

ORBITAL INTERACTIONS IN α -CARBOFUNCTIONAL SILANES*

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Orbital interactions in α -carbofunctional silanes H_3SiCH_2X ($X = NH_2, OH, F$) and corresponding carbon analogues are discussed on the basis of CNDO/2 wave functions and Mulliken's population analysis. Two parallel mechanisms of the electron acceptor action of silicon (the so-called α -effect) are proposed.

Electron acceptor properties of silyl substituents in α -carbofunctional compounds X_3SiCH_2Y were confirmed experimentally several times and were so striking that they gave rise to the term α -effect¹⁻⁵. However, confusion exists in literature as to its mechanism. Recently, Voronkov has suggested² the possibility of intramolecular ($p-d$) σ coordination, (n_x-d) or ($\sigma_{C-X}-d$) interaction. Recent revival of hyperconjugation⁶ has led to attempts to explain the α -effect in this way^{4,5,7}.

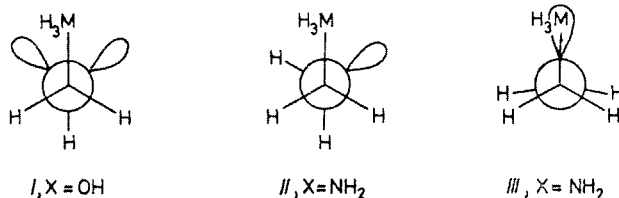
The aim of this work was to analyze possible mechanisms of intramolecular interactions in these compounds on the basis of CNDO/2 calculations. It becomes evident that inclusion of silicon d -orbitals does not lead to qualitative changes and that the acceptor properties of silicon can be well explained in terms of interaction with low lying antibonding orbitals. The possibility of such interactions was suggested by Hoffmann^{8,9} and lately also by Pitt⁷.

CALCULATIONS

Quantum chemical calculations of compounds H_3MCH_2X ($M = C, Si; X = NH_2, OH, F$) were performed by CNDO/2 method¹⁰ with and without inclusion of silicon d -orbitals for idealised tetrahedral geometries with bond lengths taken from literature^{10,11}. In cases where several conformers could exist, geometry with respect to rotation around the C—X bond was optimized. Calculated optimum conformations for carbon analogues agreed both with available experimental data and with results of *ab initio* calculations¹². Calculated optimum conformations for silicon derivatives were identical with those of corresponding carbon analogues. Calculated most stable conformations are *I* and *II*. Conformation *III* does not differ too much in energy from conformation *II*. Therefore when symmetry had to be considered the analysis of wave functions was based on conformation *III*. Results of Mulliken's population analysis¹³ were considered,

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however, always for the most stable conformations *I* and *II*. The use of Mulliken's population analysis for CNDO wave functions is not fully theoretically justified. In spite of objections¹⁴ this procedure is used in literature. Some results of calculations are summarized in Table I.



RESULTS AND DISCUSSION

Important orbital interactions for studied compounds can be depicted by orbital diagrams (Scheme 1). The main interaction which determines the shape of corresponding molecular orbitals is "through space" interaction¹⁵. This interaction leads to the highest occupied HOMO orbital of the $n\text{-}\sigma + \sigma^*$ form. The orbital diagrams also

TABLE I

Calculated Total Energies, HOMO and LUMO Energies (in hartree) and Electron Densities q_M and q_X for Compounds H_3MCH_2X

Compounds	Total energy ^a	HOMO energy	LUMO energy	q_X	q_M
$H_3CCH_2NH_2$	-31.2537 ^b	-0.5140	0.2802	5.2104	4.0252
H_3CCH_2OH	-37.2457	-0.5468	7.2813	6.2550	4.0321
H_3CCH_2F	-45.7883	-0.5885	0.2633	7.2050	4.0463
$H_3SiCH_2NH_2$	-27.8062 ^b	-0.4461	0.0625	5.201	3.546
H_3SiCH_2OH	-33.7956	-0.4917	0.0568	6.247	3.448
H_3SiCH_2F	-42.3341	-0.5042	0.0473	7.196	3.463
$H_3SiCH_2NH_2^c$	-28.1957 ^b	-0.4668	0.0774	5.163	3.549
$H_3SiCH_2OH^c$	-34.1729	-0.5137	0.0707	6.210	3.531
$H_3SiCH_2F^c$	-42.7039	-0.5278	0.0595	7.156	3.532

^a Total energy of the most stable conformations. ^b For conformation *III*, ^c Silicon *d* orbitals included.

show the difference between carbon and silicon derivatives and changes caused by the change of X. It is evident that for X = OH, F the highest occupied orbitals of carbon and silicon derivatives differ in symmetry, which reflects in basicity of these

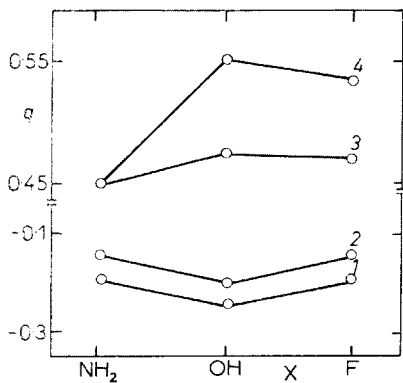


FIG. 1

Dependence of Calculated Electron Densities q_x (1 and 2) and q_{Si} (3 and 4) in Compounds H_3SiCH_2X on X

2 and 3 silicon d orbitals considered, 1 and 4 silicon d orbitals neglected.

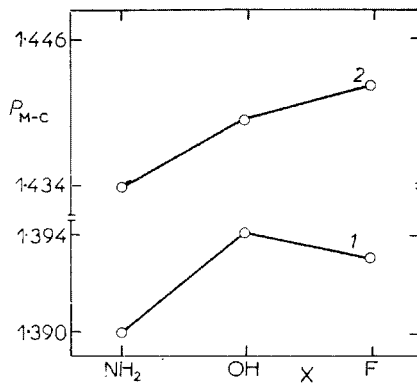


FIG. 2

Dependence of Total Overlap Population P_{M-C} in Compounds H_3MCH_2X on X (1 M=Si, 2 M=C, d orbitals neglected)

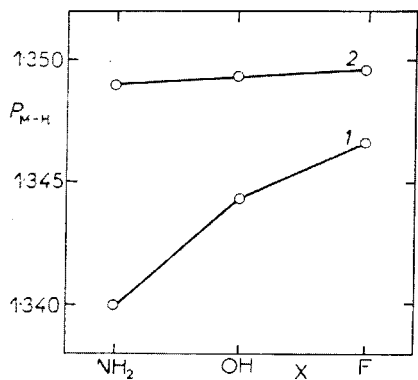


FIG. 3

Dependence of Total Overlap Population P_{M-H} in Compounds H_3MCH_2X on X (1 M=Si, 2 M=C, d orbitals neglected)

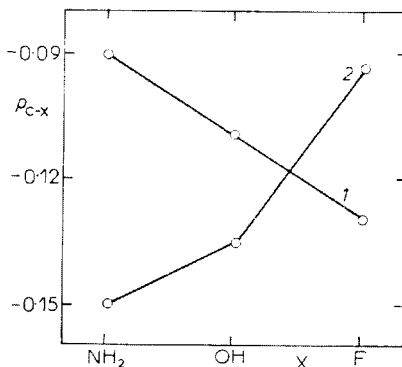
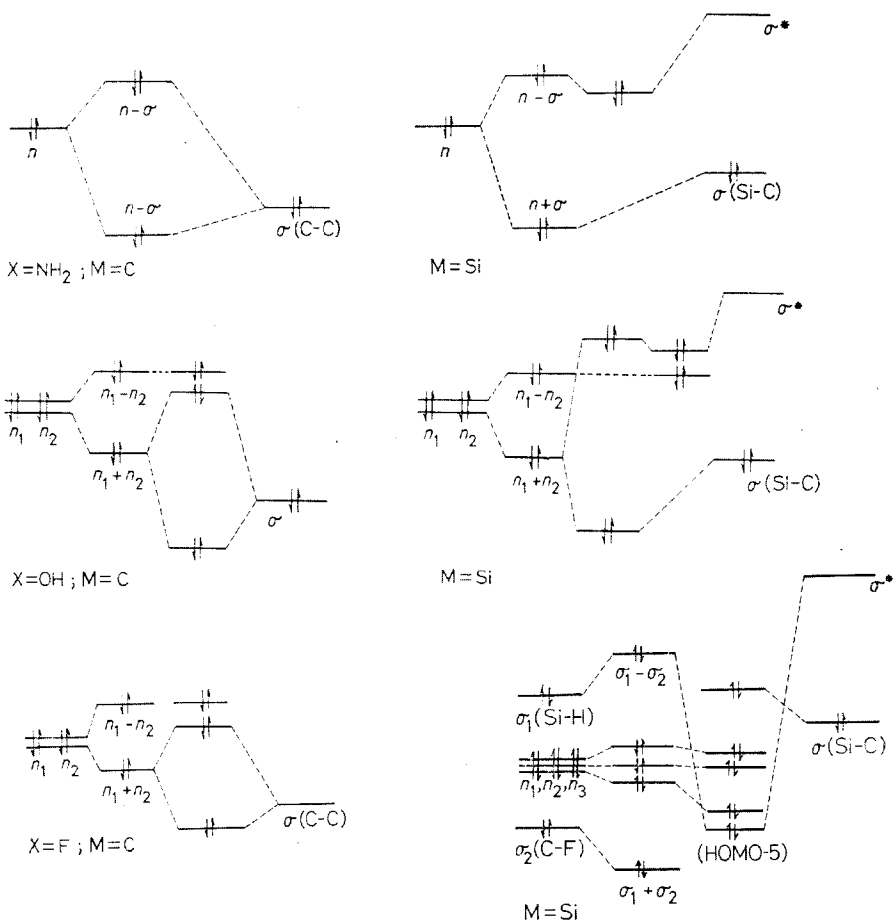


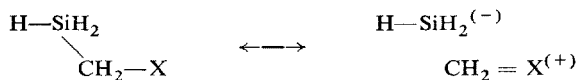
FIG. 4

Dependence of Frontier Overlap Population p_{C-X} (in HOMO) in Compounds H_3MCH_2X on X (1 M=Si, 2 M=C, d orbitals neglected)



compounds¹⁶. It is further obvious that for $X = \text{F}$ and $M = \text{Si}$ the orbital diagram is substantially modified by strong "through bond" interaction¹⁵, which influences the shape of the (HOMO-5) orbital. This interaction is strongest for $X = \text{F}$. This becomes clear from the shape of the lowest unoccupied orbital LUMO which consists of symmetrical combination of $\sigma_{\text{SiH}_3}^* + \sigma_{\text{SiC}}^* + \sigma_{\text{CX}}^*$ bonds. Due to the electronegativity of fluorine, the contribution of σ_{CF}^* to LUMO will be greatest in case of $X = \text{F}$; The interaction of the $\sigma_1 - \sigma_2$ orbital with LUMO is then sufficiently strong, which results in the energy decrease of $(\sigma_1 - \sigma_2)$ to (HOMO-5) orbital. The consequence of these interactions is a decrease of negative charge on fluorine and increase of this charge on silicon (Fig. 1), decrease in total overlap population of the C—Si bond (Fig. 2), increase in total overlap population of the Si—H bond in the sequence $X = \text{NH}_2 < \text{OH} < \text{F}$ (Fig. 3), and also decrease in frontier overlap population

p_{C-F} (Fig. 4). These consequences can all be proved by calculated values of populations and electron densities, as shown in Figs 1–6. In cases where “through space interaction” dominates in total overlap population, the results are in accordance with simple resonance theory which predicts the following limit structures (Fig. 5):



Deviations occur in those cases where “through bond” interaction plays an important role (*e.g.* $P_{\text{Si}-\text{C}}$). Frontier overlap population in HOMO, $p_{\text{Si}-\text{C}}$, follows the trend expected on the basis of resonance theory, which shows dominating role of “through space” interaction in HOMO (Scheme 1). Also possible is interaction of $(n - \sigma)$ HOMO with antibonding orbitals σ_{SiH}^* and σ_{CX}^* , which manifests itself in a decrease of frontier overlap population in HOMO, $p_{\text{C}-\text{F}}$. Interaction of HOMO with $\sigma_{\text{Si}-\text{C}}^*$ is not too advantageous from symmetry reasons, even though it could not be quite excluded, owing to low symmetry. On the other hand, the interaction of $\sigma_1 - \sigma_2$ with $\sigma_{\text{Si}-\text{C}}^*$ is symmetry preferred. It is so strong that it reflects in the total overlap populations $P_{\text{Si}-\text{C}}$.

From the shape of HOMO for silicon derivatives it is also obvious that the contribution of $\sigma_{\text{Si}-\text{H}}^*$ decreases in the sequence $\text{X} = \text{NH}_2 > \text{OH} > \text{F}$. The inclusion of d orbitals leads, of course, to a decrease of both total energy and individual orbital energies. However, contributions of d orbitals do not change qualitatively trends in the charge distribution (Fig. 1). The same conclusions were reached also in a recent

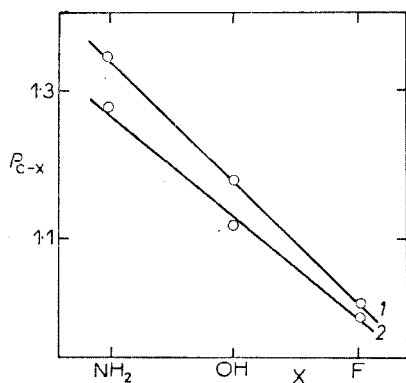


FIG. 5

Dependence of Total Overlap Population P_{CX} in Compounds $\text{H}_3\text{MCH}_2\text{X}$ on X (1 M=Si, 2 M=C, d orbitals neglected)

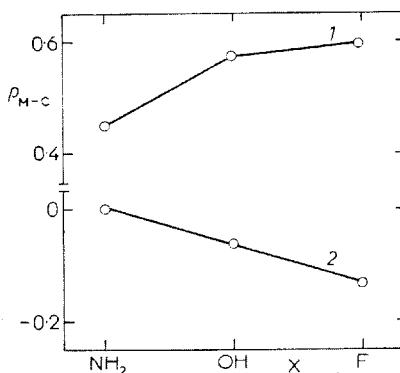


FIG. 6

Dependence of Frontier Overlap Population p_{MC} (in HOMO) in Compounds $\text{H}_3\text{MCH}_2\text{X}$ on X (1 M=Si, 2 M=C, d orbitals neglected)

study using *ab initio* method with contracted gaussian basis¹⁷. Contributions of $\sigma_{\text{Si-H}}^*$ to LUMO are substantially greater than contributions of *d* orbitals.

The results discussed above show that there are essentially two mechanisms of electron acceptor action of silicon. One is "through space" interaction of HOMO with low lying antibonding orbitals. This decreases in the sequence $\text{NH}_2 > \text{OH} > \text{F}$ (superjacent orbital interaction). The other is "through bond" interaction that is strongest in case of the fluoro derivatives. Both these mechanisms of the α -effect has to be regarded as limit cases, since due to low symmetry of studied compounds they can interact with one another. It is also seen that the so called α -effect can be explained without considering the presence of silicon *d* orbitals and further that this effect is the consequence of the higher polarisability of silicon and thus the presence of low lying antibonding orbitals.

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