH$ it amounts to only ~1 kcal mol^{-1}.[170]

At the same time the weak coordination interactions in compounds with the $E–CH_2Cl$ fragments (E = Si or Ge)[171,172] exhibit a distinct dependence on both the electronic[170–172] and steric[171] effects of the substituents at the atom E. Thus, on passing from Alk_2HSiCH_2Cl to $AlkH_2SiCH_2Cl$, i.e. on replacement of the alkyl group by the smaller hydrogen atom, the number of molecules coordinated via an intramolecular  linkage increases approximately by a factor of 1.5.[171]

(d) Compounds with E–Ar Fragments

The results of X-ray diffraction studies indicate appreciable steric effects in tetra-aryl derivatives of silicon subgroup elements. Thus, apparently owing to the steric hindrance generated by the four substituents at the silicon atom, the Si–C bond length (1.872 Å[173]) in tetraphenylsilane is greater than in phenylsilane (1.843 Å).[174] Steric hindrance at the central atom increases after the introduction of methyl groups in the *ortho*-position in the benzene ring. Thus, on passing from tetraphenylgermane to tetra(o-tolyl)germane, the Ge–C bond length increases from 1.957 Å to 1.966 Å,[175,176] while in the corresponding tin derivatives the Sn–C bond length increases from 2.144 Å to 2.160 Å.[177]

Anomalous valence angles are also observed at the central atom. These anomalies are particularly marked for the mesityl derivatives in which the aromatic rings contain two *ortho*-methyl substituents. The angles between the Mes–E–Mes bonds in the compounds Mes_3EH with E = C, Si, or Ge (Mes = mesityl) are respectively 118.3°, 116.0°, and 115.5°, i.e. they increase with decrease of the atomic number of E and with increase of the steric hindrance of the atom of the latter.[30,178] The conformation in which the mesityl substituents are arranged around the silicon or germanium atom in a propeller fashion corresponds to the minimum steric strain.[179] The barriers to internal rotation about the E–Mes bonds in Mes_3EH, which amount to 8.3, 6.0, and 3.1 kcal mol^{-1} for E = Si, Ge, or Sn respectively, apparently agree with the hypothesis of a predominant contribution to these quantities by steric interactions of the *ortho*-substituents in the neighbouring aromatic rings[179] (see also Refs. 180 and 181).

The anomalies discussed above, observed for the mesityl derivatives, are clearly manifested in their infrared spectra. Thus the frequencies and intensities in the E–H (E = Si or Ge) stretching vibration bands in the infrared spectra of Mes_3EH are extremely unusual.[182] For the vast majority of the substituents R in R_3EH, the mode of the E–H bond vibrations remains unchanged, since the substituents R influence the frequency and intensity of this highly characteristic vibration only via their electronic effects. The pronounced steric hindrance in mesityl derivatives leads to the disturbance of the mode of the given vibration and to a change in the conditions for the $(p-d)\pi$ interaction of the atom E with the aromatic ring.[182] As a result, the frequency and intensity of the E–H bond vibration no longer depend solely on the electronic effects. These anomalies are more marked for silicon derivatives than for germanium derivatives.

It follows from the NMR data for the compounds Ar_3ER, where R are various organic substituents, and Ar_4E, where E = Si, Ge, or Sn, that the activation energy for the intramolecular rotation of the aryl groups is determined both by the presence of *ortho*-substituents in the aromatic rings and by the size of the atom E.[183] Steric effects in compounds of this type make a significant imprint also on their reactivity. Thus the substitution of bromine in the bromo-derivatives of triarylgermanes and triarylstannanes with methyl substituents in the *o*-position is inhibited by steric factors to a lesser extent in the organotin compounds as a consequence of the smaller size of the tin atom compared with the germanium atom.[184]

It was established comparatively long ago[43] that the accumulation of bulky organic substituents in the aromatic ring alters significantly the thermodynamic characteristics of the charge-transfer complexes of benzene derivatives even with comparatively smaller acceptor molecules such as those of iodine chloride. In particular, this is shown by a sharp decrease of the equilibrium constant of the complex-formation of 1,3,5-tri-t-butylbenzene and to an even greater extent hexaethylbenzene, compared with the less sterically hindered alkylbenzenes. The entropy of formation of the hexaethylbenzene–iodine complex as well as the equilibrium constant are low. The acceptor apparently does not overcome the steric barrier established by the bulky substituents and is located at a distance from the donor, which is greater than the optimum distance for the donor–acceptor interaction.[43]

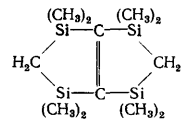
It is noteworthy that the equilibrium constant is more sensitive to steric effects than, for example, the frequency of the charge-transfer band ν_{CT} in the ultraviolet spectrum of the complex. For this reason, no anomalies associated with the steric factors are observed in the values of ν_{CT} for a series of compounds $C_6H_5CH_{3-n}[Si(CH_3)_3]_n$ (n = 1–3) and the equilibrium constant diminishes with increase of n (i.e. the size of the ring substituent).[185] However, with increase of the number of t-butyl or trimethylsilyl substituents in the ring, whereupon the role of the steric effects increases, anomalies do appear also in the values of ν_{CT}. This is manifested, in particular, by a decrease of the electron donating capacity of substituted phenols containing such groups in the formation of complexes with tetracyanoethylene.[186]

Like the decrease of the complex formation constants, the decrease of the electron-donating capacity is associated (for a molecule of a benzene derivative with bulky substituents) with the impossibility of realising the potential electron-donating properties because of the steric hindrance in the approach to the acceptor molecule to the optimum distance for electronic interactions of the complex. The fact that the distance actually attained exceeds (for steric reasons) the optimum distance can be formally regarded as a decrease of the electron-donating capacity. For this reason, the frequency ν_{CT} in the ultraviolet spectra of complexes of phenol derivatives having two or three bulky substituents [$C(CH_3)_3$, $Si(CH_3)_3$, $Ge(CH_3)_3$] with tetracyanoethylene ceases to be satisfactorily correlated with the σ^+ constants of the substituents.[186,187] This shows that both the electronic and steric effects are important in the formation of complexes by compounds of this kind. When bulky substituents are introduced into the phenol molecule (in the *ortho*-position relative to the hydroxy-group), the electron-accepting capacity of the compound in the formation of a hydrogen bond with tetrahydrofuran diminishes due to steric hindrance.[186]

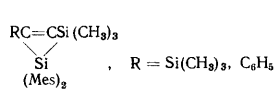
Extremely clear results have been obtained by yet another method for the estimation of the steric effects of substituents in benzene derivatives, which is based on analysis of the correlations between the ionisation potentials I_D, characterising the energy of the highest occupied molecular orbital (HOMO), and the charge-transfer band frequencies ν_{CT} in the ultraviolet spectra of the complexes of these derivatives with tetracyanoethylene.[188] It follows from the general theory[32] of charge-transfer complexes that there should be a linear relation between I_D and ν_{CT}; this has been frequently confirmed experimentally,[39] especially for compounds with related structures.[189] However, with increase of the number of organoelemental substituents in the benzene molecule, the linear relation between I_D and ν_{CT} ceases to hold. Thus, for the compounds $C_6H_{6-(m+n)}(CH_3)_m[CH_2Si(CH_3)_3]_n$ (m + n = 1–6), the points on the plot corresponding to the hexasubstituted derivatives of the type $C_6[CH_2Si(CH_3)_3]_6$, $C_6(CH_3)_4[CH_2Si(CH_3)_3]_2$, $C_6(CH_3)_3[CH_2Si(CH_3)_3]_3$, and also $C_6H_2[CH_2Si(CH_3)_3]_4$ deviate from the linear relation between I_D and ν_{CT} towards higher values of ν_{CT}, i.e. the electron-donating capacity falls due to the steric hindrance to complex formation with tetracyanoethylene.

According to the ionisation potentials of sterically hindered benzene derivatives,[188] the steric hindrance influences also the effects of the conjugation of the substituents with the ring; these results will be examined in the next Section of the review.

A number of anomalies have also been observed in the properties of sterically hindered ethylene derivatives.[20,42] Thus the ring strain in the compound



leads to an increase in the length of the multiple bond and alters the valence angles.[190] The accumulation of bulky substituents at the C=C bond is accompanied not only by an increase in its length but also by the twisting of this bond. Thus the C=C bond lengths are respectively 1.368 and 1.370 Å and the tortional angles are ~30° and ~50° in $[(CH_3)_3Si]_2C{=}C[Si(CH_3)_3]_2$ [191] and in the sterically even more hindered $[(CH_3)_3Si]_2C{=}C[Si(CH_3)_2C(CH_3)_3]_2$.[192] The sharp decrease of the reactivity of the silacyclopropenes



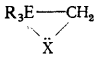
is caused by the presence in the molecule of the two bulky mesityl substituents.[193,194] It is noteworthy that electronic factors also influence the stability of compounds of this type.[195–197]

(e) The Central Atom E as the Acceptor Centre and the E–C Bond as the Donor Centre in Complex Formation

In contrast to carbon compounds, complex formation via the central atom E is characteristic of derivatives of silicon subgroup elements.[6,8,34,46,55,106] In complex formation of this type, the atom E functions as a ν-acceptor, apparently by virtue of its unoccupied *nd* orbitals.[47,55] The possibility of the realisation of the potential ν-acceptor properties (determined by the nature of the atom E and the electronic effects of the substituents linked on it) depends also on the steric shielding of the atom E by these substituents and on the steric situation at the donor centre of the donor molecule. In the absence of the complicating influence of steric effects, the ν-acceptor capacity increases with increase of the atomic number of E (on passing from Si to Ge, Sn, and Pb) and with increase of the effective positive charge on E, which is ensured by the addition of electron-accepting substituents to E.[55,106] The influence of steric effects is manifested both by the breakdown of these characteristics of complex formation and by the anomalous thermodynamic characteristics of the complexes.

Although the complex-forming capacity of silicon compounds is the smallest among all the derivatives of the elements E, it has been established by infrared spectroscopy[198] that even triethylsilane is solvated specifically by electron-donating solvents and that steric effects are then manifested to an appreciable extent. These effects are smaller for oxygen-containing solvents than for nitrogen-containing solvents, in which the donor centre (the nitrogen atom) is more shielded by the substituents. On passing from triethylsilane to triethylgermane, the solvation intensifies, but the steric effects in the formation of donor–acceptor complexes hardly change.[198]

It is striking that, judging from the infrared spectra, a fairly profound analogy is observed between the formation of the solvate complexes $R_4E...L$, where L is an electron donating solvent,[198] and the intramolecular coordination of the type



examined above.[106,170-172] The analogy holds also from the standpoint of the steric effects of E and the substituents R linked to L in complex formation. In addition, competition between these two types of complexes is well known.[170-172,199] With increasing electron-donating capacity of L or with increase of the concentration of the latter in solutions, the intramolecular coordination probably breaks down and the concentration of the solvates $R_3(XCH_3)E...L$ rises; however, the role of the steric effects under these conditions has been inadequately studied.

Another form of simultaneous complex formation via two possible pathways is known for the phenyl derivatives of silicon and germanium.[200-202] These compounds can exhibit both π-donor (by virtue of their aromatic rings) and ν-acceptor [by virtue of the atoms E (Si, Ge)] properties in relation to molecular oxygen. It has been shown by the method of the low-temperature quenching of luminescence that in the phenyl derivatives of silicon only the π-donor capacity is realised and the steric effects are then insignificant. Phenyl derivatives of germanium behave as both π-donors and ν-acceptors in complexes with molecular oxygen. In the latter case the equilibrium constant of the complex formation reaction depends markedly on the steric effect of the substituents linked to the germanium atom. It increases, for example, on passing from $(C_6H_5)_4Ge$ to $C_6H_5GeH_3$ by a factor greater than 20,[200,202] although these compounds have similar π-donor capacities and apparently identical charges on the germanium atom.

Compared with silicon and germanium compounds, tin derivatives have more pronounced ν-acceptor properties; in addition, a higher sensitivity of these properties to the influence of substituents at the central atom is characteristic of these compounds. Therefore the study of the donor–acceptor complexes involving tin compounds yielded extremely clear information about the steric effects in the donor and acceptor molecules. Thus calorimetric investigations of the complexes $Alk_{4-n}SnCl_n$ with different N- and O-donors established an increasing enthalpy of complex formation (i.e. of the strength of the donor–acceptor bond) with increase of n.[203]

At the same time a significant dependence of ΔH and of the composition of the complex on the steric hindrance in the donor molecule has been observed.[203] For donors generating an intense steric hindrance, for example, $(C_4H_9)_3N$, even the strongest acceptor $SnCl_4$ forms complexes in which the donor : acceptor ratio is 1 : 1 (and not 2 : 1).[203] The influence of the steric effects of the alkyl groups in tetra-alkylstannanes is very strong in the formation of complexes with molecular oxygen,[204] iodine,[205-208] and tetracyanoethylene.[37] It has been established by the method of low-temperature quenching of luminescence, even in relation to the comparatively weak complexes with molecular oxygen, that the equilibrium constant of complex formation decreases with increase of the size of the alkyl group in the tetra-alkylstannanes in the sequence $CH_3 > n\text{-}C_4H_9 > n\text{-}C_5H_{11}$.[204]

For the stronger charge-transfer complexes with iodine and tetracyanoethylene (acceptors), in which the Sn–C bond having a comparatively low ionisation potential (8.2–9.7 eV [37]) functions as the donor, the influence of steric effects has been studied very thoroughly. It has been shown that comparison of the ionisation potentials of the compounds Alk_4Sn, obtained by photoelectron spectroscopy, and the ultraviolet spectra of the complexes of these compounds with iodine[205-207] and tetracyanoethylene[37] permits a quantitative estimation of the steric effects of the alkyl groups at the tin atom.

In these studies it has also been established that the steric effects influence not only the formation equilibrium constant of the charge-transfer complex[206] but also the rate constants for the subsequent process, for example the insertion of tetracyanoethylene in the tin–carbon bond in Alk_4Sn.[37] Under these conditions, both in the formation of the complex and in its subsequent reaction, the character of the influence of the steric effects does not change qualitatively. In both cases these effects intensify if the alkyl groups are replaced in the sequence $CH_3 \ll C_2H_5 < iso\text{-}C_3H_7 < iso\text{-}C_4H_9 < t\text{-}C_4H_9$; in contrast to other tetra-alkylstannanes, tetraneopentyltin, in which the central atom is most shielded by bulky substituents, does not react with tetracyanoethylene.[37] On the other hand, the increase of the size of the central atom on passing to lead compounds and the increase of the E–C interatomic distance should reduce steric hindrance, which is in fact observed for the complexes $(CH_3)_{4-n}(C_2H_5)_nPb$ with tetracyanoethylene.[37]

The equilibrium constants of the complex formation reactions of tetra-alkylstannanes with iodine, complicated by the steric effects of the bulky alkyl groups, are comparatively low.[207] The constants are very much greater for the formation of charge-transfer complexes between iodine (acceptor) and Alk_3SnX, where X = Br or I (donors).[209] In contrast to tetra-alkylstannanes, in this case the hydrogen atom X functions as the donor centre in complex formation and not the tin–carbon bond.[209,210]

It is to be expected that the role of the steric effects in complexes involving tetra-alkyl derivatives of silicon or germanium as well as compounds containing the silicon–silicon and germanium–germanium fragments as donors is greater than in tetra-alkylstannanes and distannanes. However, systematic studies of this kind have not been carried out and there exist only fragmentary factual data on the spectra of the complexes.[39,211] Appreciable steric effects are manifested in cyclic polysilanes.[212,213] Thus the polysilane $[(CH_3)_3C(CH_3)Si]_4$ whose electronic transition band occurs at an extremely high wavelength and which has a very low ionisation potential is nevertheless resistant to oxidation. The unusual properties of this compound are caused not only by electronic but also by steric effects of the four t-butyl substituents.[212,213]

Anomalously long Si–Si and Si–C bonds are observed in cyclotrisilanes $(R_2Si)_3$ with bulky substituents R: 2,6-dimethylphenyl,[214] neopentyl,[215] and t-butyl.[216]

Important information about steric interactions between the silyl substituents and saturated cyclic systems,[217] including highly strained silacyclopropane derivatives,[218] has been obtained by ^{29}Si NMR.

2. The Influence of Steric Effects on Conjugation in Compounds of Silicon Subgroup Elements

As shown above, the presence of bulky substituents in the donor and/or acceptor molecules exerts a significant influence on the spectroscopic and thermodynamic characteristics of DA complexes.

Steric factors can influence the donor and acceptor centres of the complex by regulating the degree to which these centres approach one another in complex formation, as a result of which the potential complex-forming capacity is not fully realised. Furthermore, steric effects can alter the electronic intermolecular interactions already in the initial

donor or acceptor molecules. As an example, one may quote the steric inhibition of conjugation[2,4,13] or, conversely, the establishment of favourable conditions for conjugation[42] in the molecule. These phenomena, which are well known for organic compounds,[2,4,7,13,15,45] are observed also in organoelemental chemistry.[42]

We shall consider the influence of steric factors on the extremely specific effects of the $(p-d)\pi$ interaction and hyperconjugation, especially for compounds of the silicon subgroup elements. The problem of the $(p-d)\pi$ interaction with participation of the unoccupied *nd* orbitals of the E atoms has been studied in detail.[46,47,53-55] It follows from these studies that the π-acceptor properties of the atoms E in relation to the substituents X (an atom with unshared electron pairs or an αβ-unsaturated hydrocarbon group), which have been thoroughly investigated experimentally, can be interpreted as $(p-d)\pi$ interaction in the E–X fragments via the partial transfer of electron density from the atom X to the unoccupied *nd* orbitals of the atom E. Under these conditions, the E–X bond acquires partial double bond character and the degree of the latter depends on the ratio of the electron-donating properties of the atom X and the electron-accepting properties of the atom E. The ratio of these properties in the atoms involved in the E–X bond depends in its turn on the other substituents attached to the bond.

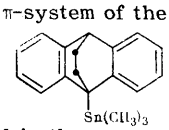
From the standpoint of the influence of stereoelectronic factors on $(p-d)\pi$ interaction, it is possible to consider two cases. The first case is that of compounds of the type R_3EX in which the substituents R are incapable of forming $(p-d)\pi$-bonds with E, i.e. the molecule has only one substituent X involved in the $(p-d)\pi$ interaction with E. In this case it has been shown for E = Si[219] and Ge [220] that the relative capacity of the substituent X for the formation of $(p-d)\pi$-bonds with E is determined exclusively by the resonance constants σ_R,[46] characterising the conjugation of these substituents with the benzene ring and a double or triple bond.[221] This confirms yet again the profound analogy, established a long time ago,[49] between the conjugation effects in organic and organoelemental systems and also the wide-scale applicability of the constant σ_R as a quantitative measure of these effects.

The second case is that of compounds of the type R_2EX_2, REX_3, and EX_4 with several substituents X involved in the $(p-d)\pi$ interaction with the atom E. In such compounds two additional factors (compared with the derivatives R_3EX) influence the $(p-d)\pi$ interaction in the molecule, namely the effective charge on E, which depends on the inductive and mesomeric effects of X, and the overlap integral of the interacting p_π and d_π orbitals of the atoms X and E. The complex situation arising in the $(p-d)\pi$ interaction of the atom E with several atoms X is associated, in particular, with the impossibility of the interaction of E with each of the several X just as strong as with a single X in the molecule. Indeed, as a result of the difference between the valence angles in the molecule (~109.5°) and the angles between the maximum intensity vectors of the d_π orbitals (90°), the interaction of E with several X takes place if the orientation of the d_π orbitals is such that it does not ensure the maximum overlap integrals of the p_π–d_π type in any of the E–X bonds.[53] This is one of the two causes (the second cause is the change in the effective charge on the atom E under the influence of X) of the non-additive dependence of the overall effect of the $(p-d)\pi$ interaction in the molecule on the number of substituents X linked to E. For example, the group overlap integrals of the EX_2 fragment are linked to the two-centre integrals (*s*) of the E–X bonds by the relation $S = (\frac{4}{3})^{1/2}s$.[53]

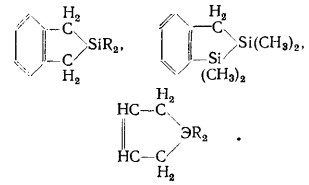
Analysis of the dependence of the frequencies of the highly characteristic stretching vibrations of the E–H bonds in the infrared spectra of the derivatives $AlkX_2EH$, where E = Si [222] or Ge,[220] on the electronic effects of the substituents has shown that, only when account is taken of the above relation between the group and two-centre integrals, is it possible to derive information from spectroscopic data about the influence of the purely electronic factors on the strength of the $(p-d)\pi$-bonds in the EX_2 fragment. In particular, the important conclusion has been reached that the degree of the $(p-d)\pi$ interaction increases with increase of the effective positive charge on the central atom E (Si, Ge).[220,222]

The resonance hyperconjugation effect and particularly its most thoroughly studied variety, namely σ,π-conjugation, are subject to an even more pronounced influence by stereoelectronic factors than $(p-d)\pi$ interaction.[42] By means of a specific alteration of the molecular geometry, it is possible to ensure virtually any spatial disposition of the orbitals interacting via the σ,π-conjugation mechanism and hence achieve both the maximum manifestation of these effects and any of its intermediate values up to its complete absence. Such extensive possibilities for the variation of the effect can be accounted for by the following characteristics of the σ,π-conjugation. The σ,π-conjugation is most pronounced for the maximum overlap of the π orbital of the E–C bond with the π orbital of the C–C or Ar group in compounds with the E–C–C–C or E–C–Ar fragments. Such overlap is attained when the E–C bond and the axis of the π orbital are arranged coplanarly, i.e. when the E–C–C angle is 90°. It has been demonstrated unambiguously for benzyl and allyl derivatives of mercury that the Hg–C–C angle is close to 90°.[223-225] Spectroscopic studies of similar derivatives of silicon subgroup elements have also supported unambiguously similar values of the E–C–C angle,[51,226,227] although direct X-ray diffraction measurements have not in fact been carried out.

Detailed analysis[42] of the factors determining the σ,π conjugation has shown that, in the compounds R_3E-CH_2-X, where X is an αβ-unsaturated substituent, the above conjugation intensities with increase of the electron-donating capacity of R and the electron-accepting capacity of X, with increase of the atomic number of E, and also in the presence of a positive charge on the orbital of the substituent X. The same factors regulate the degree of the σ,π conjugation also in compounds with a more complex structure, where the molecular geometry can ensure the approach of the angle E–C–C to 90°; for other molecular conformations, σ,π conjugation breaks down. Thus the rigid fixation of the Sn–C bond in the nodal plane of the π-system of the compound[51]



and the analogous bond in the corresponding organomercury compound[228] (see also Baidin et al.[229]) leads to the complete breakdown of the σ,π conjugation. For the same reasons, there is no σ,π conjugation in compounds containing planar rings:[230-233]



It is striking that an increase in the size of the rings, accompanied by their conformational non-rigidity, leads to the formation of conformations in which sterically favourable conditions arise for σ,π conjugation (for further details, see the earlier review[42] and in the case of organopolysilanes also Sakurai[234]). Extremely important information about the characteristic features of σ,π conjugation has been obtained for

"sterically overloaded"[40,188,235,236] benzene derivatives $C_6H_{6-n}[CH_2Si(CH_3)_3]_n$. With increase of the size (n) of bulky substituents, the requirement necessary to ensure conditions most favourable for the conjugation of these substituents with the ring break down, which is manifested in the photoelectron spectra and the EPR spectra of the radical-cations of these compounds.[40,188,235] The degree of σ,π conjugation then depends on the angle between the C–Si bond and the plane of the benzene ring or the axis of the C=C bond (for the corresponding ethylene derivatives[41,237,238]). In the latter case, when the sterically most favourable conditions for σ,π conjugation have been created, having fixed rigidly in space the fragments involved in the conjugation, it is possible to obtain ethylene derivatives with very low ionisation potentials (less than 7 eV[41]). Such high electron-donating capacity of compounds of this kind is caused by the maximum extent of σ,π conjugation; for this reason, one observes in this instance a kind of enhancement of conjugation as a result of the creation of the most favourable steric conditions.[41]

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Thus, on the one hand, studies designed to create a general theory of steric effects in chemistry are being prosecuted at the present time. Fundamental advances on these lines will apparently become possible only after a set of specific quantum-chemical investigations have been carried out; so far this problem is far from being solved. On the other hand, a planned general interpretation of an increasing amount of experimental data is being carried out in organic and organoelemental chemistry, which has led, in particular, to the development of empirical methods for the estimation of steric effects and also to the understanding of the specific features of the more varied role of these effects in organoelemental compounds.

Compounds of the silicon subgroup elements are used (at least in the chemistry of non-transition elements) as important model systems for the investigation of the steric effects both in the ground electronic state and (judging from the extensive data on reactivities which have not been included in this review) in the transition state. Together with their independent importance, spectroscopic investigations of the steric effects in the ground electronic states of such model compounds can have a direct bearing on the study of reactivity, since it has been shown for a series of organoelemental systems, for example, for tetra-alkylstannanes,[37] that steric effects in the ground and transition states differ little. Improvement of the spectroscopic research techniques for the primary stages of not too fast reactions involving organoelemental compounds is therefore likely to be useful for the prediction of the influence of steric effects on reactivity.

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