Analysis of the Ionization Potentials and the Charge Distribution of Silyl and Alkyl Substituted π-Hydrocarbons using the CNDO/2 Method

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Summary CNDO/2 molecular orbital calculations on alkyl and silyl substituted π-hydrocarbons are shown to reproduce correctly experimentally observed trends in charge distribution, despite the fact that d-orbitals are omitted from the silicon basis set.

TRENDS in the properties of derivatives of the Group IV elements are generally interpreted in terms of inductive electron supply (Sn > Ge > Si > C), coupled with electron withdrawal (Si > Ge > Sn >> C) by a p_π-d_π mechanism There is evidence of the importance of the latter in determining properties which involve antibonding orbitals such as e.s.r. and electronic spectra, and reduction potentials.[1] However, the case for rationalizing many ground state properties in terms of d-orbitals is less strong, even though abnormal molecular geometry, ionization potentials, charge distribution, and acidities and basicities have all been explained in terms of p_π-d_π back-bonding. On the basis

of energy considerations and the demonstrated[2–6] importance of σ–π mixing in Group IV compounds, we suggested[3] that differences in ground state σ–π interaction rather than p_π–d_π bonding might possibly be responsible for some of the observed trends in this Group. We now report CNDO/2 MO calculations[7] on a series of carbon and silicon compounds in order to obtain a qualitative estimate of the role of σ–π interaction in determining charge distributions, geometries, and relative acidities, and basicities. The CNDO/2 method has been shown[7,8] to be particularly successful in reproducing these experimental properties. We report here on the theoretically derived charge distributions and I.P.'s of silyl and alkyl substituted π-hydrocarbons.

The standard CNDO/2 procedures and parameters[7] have been employed, except that d-orbitals were omitted from the silicon basis set. The ethynyl system X–C≡C–H, is the simplest π-hydrocarbon which has been studied, and is particularly informative because its cylindrical symmetry

analogues are always more electron supplying. On the other hand, the –CH₂SiH₃ group is substantially more electron releasing than either the methyl or ethyl group. For the substituents with less than C_{3v} symmetry, the original equivalence of the two acetylenic π MO's is destroyed, and the resulting non-equivalent charge distribution is a reflection of the unequal σ–π mixing in these compounds.

These theoretically derived charge distributions are in good qualitative agreement with distributions derived experimentally from n.m.r. chemical shifts,[9] i.r. absorption intensities,[10] and Hammett σ constants.[1,11] While inclusion of d-orbitals increases the I^- effect of the SiX₃ group, these calculations suggest that the differences in the substituent effects of the silyl and alkyl groups are by no means uniquely associated with $(p$–$d)\pi$ bonding.

The CNDO/2 method is known to reproduce energy levels and I.P.'s poorly,[12] although trends within a series are generally satisfactory. Nevertheless these calculations do

Charge displacement of substituted acetylenes X–C≡C–H
α β

Substituent X	SiF₃	CF₃	SiH₃	SiH₂CH₃	Si₂H₅	H	CH₃	C₂H₅	CH₂SiH₃
π_α	− 34	−26	− 1	+ 1	+ 5	0	+15	+26	+35
	− 34	−26	− 1	− 4	− 2		+15	+ 5	+ 2
π_β	+ 50	+32	+ 7	+ 1	− 5	0	−32	−53	−76
	+ 50	+32	+ 7	+ 10	+ 8		−32	−21	−18
σ_α	−229	−29	−168	−174	-154	−64	−24	−27	−22
σ_β	− 77	−69	− 70	− 69	− 69	−64	−53	−50	−46
$\Sigma\Delta\pi$	+ 33	+13	+ 13	+ 8	+ 6	0	−35	−43	−57
$\Sigma\Delta\sigma$	−178	+30	−110	−115	− 95	0	+51	+51	+60

a Charge displacements are expressed as $(1.000 - q) \times 10^3$, where q is the electron population per orbital; the numbers listed for the π orbitals correspond to the displacements in the two orthogonal p_π orbitals on each of the α and β acetylenic carbon atoms; for the σ orbitals the numbers are the sum of the displacements in the corresponding s and p_σ orbital. $\Sigma\Delta\pi$ and $\Sigma\Delta\sigma$ refer to the sum of charge displacements relative to X = H. Substituents are arranged in order of π-electron supply.

facilitates separation of σ and π effects. The Table indicates that, as expected, the SiH₃ group donates electrons strongly to the acetylenic σ system (mostly $p_{Si} \to s_C$). However, the SiH₃ group also *withdraws* electrons weakly from the π system, even though d-orbitals are not included in the basis set. The same result is obtained for vinyl and phenyl silane (Figure 1). Thus, using Pople's terminology,[7]
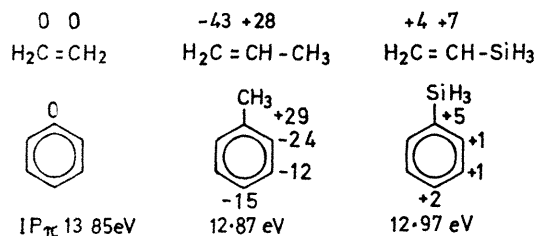
show that, because of σ–π mixing, the π-MO's will invariably be a linear combination of the hydrocarbon π-orbitals and the substituent σ orbitals of appropriate π-symmetry. The degree of mixing and splitting of these sets of σ and π orbitals will depend on their relative energies, overlap, and the resonance integral β. Thus, although there is generally better energy matching of the $\sigma(SiX_3)$ orbitals with
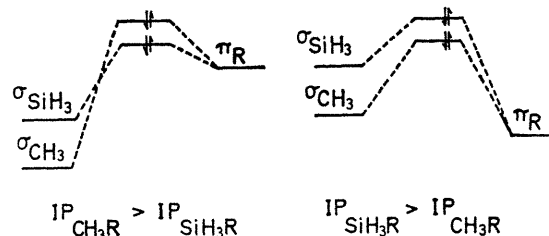

FIGURE 1. *Charge distribution of silyl and methyl benzene and ethylene.*

FIGURE 2. *Perturbation analysis of the relative I.P.'s of CH₃R and SiH₃R.*

the SiH₃ group is $+I^-$ when attached to a carbon π system, in contrast to Me which is $-I^+$. This electron withdrawal, which must result from mixing of the acetylenic π orbitals with the Si–H orbitals of appropriate symmetry, is less for the substituents –SiH₂CH₃, and –SiH₂SiH₃, but greater for SiF₃. However, the changes are small and the carbon

π orbitals, the fact that overlap is poorer and $\beta(C)$ (−21 eV) $\gg \beta(Si)$ (−13 eV) means that a silyl substituent will not necessarily perturb the energy of a π-MO to a greater extent than an alkyl substituent. The I.P. of the silyl derivative will generally only be smaller than that of the methyl derivative when the σ contribution to the MO is

dominant, *i.e.* when the energy of the σ electrons is lower than that of the hydrocarbon π electrons, and β is relatively unimportant (Figure 2).† This is clearly not the case for the phenyl system‡ and the calculated order of I.P.'s is $C_6H_6 >$ PhSiH$_3$ > PhCH$_3$ (Figure 1).

While it may be argued that results of CNDO type MO calculations may be manipulated by appropriate choice of parameters and approximations, the main point to be made is that *in principal* there are mechanisms other than $(p-d)\pi$ bonding which will at least partially explain the

trends in I.P.'s and charge distributions observed for Group IV derivatives. For example, using only a qualitative valence bond description, the structural contribution:

$$H-C\equiv C-SiH_3 \rightleftharpoons H\cdot\overset{+}{C}=C=SiH_2 + H^- \quad \text{can explain the}$$

contrasting charge distributions, where the difference in behaviour of the CH$_3$ and SiH$_3$ groups stems from the reversed polarity of the C–H and Si–H bonds.

† This is equally true for other π systems, *e.g.* R$_3$SiX, X = halogen, O, N, etc.
‡ A useful guide is the relative I.P.'s of the parent hydrides, *i.e.* C$_6$H$_6$, 9·24 eV; SiH$_4$, 12·2 eV; CH$_4$, 12·7 eV.[13]

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