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(*p*-*d*) π-Bonding and Hyperconjugation in Vinylsilane*

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Ab initio calculations were performed for $SiH_3{-}CH{=}CH_2$ and $CH_3{-}CH{=}CH_2$. They lead to the result that the bathochromic shift observed in the spectra when replacing the methyl group of propylene by a silyl group can be explained by differences in the hyperconjugation between the silyl- or methyl-group and the vinyl rest of the molecules. This result is gained qualitatively correct already without including silicon *d*-functions. The inclusion of silicon *d*-functions is helpful for a quantitatively accurate description. The *d*-function participation gains within the functional basis employed here considerable weight in the excited states only.

Key words: Vinylsilane – Hyperconjugation

If the bonding properties of elements of a principal group of the periodic system are compared, then an especially large change of these properties from an element of the first period to an element of the second period is observed. In interpreting this fact within the framework of the LCAO-MO-theory the consideration plays an important role that for elements of the second period the lowest excited states of the free atoms are energetically very much closer to the ground state than for elements of the first period. One assumes that the description of the ground state of compounds of these elements of the second or higher period by single-determinant LCAO-MO-functions is more strongly influenced, by including in the SCF-calculations atomic orbitals which are not populated in the ground state of the free atoms of these elements, than is the case for compounds of elements of the first period. For covalent compounds of elements of the 4th to the 7th group especially *d*-functions play an essential role within this concept.

In his classical paper on the hybridization of atomic functions Pauling showed more than 40 years ago that the description of covalent bonds by hybridized functions requires the use of *d*-functions as well as *s*- and *p*-functions for certain stereochemical conformations.

During the intervening years a wealth of experimental material has been assembled from a variety of sources [1], which is interpreted as proof of the *d*-function participation in building up σ-bonds (e.g. in order to explain stereochemical facts, as mentioned above) as well as π-bonds.

There are virtually no recent publications on the bonding properties of such elements as silicon, phosphorus, sulfur, and chlorine which do not treat this subject.

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* Dedicated to Professor H. Hartmann on the occasion of his 60th birthday.

However, all of the significant experimental data for this subject allow various interpretations. The question of the *d*-function participation is to a certain degree a fictitious problem. The extension of a given set of basis functions generally should improve the results of an SCF calculation. Moreover the significance of the correction depends upon the physical quantity considered: e.g. the calculated results for the dipole moment of a molecule are much more sensitive to alterations of the description of the valence shell than results for the total energy. Therefore the aim of the investigation presented here must be defined more precisely. It seems obvious that semi-empirical calculations cannot give essential contributions to solve the problem. Therefore results of all-electron *ab-initio* calculations are presented here. Two compounds, propylene $CH_3{-}CH{=}CH_2$ and vinylsilane $SiH_3{-}CH{=}CH_2$, will be compared. For propylene, a set of basis functions will be used which proved to be large enough to give reasonably good results in previous calculations on similar compounds (Clementi, Moskowitz). An analogous set of functions then is used for vinylsilane, too. In a next step, both basis sets are extended a) by using more *s*- and *p*-type functions, b) by using *d*-type functions. Comparing the results of SCF-computations using these different sets of basis functions, the question of a *d*-function participation—especially of silicon-*d*-functions in this case—can be answered depending on the weight the *d*-functions gain in the SCF-orbitals (population analysis) and on the possibility to reproduce those experimental data which led to the assumption of a *d*-function participation.

Ebsworth has published a summary of reasons for assuming a silicon-*d*-function participation in various silicon compounds. Particularly for vinylsilane a (*p*-*d*) π-interation between silicon and the π-electron system of the vinylgroup is predicted on the basis of spectral effects. The compound $SiH_3{-}CH{=}CH_2$ shows, like α-silylketones $SiR_3{-}COR$, a very pronounced bathochromic shift in the UV absorption spectrum [2–4] compared to the corresponding carbon analogs. The shift affects that band which corresponds to the ($\pi{-}\pi^*$) transition of the vinylgroup (or in the ($n{-}\pi^*$) transition of the carbonyl group respectively. It has a magnitude of approx. 5000 cm^{-1}, or 0.6 eV, – a large effect [1]). The bathochromic shift is assumed to occur if the silicon atom participates through its *d*-functions in the π-electron system of the molecule. Thus the π-electron system of these silicon compounds is more spread out than is the case in the carbon analogs.

In the literature various estimates of the degree of such a (*p*-*d*) π-interaction have been given. Several authors hold it for significant [5–7], others for negligible [8], and still others assume a strong (*p*-*d*) π-interaction only in the excited molecular states, while it is assumed to be negligible in the ground state [2, 4, 9].

Method of Investigation

The calculations were carried out according to the Roothaan SCF-method with the aid of a slightly modified version of the program IBMOL written by Clementi, Davis, and Veillard [10]. The calculations include all electrons of all atoms of the molecules.

All integrals which appear are calculated directly by IBMOL. Electron interaction integrals whose value fall below a set limit were not considered. This threshold was set equal to 10^{-14} here. Atomic units were employed.

Configuration interaction calculations were not carried out. The atomic functions used were of the Boys type [11]. Slater functions, which were determined for atoms by Clementi and Raimondi [12] using Hartree-Fock calculations were approximated using linear combinations of Boys functions with the help of data given by Huzinaga [13].

Hehre, Stewart, and Pople show that expansions of Slater-type radial functions in Gaussian functions converge rapidly [14]. The use of 4 Gaussian functions for the approximation of one *p*-type slater function gives excellent results, and already an expansion using 3 Gaussian-type-functions is such a good approximation that the authors recommend such a representation for molecular calculations even when attempting to achieve a high accuracy.

In the calculations presented here 3 Gaussian-type-functions are used to represent one p_x- (or on p_y- or one p_z-) atomic function, and 2 (H-atoms), 4, or 6 (C- and Si-atoms, resp.) Gaussian type functions to represent the *s*-type atomic functions. The range of this basis corresponds for the H-atoms and for the outer shell of the carbon atoms to the basis used by Clementi and coworkers for their investigation of aromatic systems [15, 16].

A comperatively better description of the chemically and spectroscopically interesting outer MO's [18], here especially of the π-bonding MO's of the molecule, is achieved by using uncontracted atomic functions here, i.e. the atomic functions which participate in this bond are not restricted in their flexibility by using fixed linear combinations of the Gaussian type functions (called "contracted" functions by Clementi); here the expansion coefficients for these functions are determined within the SCF molecular calculation. Moreover some calculations were made using 4 instead of 3 Gaussian-type functions for the carbon-p_z-functions involved in the π-bond.

For the coordinate system selected as shown in Fig. 1, only the d_{xz}- and d_{yz}-functions of the silicon-*d*-functions have symmetry siuted to a (*p-d*) π-interaction with the p_z-functions. The d_{xz}-function gives the maximum and the d_{yz}-function the minimum overlap with the carbon p_z-function. For this reason only *d*-functions of d_{xz}-type were used in the calculation.

Because no criteria existed for the selection of suitable exponential coefficients for the *d*-functions, a preliminary calculation with five d_{xz}-functions with the exponential coefficients 0.005, 0.03, 0.18, 1.0, and 6.5 was carred out. The anomalies which occur for the first virtual orbital when the function with the exponential coefficient 0.005 is used were treated in a separate publication [19]. Further studies were therefore carried out without the use of this function. The results of the calculations suggested that only two d_{xz}-functions with the exponential coefficient 0.06 and 0.15 should be used.

For the bond lengths experimental data were used [20] (Fig. 1, distances in atomic units). One H-atom of the SiH_3 group (H_1 in Fig. 1) lies in the SiCC plane so that the molecule has C_s symmetry. The conformation of the SiH_3 group which can be seen in the figure was determined by O'Reilly and Pierce [20].

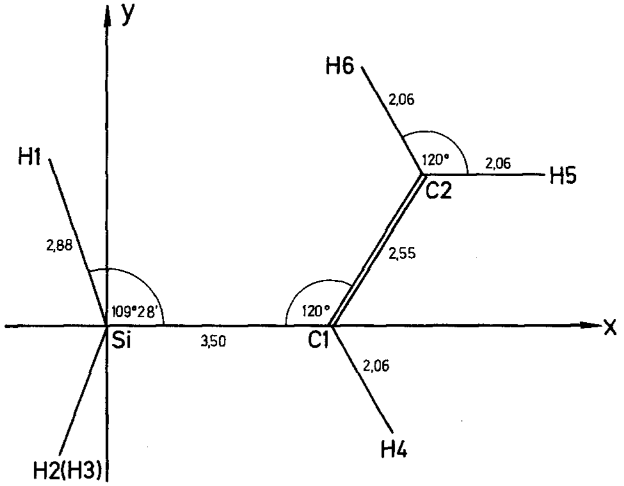

Fig. 1

In the comparative calculations for propylene, too, experimental data were used for the bond distances (2.82 atomic units for the C—C distance between the carbon atom of the methyl group and the neighbouring carbon atom of the vinyl group, 2.06 atomic units for the C—H distance in the methyl group, 125° for the CCC angle) [19]. The conformation of the methyl group in propylene corresponds to that of the silyl group given in Fig. 1 [20, 21].

Results and Discussion

Table 1 gives the gross population $N(r_k)$ and the partial gross population $N(i; r_k)$ of the silicon d_{xz}-functions. $2a''$ and $3a''$ are occupied orbitals in the ground state, $4a''$ is the first virtual orbital. The table shows that the more contracted d-function gains a higher weight in the ground state that the more diffuse d-function. In total the participation of the d-functions in the ground state is small.

Stronger influenced by d-function participation is the electronic excitation energy of vinylsilane. The following values were obtained for the lowest singlet-singlet excitation energy (π—π^*-transition): Vinylsilane with d-function participation 0.349 a.u., vinylsilane without d-function participation 0.358 a.u., propylene 0.369 a.u. The experimentally observed difference between the excitation energies of propylene and vinylsilane is about 0.02 a.u.

Table 1. Gross populations $N(i; r_k)$ and $N(r_k)$. Vinylsilane

r_k	$N(i; r_k)$ in Orbital i			$N(r_k)$
	$2a''$	$3a''$	$4a''$	
$d_{xz}(\zeta = 0.06)$	0.001	0.006	0.126	0.007
$d_{xz}(\zeta = 0.15)$	0.003	0.036	0.148	0.039

Calculations for propylene with inclusion of carbon *d*-functions brought no noticeable participation of *d*-functions in the ground state (for numerical values see [22]) and no influence on the energy difference between the highest occupied and the first virtual orbital. In the case of vinylsilane, on the other hand, it was not possible to reproduce the effect of *d*-function participation by the use of a functional basis which contained instead of 2 *d*-functions 2 additional *p*-functions. It was not checked so far how much the *s*- and *p*-function basis must be enlarged to compensate the effect of the two *d*-functions used in the calculations here.

As from experiment the most important argument for the assumption of a silicon *d*-orbital participation is the observed bathochromic shift in the transition from propylene to vinylsilane, it is interesting that within these calculations this shift is obtained qualitatively correct already without *d*-functions. For the quantitatively correct description of the effect, however, the participation of *d*-functions is necessary within the framework of this calculation.

These results indicate that there should be found another interpretation of the experimental facts, so that the *d*-orbitals play the role of corrective terms only. Such an interpretation is possible on the basis of the hyperconjugation concept. The (p-d) π-interaction can be considered as a special form of a more general type of interaction, the hyperconjugation interaction [23].

Hyperconjugation has meaning in terms of a picture of localized bonds, so that it at first appears that one must go from the delocalized orbitals – as given by the SCF calculation here – by means of an orthogonal transformation to localized orbitals in order to study the hyperconjugation problem. It is possible, however, to discuss some aspects of delocalisation and hyperconjugation by using overlap populations $n(k, l)$ between two centers k and l, gained by Mullikens population analysis [24], without performing transformations of the orbitals.[1] Scherr [25] showed, that some of the quantities defined by Mulliken are invariant with respect to orthogonal basis transformations. In particular this is true for those quantities which include sums over all orbitals or over all orbitals of a given symmetry species, e.g. for $n(k, l)$ calculated by summing the orbital quantities $n(i; k, l)$ over all orbitals i of one symmetry.

Mulliken [24] showed that the overlap population $n(k, l)$ between the centers k and l is a measure of the bonding or non bonding interaction between these centers. For centers which in the sense of a concept of localized bonding are bound, as e.g. for the hydrogen atom and the oxygen atom in the H_2O molecule, $n(k, l)$ has a positive value, which becomes greater the stronger the bond between the centers is. For the non-bonded centers as the two hydrogen atoms in the H_2O molecule, $n(k, l)$ has a negative value.

If these considerations are extended to molecules with conjugated double bonds, as e.g. for butadiene,

$$\underset{a}{CH_2}{=}\underset{b}{CH}{-}\underset{c}{CH}{=}\underset{d}{CH_2},$$

then one finds, that the interaction of the conjugated double bonds is expressed as a positive value of the overlap population between the carbon atoms b and c,

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[1] Investigations with localized orbitals were performed, too. The results agree with the results presented here.

Table 2. Overlap populations $n(i, k, l)$ for vinylsilane (d-functions included)

Orbital i	k, l	$n(i; k, l)$
$1a''$	Si, C_1	-0.002
	C_2, C_1	0.0
	Si, $H_2(H_3)$	-0.006
	C_1, $H_2(H_3)$	0.0
$2a''$	Si, C_1	0.045
	C_2, C_1	0.032
	Si, $H_2(H_3)$	0.155
	C_1, $H_2(H_3)$	0.008
$3a''$	Si, C_1	0.002
	C_2, C_1	0.203
	Si, $H_2(H_3)$	0.046
	C_1, $H_2(H_3)$	-0.011

Table 3. Overlap populations $n(i, k, l)$ and $n(k, l)$ for vinylsilane (without d-functions). $k = C_1$, $l = Si$

	Orbital i			
	$1a''$	$2a''$	$3a''$	$4a''$
$n(i; k, l)$	-0.001	0.040	-0.029	0.100
$n(k, l)$		0.010		

$n(b, c)) > 0$, where in $n(b, c)$ is summed over the occupied π-orbitals. Mulliken shows that for localized double bonds with negligible interaction with one another this value must be negative. Applied to the present question, – hyperconjugative interaction between the silyl or the methyl and the vinyl group –, this means that the overlap population $n(k, l)$ between the silicon atom [or the carbon of the methyl group (C_3)] and the carbon atom C_1 (cf. Fig. 1), calculated as the sum of the partial overlap populations in the occupied π-orbitals, must have a positive value when a hyperconjugative interaction is present. Tables 2–4 give the partial overlap populations $n(i; k, l)$ for the three occupied orbitals which belong to the irreducible representation A''.

If one adds the values for the partial overlap populations $n(i; k, l)$ between the centers Si(k) and $C_1(l)$ of Table 2 then the value of the desired invariant quantity $n(k, l)$ is obtained, $n(k, l) = 0.045$. This value shows a bonding interaction between the silicon atom and the neighbouring carbon atom within the framework of the π-bond system of the molecule. This can be interpreted in terms of a hyperconjugative interaction. As a comparison, the value $n(b, c)$ discussed was calculated by Mulliken by a semiempirical method to be equal to 0.038 for butadiene.

Table 3 gives for comparison the corresponding values for the case that there are no d-functions in the basis set. Here, too, a positive value of $n(k, l)$ is obtained, although it is smaller than the value obtained when d-functions were included. With respect to the hyperconjugation problem the inclusion or non inclusion of silicon d-functions produces no basically different results within the framework of the present study.

Table 4. Overlap populations $n(i, k, l)$ and $n(k, l)$ for propylene. $k = C_1$, $l = C_3$

	Orbital		
	$1a''$	$2a''$	$3a''$
$n(i; k, l)$	0.053	−0.071	−0.015
$n(k, l)$		−0.018	

It is interesting to note that from Table 4 for propylene a negative value (−0.018) is obtained for the overlap population $n(k, l)$ between C_3 (methyl group) and C_1. Thus according to this analysis no hyperconjugation appears to exist between the methyl group and the vinyl group – in contrast to numerous postulations [23], but in agreement with a hypothesis of Bartell [23, 26].

It should be emphasized on the other hand that the values one can calculate for the overlap population $n(k, l)$ are in general very sensitively dependent upon the functional basis used. One should not attempt to give too much importance to the absolute values obtained. The functional basis used is, however, so that it can be expected that the results of this comparative study for similar molecules using corresponding sets of basis functions are meaningful. That is, the conclusion seems justified, that the observed spectroscopic effects are due to the fact, that in vinylsilane a much stronger hyperconjugation interaction between the silyl group and the vinyl group exists than is the case in propylene between the methyl and the vinyl group.

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