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Stereoelectronic effects in silicon, phosphorus, and sulphur molecules. Quantum-chemical calculations and qualitative orbital models

A A Korkin
Institute of Physiologically Active Substances, Russian Academy of Sciences, Chernogolovka

ABSTRACT. The results of non-empirical quantum-chemical calculations for silicon, phosphorus, and sulphur compounds of different structure are discussed. Qualitative orbital models, which establish a relation between the distribution of electrons and molecular structure and properties, are analysed. A general definition of stereoelectronic effects is presented.

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I. Introduction

The comparative study of the structure and the electronic and energetic characteristics of silicon, phosphorus, and sulphur molecules has been traditional in quantum chemistry in view of the existence of many similar relations, problems, and trends in the chemistry of these elements.[1–23]

The concept of the "stereoelectronic effect" is widely used in both experimental and theoretical studies in organic and organoelement chemistry.[24–31] Until recently, stereoelectronic effects were indissolubly linked to ideas concerning hyperconjugation in its broad interpretation, involving the interaction of lone pairs (LP) with unoccupied σ^* and π^* orbitals. The need to introduce a general concept is associated with the fact that it has been quite firmly established that conformational effects are common to different classes of compounds.[24,32–34] The stability of certain conformations, the changes in the structural parameters and relative reactivities in a series of related compounds, as well as other characteristics can be explained in many instances and treated systematically on the basis of models which include as the initial postulates the "classical" ideas concerning localised electron pairs with allowance for the interaction between these pairs and the antibonding orbitals of neighbouring, mainly vicinal bonds. Deslongchamps[24] defined stereoelectronic effects as "the stereochemistry of particular electron pairs—bonding and anti-bonding".

It is quite evident, however, that, if one considers particular electron pairs as localised pairs, then, within the framework of the above definition, one can discuss only the molecular characteristics which have come to be referred to as cooperative: energies, dipole moments, polarisabilities, vibration frequencies in spectra, structural parameters, etc. We emphasise the term "have come to be referred to as cooperative" because one-electron characteristics such as ionisation potentials, electron affinities, and electronic transition energies are also in essence functions of the entire multielectron system of the molecule. However, the one-electron characteristics and different "effects" coupled with them are not embraced by the definition of "stereoelectronic effects" if the latter are considered within the framework of the model of localised electron pairs, because one-electron characteristics are determined by the properties of delocalised molecular orbitals or, more rigorously, by the behaviour of an individual electron in the field of other electrons and nuclei of the molecule (see also Dewar[35]).

If one abandons the idea that the isolated electron pairs should be regarded from the start as localised, then the definition of stereoelectronic effects includes also the energetic and spatial changes in the frontier molecular orbitals, which occur when the molecular conformations change, this being manifested in the electronic,[36] photoelectron,[37] and X-ray electronic[38] spectra.

In the present review, we shall discuss the literature data in the context of a broader definition (compared with that given by Deslongchamps[24]), in which the stereoelectronic effect is understood as the "deviations of the characteristics of molecules from the values predicted by the base model which can be explained as a result of disregarded interactions and represented in the form of fine details of the spatial distribution of electrons".[39] This definition includes explicitly the concept of the "base model", whose equivalent in the Deslongchamps definition is "isolated electron pairs". Base models can be different in the work of different workers depending on the selected method of study and the ideas concerning the structure and properties of molecules, so that in certain cases it is important to consider beforehand the initial postulates (null approximation) on the basis of which the orbital models of stereoelectronic effects are constructed.

Orbital models of molecules with participation of Third Period atoms are constructed as a rule on the basis of analogous models of the structural analogues, including atoms of the Second Period referring to the same Group in the Periodic Table. Here account is taken of the difference between the electronegativities, the sizes of the valence orbitals, and the presence of the *d* shell in the Third Period atoms.

On passing from the Second to the Third Period, the difference between the energies of the valence *s* and *p* orbitals diminishes, which should promote the hybridisation of the atomic orbitals. However, the opposite trend, caused by the increase in the size of the atoms and in the difference between the radii of the 3*s* and 3*p* orbitals, exerts a greater influence.[17] The presence of 2*p* electrons in

the inner layer results in a greater size of the valence 3*p* orbitals than that of the 3*s* orbitals, which lowers in its turn the effectiveness of hybridisation.[40] The relative increase in the size of the 3*p* orbitals makes the 3*s* orbital "quasi-inner" and, in the presence of non-bonding electron pairs in the atom, the latter are predominantly of the *s* type (see, for example, Magnusson[41] and Korkin[42,43]). Accordingly, the contribution of *p* electrons predominates in the bonding electron pairs. The stabilisation of the "non-hybridised" state of the Third Period atoms is associated also with increase in the size of the atom and decrease of the repulsion of the ligand and the geminal electron pairs, which leads to a smaller steric strain of the bond angles formed by the "pure" *p* orbitals (~90°).

The above differences in the nature of the orbitals of the Second and Third Period atoms make it possible to explain the characteristic features of the structure and chemical properties of silicon, phosphorus, and sulphur compounds. The aim of the present review is to discuss the general trends and the comparative aspects in the development and use of orbital ideas in the chemistry of these elements. We did not attempt to embrace all the available publications on calculations for the silicon, phosphorus, and sulphur molecules. Their number is very great, which undoubtedly reflects the interest of theoreticians in this field. The review deals to a greater extent with studies in which comparative calculations are presented for silicon, phosphorus, and sulphur molecules in relation to one another and in relation to their structural analogues (carbon, nitrogen, and oxygen) and the results obtained are discussed in the language of qualitative orbital models.

II. *d* Orbitals in the chemistry of silicon, phosphorus, and sulphur

The question of the role of *d* orbitals occupies a special place in the theoretical chemistry of non-transition elements. In order to account for the structure and stability of highly coordinated molecules, Pauling[12,44] put forward the hypothesis of the involvement of *d* orbitals in the formation of hybrid atomic orbitals (sp^3d, sp^3d^2). However, whereas in the case of transition metal atoms one is concerned with the hybridisation of *ns*, *np*, and $(n-1)d$ orbitals which have similar energies, the excitation of an electron to the 3*d* shell in the silicon, phosphorus, and sulphur atoms requires an energy of the order of 10 eV, which is close to the ionisation potential of 3*p* electrons.[17,45] In neutral atoms the 4*s* orbitals have lower energies under these conditions than the 3*d* orbitals by an amount of the order of 2eV.[46] When electrons are abstracted, the energy of the 3*d* orbitals decreases to a greater extent than that of the 4*s* orbitals and in the dication M^{2+} the positions of the 4*s* and 3*d* orbitals are reversed.[46] The abstraction of electrons is accompanied by a decrease in the diffuseness of the 3*d* orbitals and their sizes approach those of the valence 3*s* and 3*p* orbitals.

The increase in the coordination number and the increase in the electronegativity of the substitutuent entail an increase in the effectiveness of the charge on the central atom. In this case, as in ionisation, the effective charge of the 3*d* orbitals diminishes and their population increases.[1,17,47]

The fraction of electrons occupying *d* orbitals depends not only on the molecular structure but also on the initial basis set and the exponents of the Gaussian or Slater functions. Since the *d* orbitals of silicon, phosphorus, and sulphur atoms in the ground state are unoccupied, the choice of the exponents of the *d* functions is usually made by optimising the energies of a series of molecules.[47,48] Depending on the nature of the problem and the computational facilities available to the investigator, the *d* orbitals are added to all the atoms of the Second and Third Period or only to those of the Third Period (for further details, see Clark[49]).

The question arises whether one should consider the *d* orbitals of silicon, phosphorus, and sulphur atoms as "normal" valence orbitals, as in the case of transition elements, or as polarisation functions. This problem has been discussed to some extent in numerous publications devoted to non-empirical calculations for silicon, phosphorus, and sulphur molecules. In the general case, an unambiguous answer is apparently not available to this question, because, firstly, the role of the *d* orbitals depends significantly on the molecular structure and the nature of the characteristic investigated and, secondly, the very concept of "valence orbital" permits different interpretations.

Comparative non-empirical calculations in terms of *sp* and *spd* basis sets have shown (see, for example, Refs. 1, 2, 6, and 48–50) that the influence of the *d* orbitals on different molecular characteristics increases with increase in the coordination number of the atom, but the populations of the *d* orbitals are then much smaller than the values which are attributed to the sp^3d^n hybridisation and do not exceed 0.3 of an electron even for SF_6.[51]

The influence of *d* orbitals on molecular geometry has been studied most thoroughly. Calculations using the 3-21G* and 6-31G* basis sets make it possible to determine the bond lengths and bond angles, on average, to within 0.01 Å and 1° respectively,[48] while the 3-21G and 6-31G basis sets lead to much too high bond lengths. This applies to both single bonds in molecules of the type PF_5 or SF_6 and to semipolar or multiple bonds of the type of the phosphoryl or sulphoxide bonds, for example, in the F_3PO and F_2SO_2 molecules. The multiplicity of the P=O abnd S=O bonds in these molecules is due to the reverse transfer of electron density from the O atom to the P or S atom, the contribution of *d* orbitals in this bond not exceeding 25%.[1,52]

The majority of conformational effects in silicon, phosphorus, and sulphur molecules can be described satisfactorily at a qualitative level also without taking into account *d* orbitals, within the framework of hyperconjugation ideas (see the next Section), but the quantitative results as a rule agree best with experimental data when account is taken of *d* orbitals.[48] Exceptions may arise as a consequence of the cancelling of errors due to the incompleteness of the basis set and failure to take into account correlation effects. The presence or absence of *d* orbitals in the basis set can alter the relative stabilities of conformations, but their role is then related to non-specific electrostatic and van der Waals interactions, which depend on bond lengths, bond angles, and electron populations of the atoms.[53–62] For example, allowance for 3*d* orbitals lead indirectly to an increase in the relative stability of the *cis*-conformation of the H_2NSH molecule, because the nitrogen atom becomes less pyramidal,[59] and to a decrease of the relative stabilities of the eclipsed conformation of methyl alcohol and of its S, Se, and Te analogues as a result of the increase in the steric repulsion caused by the decrease in the C–X bond length.[61] The overall populations of *d* orbitals depend only slightly on the molecular conformations.[62]

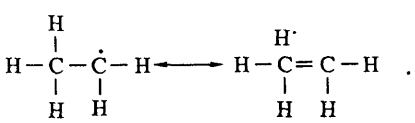
The inclusion of *d* orbitals in the basis set improves the quantitative description of electronic characteristics such as the dipole moments and ionisation potentials. Since, as already mentioned, the bond lengths calculated in terms of *sp* basis sets exceed the experimental values, dipole moments are also found to be too high.[48,62] The electronic characteristics associated with direct electron transfer to unoccupied orbitals, such as UV spectra[63,64] and

electron affinity,[65,66] are more sensitive to the quality of the basis sets and a satisfactory quantitative description of these characteristics requires the inclusion of diffuse functions and functions with a high multiplicity in the basis set. The requirements imposed on the basis set in such cases are also due to the fact that quantitative calculation of the energies of excited states and anions requires allowance for electron correlation effects whose calculation using small basis sets does not lead in many instances to an increase in the accuracy of the results.[48,49] However, it is of interest to note that, as shown by the results of calculations by the X_α method, the lowest-energy states of the SiH_4^-, PH_3^-, HCl^-,[67] R_3SiPh^-,[68] and $RSPh^-$ [69] anions correspond to the presence of an additional electron in the σ^* orbital in the initial molecules, while the σ^* orbitals of the structural analogues of these anions, containing the atoms of Third Period elements, have higher energies than the Rydberg orbitals and do not correspond to stationary states of the anions.

The idea that *d* orbitals are involved in chemical bonding has undergone a significant evolution as computational quantum-chemical methods developed. At the present time, it is possible to test directly many postulates and corollaries of qualitative orbital theories, including also "*d*-orbital effects", by calculating molecular characteristics in terms of *sp* and *spd* basis sets. At the same time, the usual practice in the organic chemistry of silicon, phosphorus, and sulphur is to formulate orbital ideas on the basis of the analysis of molecular characteristics (obtained from experimental studies) using correlation analysis. If any molecular characteristics do not vary in conformity with linear relations of the Hammett–Taft type under these conditions, then this is explained by the effects of $p_\pi-d_\pi$ conjugation, a decrease in the diffuseness of the *d* orbitals under the influence of electronegative substituents, the involvement of *d* orbitals in chemical bonding on the grounds of symmetry considerations, etc. (see, for example, Refs. 23 and 70–75 and the literature quoted therein). Attempts are then made at a quantitative determination of the contribution of *d* orbitals to the measured characteristics and at a comparative estimation of the reliability of alternative orbital models (for example $d_\pi-p_\pi$ or n,σ^* conjugation) from the results of experimental studies.[76–79] Such empirical models can undoubtedly be useful for the classification of particular sets of experimental data, but their importance for the theoretical justification of ideas concerning the nature of chemical bonding should not be overestimated. The majority of "*d*-orbital effects" can be explained in a different way within the framework of models taking into account only valence *s* and *p* orbitals.[27,45]

III. Structural and energetic manifestations of hyperconjugation

The idea of the involvement of C–H σ-bonds in resonance interactions was put forward in the middle of the 1930s[80–82] to explain the structural features and reactivity of hydrocarbons. Wheland[80] attributed the increased stability of the ethyl radical relative to the methyl radical to the resonance stabilisation of the $CH_3CH_2^\cdot$ radical with participation of the so called "non-bonded structures":



Similar structures but with resonance of the ionic type were put forward by Baker and Nathan[81] to explain the reactivity in the series of *p*-alkyl-substituted bromotoluenes. The orbital model for the description of the resonance interaction of this type was developed by Mulliken,[83] who suggested that the term hyperconjugation be used for the description of the resonance interaction of C–H σ-bonds with unsaturated fragments. From the standpoint of the molecular orbital method, hyperconjugation arises as a consequence of the non-orthogonality of the σ and π orbitals, which leads to their mutual delocalisations. For the coplanar disposition of the sp^3 and p_π orbitals of two carbon atoms forming a chemical bond, their overlap amounts to 80% of the $p_\pi-p_\pi$ overlap.[84] However, the energetic and structural manifestations of hyperconjugation in the molecules of unsaturated hydrocarbons are not quite so pronounced as those of the formation of π-bonds in the ethylene molecule or of the conjugation in the benzene or even butadiene molecule, which is associated with the large energy gap between the occupied (σ) and unoccupied (π^*) orbitals.

Immediately after its appearance, the idea of hyperconjugation gained wide currency for the interpretation of various features observed experimentally, which, as shown in Dewar's critical review,[84] were either incorrectly interpreted or were susceptible to an equally acceptable qualitive description within the framework of other models. Dewar's review[84] resulted in appreciable cooling of the chemists' enthusiasm as regards hyperconjugation ideas, the development of which underwent a fresh start only after the appearance of modern computer programmes for non-empirical LCAO-MO calculations with automatic optimisation of the geometry. In particular, many structural features and spectroscopic and chemical properties of silicon, phosphorus, and sulphur compounds, which had been previously explained within the framework of the *d*-orbital model, could be interpreted as hyperconjugation effects.[1,18,85–90]

Three types of resonance stabilisation are considered within the framework of the hyperconjugation ideas: radical (I), cationic (II), and anionic (III):

$$\underset{\text{(I)}}{Y-E-\dot{X}\longleftrightarrow\dot{Y}\ E=X}\ , \qquad \underset{\text{(II)}}{Y-E-\overset{+}{X}\longleftrightarrow Y\ E=X}\ ,$$

$$\underset{\text{(III)}}{Y-E-\bar{X}\longleftrightarrow Y\ E=\bar{X}}\ .$$

For molecules with a closed shell, the direction of the shift of electron density [resonance of type (II) or (III)] is determined to a first approximation by the deficiency or excess of electron density on the group X and the polarised bond E–Y.

The general structural and chemical consequences of hyperconjugation have not been discussed in detail in the studies quoted above and we shall consider here the characteristic features of its manifestation in non-empirical calculations for silicon, phosphorus, and sulphur molecules and their structural analogues containing Second Period atoms.

One of the ways of investigating hyperconjugation effects involves the calculation of the energies of isodesmic reactions. This method was used by Schleyer, et al.[91] to calculate the energies of isodesmic reactions involving disubstituted methanes CH_2XY (X, Y = NH_2, OH, F, PH_2, SH, Cl):

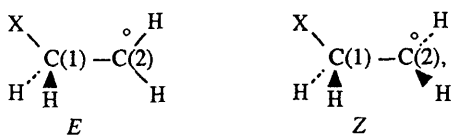
$$CH_4 + XCH_2Y = CH_3X + CH_3Y + \Delta E.$$

According to their data,[91] the stabilisation energy diminishes following the replacement of the group X and/or Y containing Second Period atoms by its structural analogue containing Third Period atoms. When X, Y = PH_2 or SH, the stabilisation energy is small ($0 < \Delta E < 0.5$ kcal mol^{-1}), whereas in the case where X = Cl and Y = PH_2, SH, or Cl, ΔE assumes negative values. A more detailed analysis shows that hyperconjugation involving the lone pairs of the Second Period atoms X predominates (NH_2 > OH > F), decreasing with decrease in the electronegativity of Y (F > OH > NH_2 > Cl > SH > PH_2).

Another way of estimating the effectiveness of hyperconjugation involves the study of the behaviour of structural parameters and molecular energies in the study of conformations. Such study has been described by Magnusson[92] for the series of molecules $X-CF_3$ (X = SiH_3, SiH_2^-, PH_3^+, PH_2, PH^-, SH_2^+, SH) and their structural analogues (X = CH_3, CH_2^-, NH_3^+, NH_2, NH^-, OH_2^+, OH). As in the study of Schleyer, et al. mentioned above, it was concluded here that hyperconjugation weakens on passing from Second Period atoms to Third Period atoms.

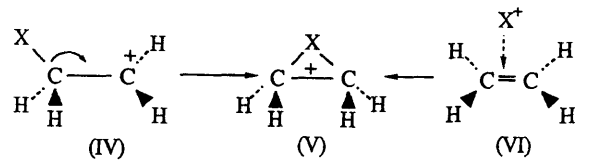
This conclusion is not, however, universal. For example, in the cations $X-CH_2^+$ the π-donor capacity of X = SH and Cl is higher than that of X = F and OH, whereas in the neutral molecules Ph−X, HC≡C−X, and $H_2C=CH-X$ the opposite picture is observed.[93] The authors[93] explained this by the fact that in neutral molecules the resonance integral of the interaction of the lone pair of X and the *p* orbital of the carbon atom of the unsaturated fragment is decisive, its values being higher for Second Period atoms, whereas in the cations the energy gap between the occupied orbital (*n* orbital of X) and the unoccupied orbital (*p* orbital of the carbon atom) is decisive, diminishing on passing from Second Period atoms to Third Period atoms.

The structural and energetic manifestations of hyperconjugation are well illustrated by the relative stabilities of (*E*)- and (*Z*)-conformations of β-substituted ethyl cations, radicals, and anions:[60,93,94]



where the circle denotes "plus" and "minus" signs or the "radical". The cation is stabilised as a result of the interaction of the σ_{CH} and σ_{CX} orbitals with the unoccupied *p* orbital of the C(2) atom. An increase in the electronegativity of the substituent *X* diminishes the contribution of the atomic orbital of the C(1) atom to the σ_{CX} orbital and hence weakens the conjugation with participation of the C−X bond. As a result, the (*E*)-conformation, where σ_{CH} orbitals are involved in conjugation, is more stable for electronegative substituents.[94] The opposite picture is observed in the anions, because in this case stabilisation is achieved as a result of $n-\sigma^*$ interaction. An increase in the electronegativity of the substituent X increases the contribution of the atomic orbital of the C(1) atom to the σ_{CX} orbital and increases the effectiveness of its interaction with the occupied *n* orbital of the C(2) atom.[94,95] In radicals, the interaction of the singly occupied *p* orbital of the C(1) atom with both σ and σ* orbitals is stabilising.[32,96] As a result of this, the electronegativity of X has only a weak influence on the relative stabilities of the (*E*) and (*Z*)-conformations. If X includes Second period atoms, then virtually free rotation about the C(1)−C(2) bond is observed in radicals,[60,97–99] but if X contains Third Period atoms[60] the (*Z*)-conformation is more stable owing to the greater polarisability of the C−X bonds. Analysis showed that under these conditions an increase in the electronegativity of the group X entails a decrease in the contribution of the $\sigma_{CX}-p_C^*$ interaction to the stabilisation of the (*Z*)-conformation, while the contribution of the $\sigma_{CX}^*-p_C^*$ interaction increases.[60]

However, in reality, the situation is more complex. For example, high level *ab initio* calculations with complete optimisation of the geometry (see, for example, Ford and Raghuver[100] and the references therein) have shown that in cations a competition is observed between the "classical" structure (IV) and the "non-classical" structure (V):



Structure (V) can apparently be regarded as a result of very effective $\sigma_{CX}-p_C$ interaction, although at a qualitative level the model of the complex of X^+ with the molecule of ethylene (VI) is no less justified. In β-substituted ethyl anions with electropositive substituents X, the (*Z*) conformation is additionally stabilised as a result of the overlap of the unoccupied atomic orbitals of the atom X (Li, Be, Na, Mg) and the doubly occupied orbital of the carbon atom.[95]

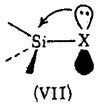
In the Introduction, we already noted that one of the important elements of the construction of orbital models of the structure of molecules containing atoms of non-transition elements of the Third and subsequent Periods is the idea of the decrease of the effectiveness of hybridisation for heavy atoms.[17] This is perhaps most clearly manifested when the structures of molecules comprising tricoordinate nitrogen and phosphorus atoms are compared. In the molecules of tetracoordinate silicon, the "enforced" sp^3-hybridisation of the atomic orbitals is observed by virtue of symmetry, which brings it closer to carbon. In the molecules of dicoordinate sulphur, as in those of oxygen, there is, apart from the predominantly *s*-type hybridised lone pair, a second lone pair formed by the pure *p* orbital capable of participating effectively in conjugation.[56,89,101–103]

The lone pairs of the nitrogen and phosphorus atoms differ significantly in their capacities for $n-\sigma^*$ and $n-\pi^*$ interactions.[41–43,103–107] In the ammonia molecule, the lone pair of the nitrogen atom is localised predominantly in the *p* orbital of the nitrogen atom, whereas in the phosphine molecule the lone pair is localised mainly in the *s* orbital of the phosphorus atom.[43] The energy expenditure on the transition from the pyramidal tricoordinate nitrogen atom to the planar atom, in which the hybrid orbital of the lone pair becomes a pure *p* orbital, is readily "made good" by the energy gain as a result of conjugation with the low-lying unoccupied σ* or π* orbitals of the substituents at the nitrogen atom. On the other hand, the phosphorus atom in the structurally analogous molecules always retains a pyramidal structure. In terms of localised orbitals and hybridisation, this can be explained at a qualitative level by the fact that energy factors are unfavourable for the planar structure involving tricoordinate phosphorus in which the lone pair occupies a *p* orbital. Within the framework of the qualitative molecular orbital theory, the same result is attributed to the smaller (compared with nitrogen) energy gap between the HOMO and the LUMO in the planar PH_3 molecule

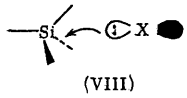
and to its instability as regards pyramidal distortion.[108] The stability of the pyramidal structure of phosphorus-containing molecules is associated, in addition, with the decrease in the steric repulsion of the ligands on passing from Second Period atoms to Third Period atoms due to the increase in size of the central atom.

The difference in the nature of the hybrid orbitals of the lone pairs of the nitrogen and phosphorus atoms is manifested in the protonation of the aminophosphine (H_2NPH_2) molecule.[42,109] The addition of H^+ to the nitrogen atom lengthens the P–N bond, whilst its addition to the phosphorus atom shortens it. This result can be explained by the different capacities of the lone pairs of the nitrogen and phosphorus atoms for $n-\sigma^*$ interaction and is used in the consideration of the mechanism of the acid catalysis of the dissociation of the P–N bond in aminophosphines.[110] The lengthening of the P–N bond on protonation of the nitrogen atom is caused by the inhibition of the $n_N-\sigma^*_{PH}$ interaction and by the increase in the steric repulsion in the coordination sphere of the nitrogen atom. When the phosphorus atom is protonated, the shortening of the P–N bond is explained by the rehybridisation of the valence atomic orbitals of phosphorus (by the increase in the contribution of the *s* orbital to the hybrid atomic orbitals participating in the formation of bonds) and by the strengthening of the $n_N-\sigma^*_{PH}$ interaction in the cation $H_2NP^+H_3$. Such qualitative analysis makes it possible to explain the influence of various substituents on the basicity of amines and phosphines.[43,105,111,112]

The π-acceptor effect of the silyl group is well known (see, for example, Egorochkin[86] and Pitt [87] and the references therein). Previously, this effect was explained by the $p_\pi-d_\pi$ conjugation, but this interpretation was not confirmed by modern non-empirical calculations, which indicate the decisive role of the σ^*_{SiX} orbitals in the π-acceptor capacity of SiX_3 groups[55,56] [$n-\sigma^*$ interaction, structure (VII)]. Another form of the manifestation of the increased acceptor capacity of the SiX_3 groups is $n_\sigma-\sigma^*$ interaction [structure (VIII)], which leads to the formation of *trans*-annular bonds in linear, cylic, and bicyclic silicon-containing molecules.[113–116]



(VII)

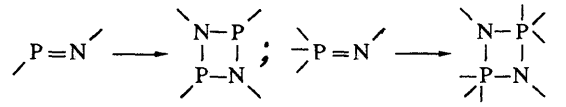


(VIII)

The influence of substituents on the length and strength of the *trans*-annular bond has been studied thoroughly in relation to silatranes.[117,118] A model calculation by the MNDO method[119] showed that the main factor determining the strength of this bond is the energy gap between the n_N and σ^*_{SiX} orbitals. Steric interactions, determining the energy of the transition from the tetrahedral structure of the silicon atom to the bipyramidal structure, also play an important role. The formation of dative bonds as a result of the $n_\sigma-\sigma^*$ interaction has been observed also in molecules of tricoordinate phosphine[120,121] and dicoordinate sulphur,[90,122,123] although not on such a broad scale as for silicon.

IV. Multiple bonds and conjugation

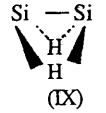
Multiple bonds can be divided into two types depending on whether the octet rule is fulfilled or infringed in the structural formula of the molecule. The first type of multiple bonds are observed in compounds of "normal" valence, in the structural formula of which the octet rule is fulfilled for each atom. For example, the P=N double bond in the iminophosphine (HP=NH) molecule is consistent with this definition, whereas the P=N bond in the iminophosphorane ($H_3P=NH$) molecule, which is usually represented as a double bond, has a different nature.[124] The difference in the nature of the P–N bonds in HP=NH and $H_3P=NH$ is manifested in the analysis of localised molecular orbitals calculated by the Boys method.[125] In the former case, the calculation leads to two equivalent localised "banana" molecular orbitals in the region of the P=N bond, whereas in the second, the presence of two lone pairs at the nitrogen atom, somewhat displaced in the direction of the phosphorus atom, is demonstrated.[124] At the same time, it is essential to note that, despite the difference in the nature of the electron distribution in the region of the PN bonds in iminophosphines and iminophosphoranes, there are also considerable structural (similarity of bond lengths) and chemical similarities between these compounds.[126,127] In particular, the dimerisation reaction



is characteristic of both.

In fact the boundary between the double bonds in "normal" and hypervalent molecules is to some extent arbitrary. For example, the SiO bond in the H_2SiO molecule is so polar that it corresponds to a large extent to the formula $H_2Si^+-O^-$; this brings it close to the PO bond in the H_3PO molecule.[52] On the other hand, hypervalent molecules of the type HPX_2 (X = CH_2, NH, O)[128–131] have a planar structure in which the double bonds are formed as a result of the overlap of the coplanar p_π orbitals, as in the ethylene molecule. At the same time, the polarity of the bonds in the HPX_2 molecules is high, so that their electron distribution is to a large extent consistent with ionic structures.

Compounds containing double bonds involving silicon and trivalent phosphorus remained for a long time chemically "exotic" in view of their instability, which was in its turn determined by the instability of the $p_\pi-p_\pi$ bonds in these compounds. The weakening of the π-bonds in the molecules involving Third Period atoms is caused by the appearance of inner *p* shells in the electronic structure of these atoms.[17,132] The instability of the π-bonds involving Third Period elements has a multiplicity of structural manifestations. For silicon-containing molecules, a series of interesting examples have been quoted in the review of Gordon and co-workers.[133] The replacement of a C atom by a Si atom increases the relative stability of the isomers containing a smaller number of multiple bonds involving silicon. For example, the main isomer of disilaacetylene has the bridged structure (IX) and disilaethylene (X) is more stable than silylsilylene (XI) only to the extent of 3.5 kcal mol^{-1}, while the structural analogue of silapropene has no minimum on the potential energy surface corresponding to the structural formula (XII).



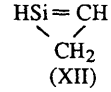
(IX)

$H_2Si=SiH_2$

(X)

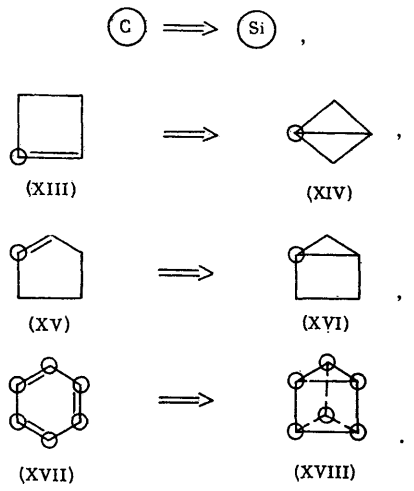
$H_3Si-\dot{S}iH$

(XI)



(XII)

In cyclic molecules the replacement of a C atom by a Si atom diminishes the stability of the unsaturated cyclic compounds (XIII), (XV) and (XVII) compared with the condensed compounds (XIV), (XVI), and (XVIII).



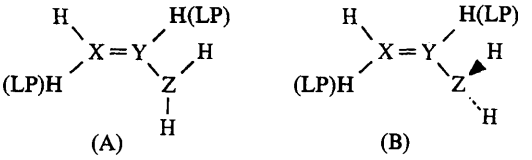
As already mentioned, on passing from Second Period to Third Period atoms, the relative contribution of *p* electrons to the hybrid atomic orbitals participating in the formation of bonds increases and there is a corresponding increase in the *s* electron fraction in the non-bonding orbitals. This factor makes the sp^2-hybridised state of the silicon atom, in which the contribution of *s* orbitals to bonding is large, unfavourable on energy grounds.[134]

As a result of the endeavour of the unpaired electrons in this instance to occupy the *s* orbital, SiH_2 has a singlet ground state, while CH_2 has a triplet ground state. The stability of the singlet state relative to the triplet state in the X_2E (E = C, Si, Ge, Sn) molecules increases with increase in the relative electronegativity of the substituents X.[135] The strength of the double bonds involving the X_2E fragment and the stability of the planar molecular structure are inversely related to the energy of the singlet–triplet transition in X_2E:.[136,137] The stability of the planar structures of unsaturated molecules involving Group IV atoms has been attributed[137] to the competition between the "triplet" and "singlet" mechanisms of the formation of the double bond:

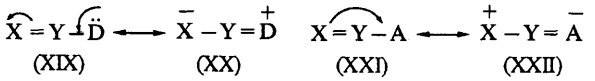


In the former case the optimum overlap of the interacting orbitals is achieved in the planar molecular structure, while in the latter it is achieved in the non-planar structure. The triplet mechanism describes best the formation of the double bond in the ethylene molecule, whereas in the disilene molecule there is a considerable contribution of the structure with dative bonding, which leads to the instability of the planar structure.[138–141]

In our view, the question of the characteristic features of conjugation with participation of double bonds involving Third Period atoms compared with the analogous bonds involving Second Period atoms is of undoubted interest. Calculations have been carried out[142] in terms of the 3-21G* basis set for the molecules $H_nX{=}YH_m{-}ZH_2$ (X, Y = C, N, Si, P; Z = B, N; n = 1, 2; m = 0, 1) in two conformations: (A) and (B).

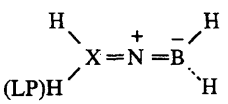


The structural, energetic, and electronic effects, associated with the conformational transitions (A)⟷(B) were analysed. The "classical" ideas concerning the conjugation of the donor (acceptor) group with the double bond are reflected in the form of the resonance of the structures (XIX)⟷(XX) and (XXI)⟷(XXII):



They can be formulated as three main corollaries: (1) conjugation lengthens the double bond and shortens the single bond participating in the conjugation (structural effect); (2) the electron density on the donor (acceptor) group diminishes (increases) in the conformation favouring conjugation (electronic effect); (3) in the absence of steric hindrance, the conformation where the p_π orbitals of the double bond in the substituent overlap to the maximum extent is energetically preferred (energetic effect).

When Y = C, conjugation takes place in conformity with the above rules when account is taken of the polarity of the X=C bond. When Y = N and Z = B, the stronger dative interaction of the lone pair of the nitrogen atom and the unoccupied *p* orbital of the boron atom is superimposed on the conjugation effect, which leads in conformation (B) to the linearisation of the molecule with formation of the allene-like structure (XXIII).

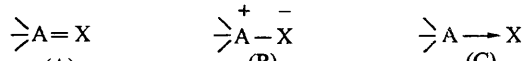


(XXIII)

When Y = Si or P, the effects of the conjugation and polarisation of the σ- and π-bonds under the influence of conformational transitions are similar in magnitude and, depending on their direction, can strengthen one another or cancel out. For example, in the conformational transition (B)→(A) in the $HN{=}P{-}NH_2$ molecule a shortening and not a lengthening of the P=N bond is observed. Similar results were detected also in X-ray diffraction studies on substituted aminoiminophosphines.[143] Analysis of the Mulliken populations has shown that the transition to the conformation (A) is accompanied by an increase in the polarity of the PN bond, as a result of which the latter is shortened. Similar effects had been observed earlier in the study of the influence of the substitution of H by F in the $HN{=}CH_2$ and $HP{=}CH_2$ molecules.[144]

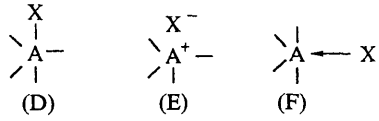
V. Hypervalent molecules and radicals

The concept of hypervalence in the chemistry of non-transition elements is associated with the description of molecular structure in which the octet rule breaks down. This means that in the structural formulae of such molecules the number of ligands and lone pairs surrounding the central atom is greater than four. Compounds containing multiple bonds of the phosphoryl or sulphoxide type (R_3PO, R_2SO, R_2SO_2, etc.) are also classified as hypervalent. Although the number of ligands in these molecules does not exceed four, the multiplicity of the bonds presupposes the involvement of more than four electron pairs in their formation [structure (A)]. The octet rule can be formally fulfilled if the structural formulae of such molecules are written using mesoionic (B) or dative (C) bonds.



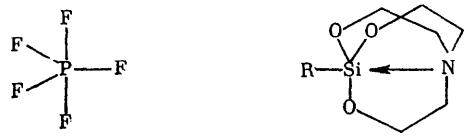
(A) (B) (C)

In many respects, the multiple bonds in the usual and hypervalent compounds exhibit similar properties (see also the previous Section). At the same time, the structural formulae (B) and (C) also reflect definite specific features of these bonds. The formulae (D)–(F), analogous to (A)–(C), are used to represent the structures of molecules in which the hypervalence is due to the increase in the number of ligands linked to the central atom.



(D) (E) (F)

As in the usual molecules, the nature of the chemical bonds in hypervalent molecules is extremely varied: ranging from weak to strong and from covalent to ionic bonds. The use of a particular formula for the representation of hypervalent molecules is determined to a large extent by the specific situation and the wish of the author to emphasise particular properties of the compound. The molecule of phosphorus pentafluoride is usually represented by the formula (XXIV), despite the high polarity of the P–F bonds, whereas in silatranes the *trans*-annular bond between silicon and nitrogen is represented by the dative formula (XXV).

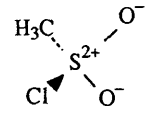


(XXIV) (XXV)

The structural formula (XXV) does not reflect the increase in the positive charge on the silicon atom on formation of a bond with nitrogen, which is observed in calculations for model molecules of pentacoordinate silicon.[145,146]

The wide variety of different types of chemical bonds in hypervalent molecules hinders the selection of the structural, energetic, or electronic parameters which could reflect quantitatively the degree of "hypervalence" of the atom in the molecule. The population of the 3*d* orbitals has been usually employed as such a parameter, although recently this criterion has been subjected to serious criticism (see Reed and Schleyer[1] and the references therein). At the same time, the important role of *d* orbitals in the description of the properties of hypervalent molecules has been emphasised in a number of studies (see, for example, Refs. 147–150). It appears evident nowadays that the quantitative description of the structural, energetic, and spectroscopic characteristics of hypervalent molecules can be achieved only using wide basis sets including 3*d* orbitals. At the same time, qualitative concepts such as that of the model of the reverse transfer of π-electron density from the ligands to the *d* orbital of the central atom (for the description of the multiplicity of bonds of the phosphoryl type) or the model of hybridisation with participation of *d* orbitals in highly coordinated molecules have not been confirmed by the results of modern non-empirical calculations.

According to the data of Reed and Schleyer,[1] based on the results of NBO (Natural Bond Orbitals) analysis,[151,152] the molecule of chlorosulphone and structurally similar hypervalent molecules have a predominantly ionic character corresponding to the Lewis structure (XXVI). The increased multiplicity of the S–O bond is due mainly to the effect of negative hyperconjugation with participation of the lone pair of oxygen and the antibonding bond orbitals σ^*_{SCl} and σ^*_{SC}:



(XXVI)

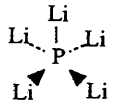
In pentacoordinate and hexacoordinate molecules, the three-centre four-electron bond model is more consistent with the qualitative concept of the hypervalent bond than the model of hybridisation with participation of 3*d* orbitals.

The method of correlation diagrams, proposed previously by Shaik[153] for the analysis of nucleophilic substitution reactions, was used to explain the stability of SiH_5^-,[154,155] sulphuranes, and sulphuranyl radicals.[156] In contrast to Walsh diagrams, in which the dependence of the molecular orbital energies on structural parameters is analysed, the Shaik diagram method is based on the analysis of the energies of the Lewis structures obtained by the valence bond method. The qualitative difference between CH_5^- (transition state in the S_N2 reaction between CH_4 and H^-) and SiH_5^- (a relatively stable intermediate[157]) can be explained by the stabilisation of the latter as a result of the involvement of the σ^* orbital of the equatorial SiH_3 fragment in bonding.

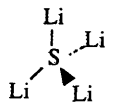
The σ^* orbital of the SiH_3 fragment has less antibonding character, in contrast to the analogous orbital in the carbon analogue, and is localised predominantly on the silicon atom. Although the *d* orbitals do in fact increase the relative stability of the bipyramid in this case, nevertheless they do not determine the qualitative nature of the effect.[158]

The stability of hypervalent molecules as a rule increases with decrease in the electronegativity of the ligands, which is consistent with the ideas based both on the molecular orbital theory and on the valence bond diagram method. At the same time, calculations for the hypervalent phosphorus- and sulphur-containing molecules with the most electropositive ligands (lithium atoms), namely PLi_5, SLi_4, and SLi_6,[159] are in our view of considerable interest.[159] When the geometry is optimised in terms of the HF/3-21G* approximation (with *d* orbitals only in the S and P atoms), all the above molecules have energy minima corresponding to the "non-classical" (from the standpoint of the Gillespie–Nyholm model[160]) structures

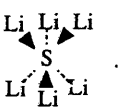
(XXVII)–(XXIX), which are stable as regards decomposition into atoms and the segregation of the Li_2 molecule. Such behaviour is caused mainly by two factors: the increase in electron density on the central atom and the effective bonding of neighbouring lithium atoms via diffuse *p* orbitals:



C_{4v} (XXVII)



C_{3v} (XXVIII)

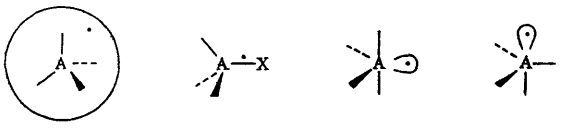


D_{3d} (XXIX)

All three molecules are structurally non-rigid. The $SiLi_4$ molecule, whose energy minimum corresponds to the C_{2v} structure, exhibits a similar behaviour.[161]

Until recently quantum-chemical calculations for molecules containing unpaired electrons were predominantly qualitative (estimates). Modern non-empirical programs for high-speed computers make it possible in many instances to calculate quantitatively the structures and energies of radical species. This increases in its turn the predictive and conceptual value of orbital models based on modern non-empirical calculations for such systems.

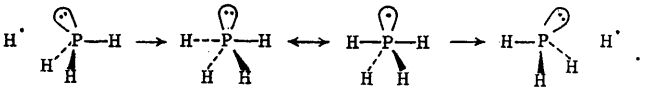
From the standpoint of orbital ideas, the excess electron in hypervalent radicals can be located in the diffuse Rydberg orbital (A) or the antibonding bond orbitals (B) or can occupy one of the coordination sites in the manner of a lone pair [(C) and (D)].



(A) (B) (C) (D)

According to non-empirical calculations, the unpaired electron in the metastable radicals $\dot{N}H_4$[162–165] and $\dot{O}H_3$[166,167] is located in the Rydberg orbital, while the radical $\dot{C}H_5$ is a transition state in the reaction of methane with a hydrogen atom.[168,169] On passing from Second to Third Period elements, the energies of the antibonding orbitals diminish and the "capacity" of the coordination sphere of the central atom increases.

The structure of phosphoranyl radicals (PX_4) is intermediate between (B), (C), and (D) and depends on the nature of the substituents. In radicals of the $Ar_3\dot{P}Cl$ type, the excess electron is located, according to EPR data, in the σ^* orbital of the P–Cl bond.[170–172] On the other hand, according to the results of *ab initio* calculations,[173] such radicals should have a trigonal-bipyramidal structure with the excess electron on the phosphorus atom in the apical position. In the $H_3P-\dot{X}$ (X = PH_3, SH_2, ClH) series, the first member is a σ^* radical with the excess electron localised on the P–P bond, whilst the third has a trigonal-bipyramidal structure, the difference between the apical and equatorial positions of the unpaired electrons amounting to only 0.15 kcal mol^{-1} in terms of the MP2/4-31G* approximation.[174] The radical $H_3P-\dot{S}H_2$ has an intermediate configuration both from the standpoint of its structure and of the distribution of the unpaired electron density. The stabilities of the radicals $\dot{S}iH_5$, PH_4, and $\dot{S}H_3$ have been analysed[175] by the method of correlation diagrams for valence bonds.[153] The phosphoranyl radical is most stable as regards decomposition with evolution of atomic hydrogen. Analysis[175] showed that the stability of hypervalent radicals increases with decrease in the A–H bond energies. The phosphoranyl radical is traditionally stabilised as a result of the involvement of the lone pair of the phosphorus atom in the redistribution of electron density on formation of the trigonal bipyramid:



In $\dot{S}H_3$ such stabilisation is less effective, owing to the greater energy of the abstraction of the lone pair electron from the H_2S molecule.

The radicals $H_2\dot{P}=X$ (X = O, S), investigated by the *ab initio* method,[176] are also hypervalent like the initial $H_3P=X$ molecule. The abstraction of a hydrogen atom from $H_3P=X$ is accompanied by lengthening of the P–X bond and an appreciable decrease in the HPX bond angles. The P–X bond lengths are intermediate under these conditions between the lengths of double ($H_3P=X$) and single (H_2P-XH) bonds. The distribution of spin density also shows that the unpaired electron in the radicals H_2PX is delocalised between the P and X atoms. Thus the structure of radicals of this kind is intermediate between $H_2\dot{P}=X$ and $H_2P-\dot{X}$.

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Modern non-empirical calculations are a source of a wide variety of qualitative and quantitative information, which makes it possible to rethink the existing ideas and formulate new ones concerning the structure of chemical bonds (especially in silicon, phosphorus, and sulphur compounds). This stimulates in its turn the development of experimental research and the synthesis of chemical compounds of new classes.

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