

PHOTOELECTRON SPECTRA AND MOLECULAR PROPERTIES XV*. THE EFFECTS OF α - AND β -SILYL SUBSTITUENTS ON π -SYSTEMS

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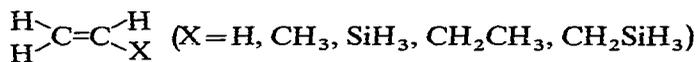
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SUMMARY

The photoelectron spectra of substituted ethylenes, $H_2C=CHX$ ($X=H, CH_3, SiH_3, CH_2CH_3, CH_2SiH_3$) are discussed in the light of results of CNDO-type molecular orbital calculations. The characteristic shifts of the first bands are explained in terms of a qualitative model for the substituent effects of α - and β -silyl groups upon π -systems.

INTRODUCTION

The dichotomous donor–acceptor effects of silyl substituents upon π -systems has long been a topic of interest^{2,3,4,5}, and the ethylene moiety—the simplest of π -systems—is well suited to their investigation. Trimethylsilyl-substituted ethylenes have already been thoroughly investigated by various other techniques^{5a,f}, and the photoelectron (PE) spectra of two such derivatives have been reported recently⁶. In order to eliminate extraneous influences and to facilitate the understanding of specific effects, the photoelectron spectra of five simpler ethylene derivatives have been studied with the aid of CNDO/2 and modified CNDO/2 MO calculations.



It should be noted at this point, that PE spectroscopy simply allows the measurement of energy differences between electronic states, and it is only via Koopman's theorem that these energies can be associated with factorized molecular orbitals⁷. The perturbation of the latter may be further partitioned into various effects (inductive, conjugative, etc.), and these in turn may exhibit some dependence on geometry (conformation). Although this simplification of the true molecular states is contrived, it does provide an instructive, if artificial, model for substituent effects, the component contributions of which may be derived from the proper comparisons within series of compounds.

* For part XIV see ref. 1.

PHOTOELECTRON SPECTRA

The PE spectra of the five ethylene derivatives are given in Fig. 1⁸. If all occupied valence basis set MO's were within the 6.00–21.21 eV range, the number of bands expected would be six ($X = H$), nine ($X = CH_3, SiH_3$) and twelve ($X = CH_2CH_3, CH_2SiH_3$) respectively. However, those MO's consisting largely of carbon 2s and silicon 3s orbitals are generally beyond the range of the He(I) source; the situation here is further complicated by the overlapping of spectral bands and ambiguous intensity ratios. Nevertheless, the molecular orbitals of prime concern, namely the highest occupied π -levels, certainly correspond to the well isolated first peaks of the five spectra; these assignments are confirmed for the three hydrocarbons by the fine

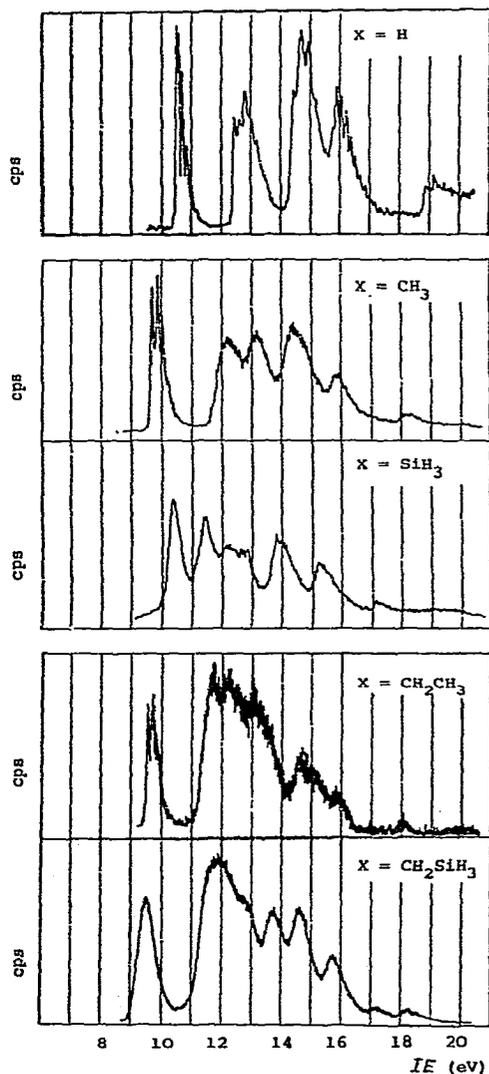


Fig. 1. Photoelectron spectra of five ethylene derivatives, $H_2C=CHX$.

TABLE 1

ASSIGNMENT OF THE IONIZATION ENERGIES OF THE MONOSUBSTITUTED ETHYLENES BASED ON MOLECULAR ORBITAL CALCULATIONS^a

$H_2C=CHCH_3$		$H_2C=CHSiH_3$		$H_2C=CHCH_2CH_3$		$H_2C=CHCH_2SiH_3$	
Orbital type	IE (eV)	Orbital type	IE (eV)	Orbital type	IE (eV)	Orbital type	IE (eV)
2 a''	9.86	2 a''	10.37	3 a''	9.72	3 a''	9.49
7 a'	12.22	7 a'	11.46	9 a'	11.75	9 a'	11.72
6 a'	13.16	6 a'	12.24	8 a'	12.24	8 a'	11.92
5 a'	14.40	1 a''	12.7	2 a''	12.52	2 a''	12.74
1 a''	14.7	5 a'	13.80	7 a'	13.05	7 a'	13.67
4 a'	15.94	4 a'	15.22	6 a'	13.68	6 a'	14.59
3 a'	18.2	3 a'	17.15	5 a'	15.83	1 a'' ?	15.61
				1 a''	18.1	5 a' ?	17.2
						4 a'	18.3

^a The symmetry assignments are for the point group C_s .

structure exhibited ($X=H$, $\nu=1230$ (ref. 9); $X=CH_3$, $\nu=1370$; $X=CH_2CH_3$, $\nu=1370$ cm^{-1}). There being no other direct evidence, tentative assignments for the remaining PE bands have been made solely on the basis of the calculated orbital sequences. (Fig. 1 and Table 1.)

DISCUSSION

The initial band of each PE spectrum, unequivocally assignable to the highest occupied π -orbital, is seen to undergo characteristic shifts; the magnitudes of the first ionization energies (IE_1) conform to the following sequence: $X=CH_2SiH_3 < CH_2CH_3 < CH_3 \ll SiH_3 < H$. When treated properly (*vide infra*), the results of the MO calculations reproduce this sequence surprisingly well. (Fig. 3.)

In the case of the α -substituted ethylenes, the introduction of a methyl or silyl group produces a destabilization of the occupied ethylenic π -orbital, which, in terms of substituent effects, arises from two factors—an inductive effect and a symmetry-allowed antibonding admixture of the out-of-plane C-H and Si-H σ -bonds (hyperconjugation). In view of the valence state ionization potentials (VSIP) (C 2s, 19.54 eV; C 2p, 11.20 eV; Si 3s, 14.76 eV; Si 3p, 7.90 eV)¹⁰, the inductive donor strength of the H_3Si group would be expected to exceed that of the H_3C substituent. Likewise, the lower VSIP's of silicon should guarantee more effective σ/π -mixing¹¹ in the silyl derivative. Nevertheless, the destabilization in vinylsilane is only a fraction of that in propylene. This observation can be explained in terms of the counter-influence of vacant Si orbitals of π -symmetry (3d and/or 4p) which afford a mechanism for delocalizing and concomitantly stabilizing the ethylene π -electrons. This description is in keeping with the results of the calculations which are qualitatively depicted in Fig. 2. Moreover, corroborative evidence for the π -delocalization is provided by the spectra, which show that while the π -band of propylene displays well resolved fine structure, that of vinylsilane is broad and featureless.

In the case of 1-butene ($X=CH_2CH_3$) and allylsilane ($X=CH_2SiH_3$), the

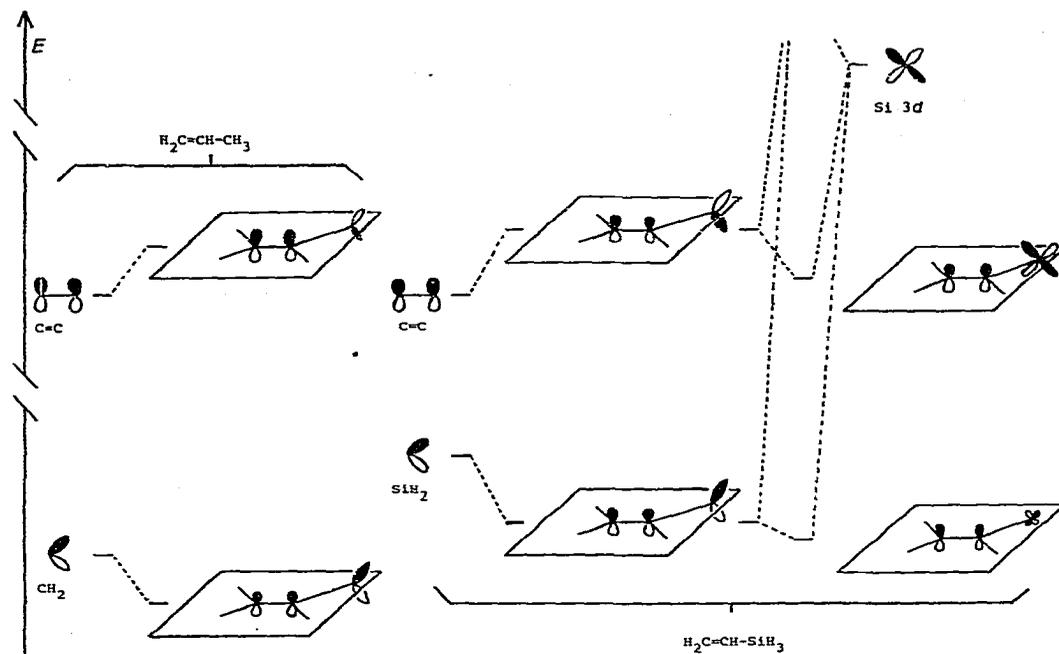


Fig. 2. Qualitative MO scheme for the perturbation of the ethylenic π -orbital by methyl and silyl substituents.

situation is complicated by the significant differences in the π -orbital energies to be expected in the three distinctive conformations I, II, III. Weidner and Schweig⁶, who considered only conformations II and III for allyltrimethylsilane, chose to interpret

	(I)	(II)	(III)
M = C			
E_{total}	937.7699	937.8407	937.7129 (eV)
M = Si			
E_{total}	855.6994	855.2013	855.0325 (eV)

their results solely in terms of II on the basis of a calculated 3–5 kcal/mole difference in total energies. While conformation (I) may be reasonably excluded in light of steric considerations in the instance of the trimethylsilyl derivative, the calculated total energies of the simpler allylsilane and 1-butene favour a free rotation model. The energies of the π -orbitals within such a model can be roughly approximated by the simple, statistically weighted average given in eqn. 1.

$$\varepsilon_{\pi}(\text{ave}) = \frac{\varepsilon_{\pi}(\text{I}) + 2\varepsilon_{\pi}(\text{II}) + \varepsilon_{\pi}(\text{III})}{4} \quad (1)$$

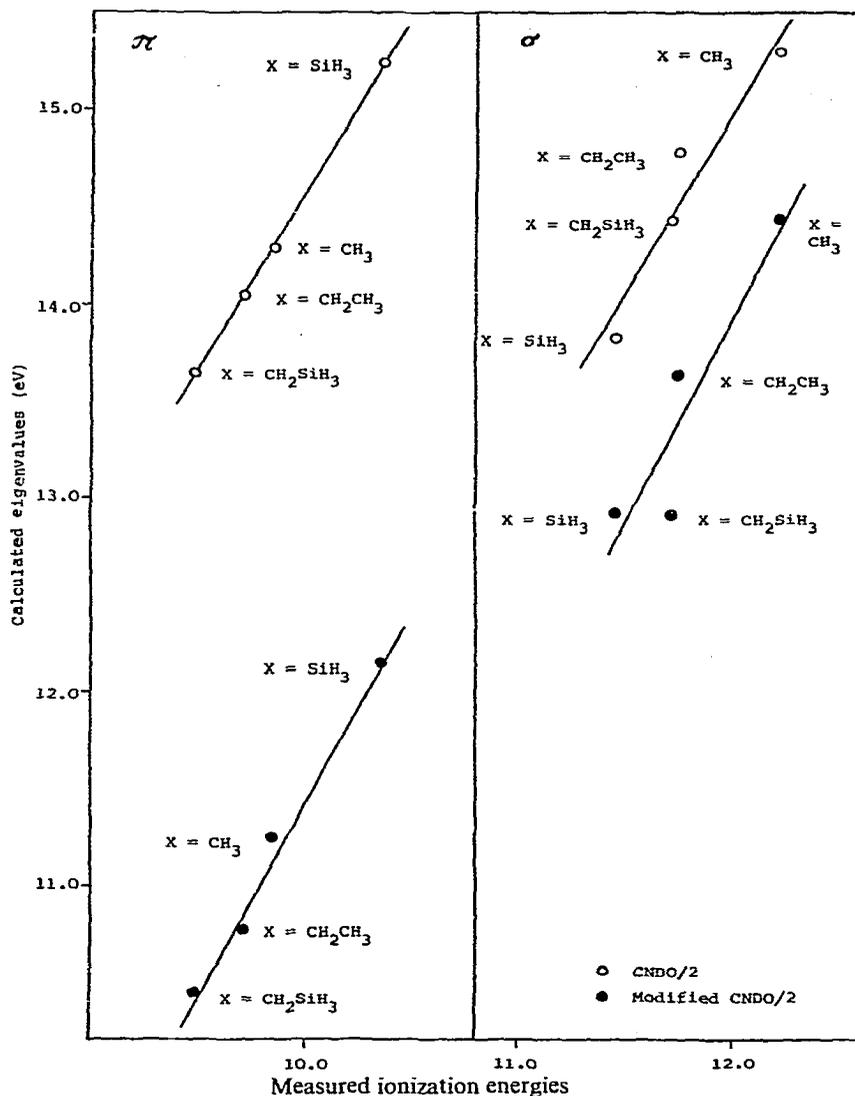
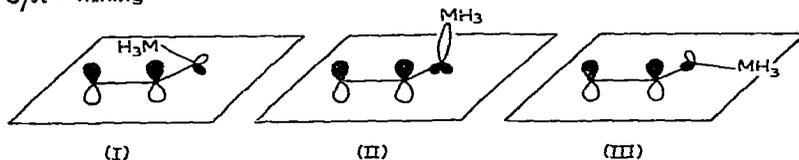


Fig. 3. Correlation of calculated eigenvalues with measured ionization energies of the two highest occupied orbitals in the monosubstituted ethylenes, $H_2C=CHX$.

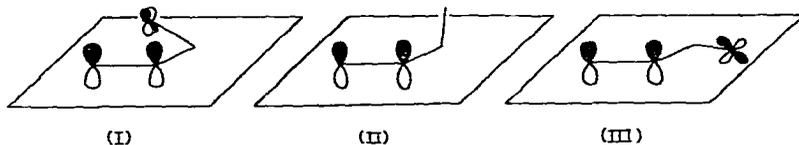
As indicated in Fig. 3, the results obtained by this method are in good agreement with the measured vertical ionization energies*.

With the aid of the following simple diagrams, the influences governing the energies of the first π -orbitals may be assessed:

* Figure 3 clearly illustrates one of the primary differences between the two methods of calculation: the reparametrization in the modified CND0/2 technique tends to destabilize π -type orbitals. In addition, it should be noted that while the normal CND0/2 results appear to provide better numerical correlations with the experimental data, they also reverse the order of the two highest occupied orbitals in vinyl- and allylsilane; the modified CND0/2 calculations correctly predict this π/σ -ordering, while the remaining orbital sequences are similar for both methods.

σ/π - mixing

Participation of Si 3d orbitals



1. The major σ/π -mixing in conformations (I) and (III) involves the C-H bonds of the methylene unit, and is likely to provide comparable degrees of destabilization in 1-butene and allylsilane.

2. The σ/π -mixing in (II) consists primarily of the anti-bonding admixture of the $\text{CH}_2\text{-M}$ single bond (*i.e.*, $\text{CH}_2\text{-CH}_3$ or $\text{CH}_2\text{-SiH}_3$) into the ethylenic π -bond, where the higher-energy carbon-silicon bond (ΔVSIP) should yield a considerably greater destabilizing contribution.

3. Conformations (I) and (III) allow a certain amount of *d*-orbital participation in allylsilane, the effect of which should be to mitigate the destabilizing effects of σ/π -mixing.

Not only is this interpretation consistent with the CNDO/2 calculations, but it is also supported by the PE spectra: despite the much larger destabilizing inductive and hyperconjugative effects to be anticipated in allylsilane on the basis of VSIP's, the highest occupied molecular orbital is only moderately destabilized relative to that in 1-butene; furthermore, the first band of the spectrum of the former is very broad and devoid of fine structure, just as was the case in the spectrum of vinylsilane.

A distinct disadvantage inherent in monosubstituted ethylenes as a model system is their low symmetry: the only possible classification of orbitals is the distinction between π and σ (a'' and a' in C_s), and even this becomes unclear for 1-butene and allylsilane in conformation II (C_1). The association of particular molecular orbitals with specified units of the molecules becomes especially difficult (Fig. 4), and the applicability of a simple perturbation model is thereby severely limited. It is seen in Fig. 4, however, that the highest occupied σ -orbital of each the 4 substituted ethylenes contains major contributions from the specific valence bonds—the $\text{H}_2\text{CCH-C}$ and $\text{H}_2\text{CCH-Si}$ bonds in propylene, 1-butene, and vinylsilane, and the $\text{CH}_2\text{-Si}$ bond in allylsilane. Assuming that the second ionization energies (IE_2) of the corresponding spectra are essentially due to the expulsions of electrons more or less localized in these bonds, they are then found to display an intelligible pattern. The second ionization energy of allylsilane is greater than that for vinylsilane, due to the stabilization of the carbon-silicon bond of the former stemming from its interaction with the $2p\pi$ orbitals of the ethylene moiety. In contrast, IE_2 in 1-butene is smaller than IE_2 in propylene since the highest occupied σ -orbital of the former corresponds mainly to a bond which cannot be directly involved in σ/π -mixing, but which is destabilized by the inductive effect of the terminal methyl group. The correlation of the calculated and measured

second ionization energies (treated exactly as were the IE_1 values, *cf.* eqn. 1) is also given in Fig. 3.

From Fig. 4, it can also be seen that a second π -orbital should occur within the PE spectra of the substituted ethylenes. The ionization energies of these MO's would be of interest, inasmuch as π -type back-bonding involving Si $3d$ and/or $4p$ orbitals could be expected to be minimized at deeper energy levels. However, the uncertainty involved in assigning the remaining portions of the spectra does not warrant their further consideration.

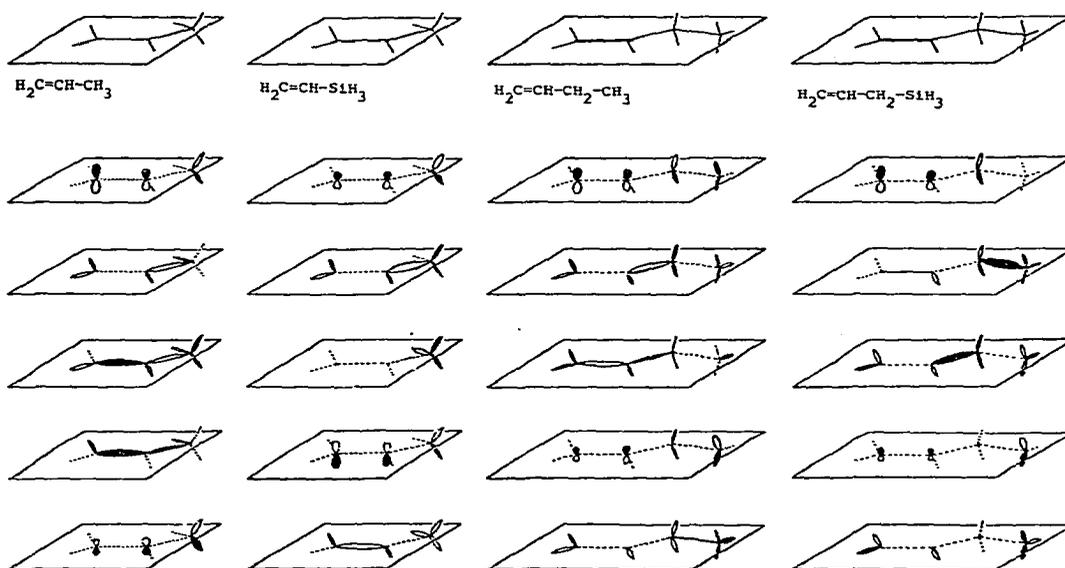


Fig. 4. Diagrams of the five highest occupied orbitals in the monosubstituted ethylenes, based on SCF-MO calculations.

In conclusion, it should be stated that the energy shifts of the first two bands of the PE spectra of the ethylene derivatives $H_2C=CHX$ (reproducible by CNDO/2 calculations) allow the development of a qualitative perturbation model for substituent effects. The well known arguments concerning the donor-acceptor influences in α -silyl derivatives of π -systems are once more substantiated. The properties of the β -silyl derivatives, which have been variously explained in terms of inductive effects⁵, σ/π -mixing¹¹, and 1,3- $p \rightarrow d\pi$ interactions, appear to require consideration of all three for proper understanding. We emphasize again, however, that the separation of these several effects is only a model—a means for gaining some insight into the nature of the states whose energies are the only measurable quantities.

EXPERIMENTAL

Calculations

SCF-MO calculations of two types were obtained for all molecules: CNDO/2¹²⁻¹³ and modified CNDO/2, the latter having been reparametrized according to the method of Jaffé and Del Bené¹⁴. Both types of calculations included Si $3d$ orbitals in the basis set.

Spectra

The spectrum of ethylene was taken from the literature⁸. All other spectra were recorded with a Perkin-Elmer PS-16, employing a 127° electrostatic deflection-type analyzer, and were calibrated with argon. The samples of vinyl- and allylsilane were introduced into the spectrometer without exposing them to air.

Synthesis

The preparations of vinyl- and allylsilane were carried out by established methods^{1,5}.

Vinylsilane was obtained in 90% yield via the LiAlH_4 reduction of vinyltrichlorosilane in n-butyl ether¹⁶. The reduction was followed by fractional condensation, in which the product was collected by trapping with a cold bath at -136° . Purity was ascertained by molecular-weight determination (found: 58.5; calcd.: 58.1), as well as by NMR and IR spectroscopy¹⁷.

Allylsilane was prepared via the synthesis and subsequent reduction of allyltrichlorosilane. Allylmagnesium chloride reacted in ether with a 2.5-fold excess of SiCl_4 to give allyltrichlorosilane in 28% yield^{18,19}. This was then reduced with LiAlH_4 in n-butyl ether¹⁹ to form allylsilane, which was isolated by fractional condensation and collected at -116° . The product exhibited the correct NMR spectrum and molecular weight (found: 72.6; calcd.: 72.2).

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