

HYPERCONJUGATION IN ORGANOSILICON CHEMISTRY

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The extent of delocalization interactions in organosilicon compounds was investigated by using the projection method of maximum localization. The results confirm that the accuracy of the localized model for organosilicon compounds is lower than that for analogous carbonyl compounds.

The existence of resonance interactions in saturated compounds (hyperconjugation) belongs to those problems of modern organic chemistry, which have initiated an exceptionally wide discussion and led to a number of controversial views. A critical review of this topic can be found in the already classical book by Dewar¹.

The concept of hyperconjugation has been introduced into chemistry early in the fourties by Mulliken², who suggested to describe the structure of aliphatic free radicals as a resonance hybrid of several mesomeric structures. From the Mulliken concept of resonance stabilization it follows that there is not a substantial difference between the classical conjugation and the hyperconjugation, except for the magnitude of effects that they may cause. These effects manifest themselves as deviations from rules of exact additivity for various molecular properties like bond lengths (additivity of covalent radii), heats of formation (additivity of bond energies) *etc.* The existence of these mostly empirical rules is stipulated by the possibility of describing the electronic structure of molecules in terms of localized orbitals corresponding to individual chemical bonds. However, from the quantum-chemical treatment of the problem of localization it follows that the real structure of a molecule can never be completely reflected in terms of strictly localized orbitals (chemical bonds). This implies that the real structure of a molecule cannot be described exactly by a classical structural formula. Attempting to preserve still the concept of localized chemical bonds, because chemistry lacks at present a more convenient tool for the structure description, we realize the necessity of admitting always a resonance of several mesomeric structures. Nevertheless, this does not mean that the phenomenon of resonance (and thus also that of hyperconjugation) really exists. On the contrary, we can speak of the resonance only in consequence of an effort to preserve the simple concept of localized bonds. The resonance concept can be completely eliminated, for instance, by describing the molecular structure in terms of wave functions. However, such a description can hardly compete in elegance and simplicity with the classical structural formulas; the latter will certainly remain a fundamental tool for the qualitative description of a chemical structure even at the expense of preserving auxiliary concepts like resonance, hyperconjugation *etc.*

In our opinion, the exact theory of chemical bonding can unambiguously contribute to the elucidation of numerous problems and misunderstandings associated with

hyperconjugation, simply by determining the limits of validity of the localized description.

The remarkable success of various empirical rules of additivity shows, particularly in the series of saturated and nonconjugated compounds, that in these cases the localized description is very close to reality. Just in this sense we feel the necessity of interpreting a number of earlier conclusions about the negligible role of hyperconjugation¹. During the past decade, there has come a renewed interest in hyperconjugation; this renaissance originated from the chemistry of organometallic, particularly organosilicon compounds. A number of experimental results evidencing the significant role of hyperconjugation in the organosilicon chemistry can be found in the review by Pitt³, regardless of the sometimes simplified understanding of the hyperconjugation concept. In our opinion, the interaction of bonding (localized) σ - and π -orbitals cannot be identified with hyperconjugation; it is merely a unitary transformation of a basis which can never lead to stabilization of a molecule or to disclosure of deviations from the additivity of molecular properties. Only interactions with the antibonding orbitals ($\sigma-\pi^*$, $\sigma-\sigma^*$, $\pi-\sigma^*$) are responsible for all these deviations. Therefore, molecules showing small energy difference between the occupied and unoccupied orbitals can be expected to display a more pronounced hyperconjugation. Thus it seems to be fully obvious that the renaissance of the hyperconjugation concept comes just from the chemistry of considerably polarizable organosilicon compounds⁴⁻⁶.

The goal of this study was to determine, on the basis of a quantum-chemical approach, the limits of accuracy of a localized model for the description of the electronic structure of organosilicon compounds and thus to examine theoretically a number of experimental results indicating an increased importance of hyperconjugation in organosilicon chemistry.

CALCULATIONS

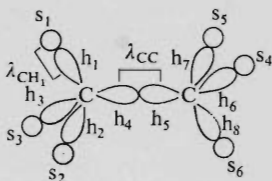
Two types of calculations are to be performed in order to judge the extent of resonance interactions for each molecule. The first one is a standard quantum-chemical calculation using the *ab initio* or a semiempirical method yielding, within the framework of a given approximation, the "exact" wave function. At the SCF level, this function is represented by the Slater determinant Φ_0 constructed from canonical molecular orbitals φ (Eq. (1)).

$$\Phi_0 = \frac{1}{\sqrt{N!}} (\varphi_1 \bar{\varphi}_1 \dots \varphi_{N/2} \bar{\varphi}_{N/2}). \quad (1)$$

This standard quantum-chemical treatment continues in the next step by construction of a localized wave function A_0 . We are arranging this function in the form of the Slater determinant from the individual strictly localized orbitals λ (Eq. (2)).

$$A_0 = \frac{1}{\sqrt{N!}} (\lambda_1 \bar{\lambda}_1 \dots \lambda_{N/2} \bar{\lambda}_{N/2}). \quad (2)$$

Each of these orbitals corresponds to one chemical bond, as represented by a line in the classical structural formula, and is expressed as a linear combination of suitable hybrid orbitals centered on bond-linked atoms and directed along the bond. The construction of strictly localized orbitals can be demonstrated by using a molecule of ethane as an example (Scheme 1).



SCHEME 1

In this example, the orbital λ_{CC} is described by equation (3a) and the orbital λ_{CH_1} by equation (3b).

$$\lambda_{CC} = ah_4 + \sqrt{(1 - a^2)} h_5 \quad (3a)$$

$$\lambda_{CH_1} = bh_1 + \sqrt{(1 - b^2)} S_1. \quad (3b)$$

The values of the expansion coefficients a , b etc. for each individual orbital are obtained by solving the equations (4a) and (4b) (analogous equations hold also for other coefficients).

$$a(q_{h_4} - q_{h_5}) + \frac{(1 - 2a^2)}{\sqrt{(1 - a^2)}} p_{h_4h_5} = 0 \quad (4a)$$

$$b(q_{h_1} - q_{s_1}) + \frac{(1 - 2b^2)}{\sqrt{(1 - b^2)}} p_{h_1s_1} = 0. \quad (4b)$$

These expressions represent the criterion of maximum localization suggested by Polák⁷. Having in hand the overall approximate wave function A_0 , the accuracy of the localized model is described by value of the overlap integral Σ defined by equation (5)

$$\Sigma = \int \Phi_0 A_0 d\tau \quad (5)$$

which can be expressed in the form of a determinant (Eq. (6))

$$\Sigma = \begin{vmatrix} s_{11} & s_{12} & \dots & s_{1n} \\ s_{21} & s_{22} & \dots & s_{2n} \\ \vdots & & \ddots & \\ s_{n1} & s_{n2} & & s_{nn} \end{vmatrix}^2 \quad (6)$$

by using the orbital overlap integrals s_{ij} (Eq. (7)).

$$s_{ij} = \int \varphi_i \lambda_j d\tau \quad (7)$$

In this study, the calculations were carried out at the level of the semiempirical CNDO/2 method. The molecules were assumed as having idealized tetrahedral geometries with standard⁸ or experimental⁹ bond lengths ($r_{\text{SiC}} = 0.187$ nm, $r_{\text{SiH}} = 0.148$ nm). *d*-Orbitals on silicon were not considered.

RESULTS AND DISCUSSION

The preceding analysis reveals that the most general criterion for determining the extent of the resonance interactions is the magnitude of deviations from the rules of additivity of molecular properties. However, these deviations are small, particularly in the series of saturated compounds, and often lie within the limits of experimental error. This certainly points to impossibility of demonstrating unambiguously even the existence of resonance interactions. For this reason we believe that the hyperconjugation and determination of its extent can be approached rather theoretically by comparing the wave function of a real molecule to a localized wave function pertaining to a standard structure with completely absent resonance interactions. It is evident that this standard cannot correspond to any actually existing molecule and that this structure is fully hypothetical. Nevertheless, its wave function can be constructed, for instance, in the form of a Slater determinant which consists of strictly localized orbitals λ corresponding to individual chemical bonds (Eq. (2)). However, from equations (3a) and (3b) it is apparent that the actual form of the localized orbitals λ depends upon the values of coefficients $a, b \dots$ and that various sets of the strictly localized orbitals λ can be constructed for various values of these coefficients. At this point a question arises whether there exist such localized orbitals λ which would yield a localized wave function A_0 approaching as closely as possible to the exact function Φ_0 . A positive answer is given by the method of variational optimization of expansion coefficients of localized orbitals suggested by Polák⁷ and based on projection properties of the density matrix. The orbitals thus obtained can be expected to correspond in a certain sense to maximum localized orbitals, *i.e.*, to orbitals displaying a minimum deviation from the additivity of molecular properties. In other words, the localized description of a molecular structure with the aid of these orbitals will approach most closely to the exact description. These orbitals can thus be utilized for estimating the upper limit of accuracy of the localized model of a chemical structure.

The quantitative characterization of accuracy of the localized description can take advantage, for example, of the value of the overlap integral \sum as defined by equation (5). The value of this integral varies in the range from zero to unity; the better the localized function A_0 reflects the actual structure of a molecule given by the function Φ_0 , the closer is the value of this integral to unity. Moreover, the usefulness

of the overlap integral Σ in characterizing the accuracy of the localized model follows from the fact that its square, Σ^2 , can simply be interpreted physically as a probability that the classical structural formula corresponding to a localized function A_0 does express the real structure of a molecule. The value of Σ^2 thus represents a very objective measure of accuracy of the localized model. Alternatively, this accuracy can be defined by means of the expression $\xi = 100(\Sigma^2 - 1)$, which gives the percent error in the localized wave function A_0 reflecting the actual structure of a molecule.

In this study, both criteria were used to characterize the extent of hyperconjugation interactions concerning the organosilicon compounds. The results of these calculations are presented in Table I which contains for comparison also the data relating to several carbon compounds.

From the Table I it can be seen that there is a quite large accuracy of the localized model used to describe the structures of saturated and nonconjugated molecules. For instance, the structures of methane, ethylene and acetylene are described by the classical structural formulas with an accuracy of 99.9, 93 and 98%, respectively. Larger deviations are encountered only in classically conjugated systems such as toluene and benzene.

TABLE I

Comparison of accuracy of the localized description of a chemical structure in the series of organosilicon and carbon compounds

Compound	Σ^2	$\xi, \%$	Compound	Σ^2	$\xi, \%$
SiH_4	0.97	3	CH_4	0.999	0.1
Si_2H_6	0.90	10	C_2H_6	0.94	6
Si_3H_8	0.66	34	C_3H_8	0.89	11
—	—	—	$\text{CH}_2=\text{CH}_2$	0.93	7
$\text{SiH}_3-\text{CH}=\text{CH}_2$	0.85	15	$\text{CH}_3-\text{CH}=\text{CH}_2$	0.86	14
—	—	—	$\text{CH}\equiv\text{CH}$	0.98	2
$\text{SiH}_3-\text{C}\equiv\text{CH}$	0.90	10	$\text{CH}_3-\text{C}\equiv\text{CH}$	0.88	12
—	—	—	C_6H_6	0.25	75
$\text{SiH}_3-\text{C}_6\text{H}_5$	0.23	77	$\text{CH}_3-\text{C}_6\text{H}_5$	0.22	78
SiH_3F	0.90	10	CH_3F	0.95	5
$\text{SiH}_3\text{CH}_2\text{F}$	0.89	11	$\text{CH}_3\text{CH}_2\text{F}$	0.89	11
SiH_3OH	0.89	11	CH_3OH	0.93	7
$\text{SiH}_3\text{CH}_2\text{OH}$	0.87	13	$\text{CH}_3\text{CH}_2\text{OH}$	0.88	12
$\text{SiH}_3\text{CH}_2\text{NH}_2$	0.87	13	$\text{CH}_3\text{CH}_2\text{NH}_2$	0.88	12
SiH_3NH_2	0.91	9	CH_3NH_2	0.93	7

In agreement with numerous experimental studies which point to a significant importance of hyperconjugation in the organosilicon chemistry, the results in Table I show a markedly decreased accuracy of the localized description for n-polysilanes when compared with n-alkanes. Another general conclusion follows from the fact that the substitution in an arbitrary molecule by alkyl (or silyl) groups manifests itself by a decrease in the accuracy of the localized model; the accuracy decreases with the increasing length and branching of the corresponding alkyl group.

The comparison of a series of closely related methyl- and silyl-substituted compounds reveals that silyl substitution evokes in most cases larger deviations from the localized description than does the substitution by a methyl group; this again provides evidence indicating a more pronounced role of hyperconjugation in the organosilicon chemistry. These results can be interpreted qualitatively on the basis of the following considerations. The extent of deviations from the localized description is determined first of all by the magnitude of interactions between the bonding and antibonding localized orbitals. On the basis of the perturbation theory one can expect that the magnitude of these interactions will be roughly inversely proportional to the energy difference between the corresponding orbitals. In the light of these considerations it seems to be quite obvious that the largest deviations from the localized model are encountered just in the more polarizable molecules, for which this difference is small.

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