Photoelectron Spectra and Transannular Interactions in 1-Silacyclopent-3-enes

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The 1-silacyclopent-3-enes $C_4H_6(SiX_2)$ (X = H, F, or Cl) have been studied by ultraviolet photoelectron spectroscopy. No evidence for transannular interactions has been found despite comparison of the spectra with those of cyclopentene and its dichloro-derivative.

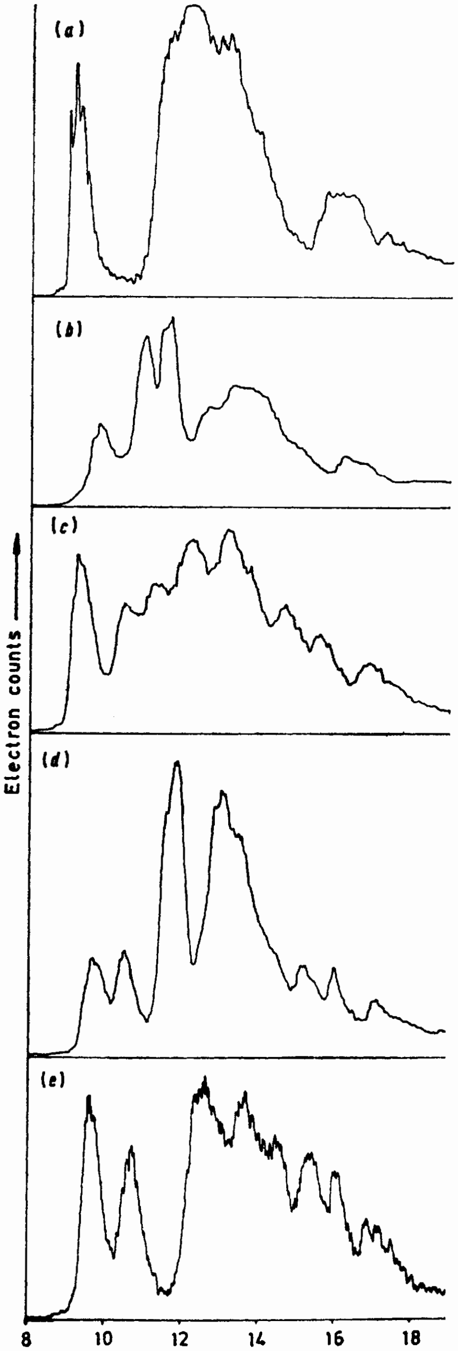
VALENCE-SHELL photoelectron spectroscopy is in principle a powerful aid to our understanding of intramolecular interactions, as individual molecular energy levels can be compared within a set of related molecules. Unfortunately it is often found that other interactions between the energy levels mask the effects sought, and only in a few cases [1,2] has it been possible to demonstrate clearly the importance of such effects as, for instance, $(p \rightarrow d)$ π bonding to silicon. Some of the interference can be eliminated if molecules of fixed conformation are studied, so that a strict symmetry separation of σ and π orbitals, for instance, can be assumed. If this is not possible interactions such as ' hyperconjugation ' must be considered.[3]

With these considerations in mind we have sought to investigate ' β π-bonding ' to silicon in 1-silacyclopent-3-enes, where the effectively planar ring defines the σ and π symmetry sets, eliminating some possibilities of hyperconjugation. A similar investigation [4] of 1,1-dimethyl-1-silacyclopent-3-ene failed to elicit evidence for such an effect; this is not entirely unexpected, as electron-donating methyl groups are likely to reduce the extent of participation of Si 3*d* orbitals in any case.

EXPERIMENTAL

1,1-Dichloro-1-silacyclopent-3-ene was kindly supplied by Dr. G. Bokerman of the Dow Corning Corporation, Midland, Michigan, U.S.A. Reduction with $Li[AlH_4]$ in dry di-n-pentyl ether under nitrogen gave the hydride, 1-silacyclopent-3-ene. The difluoro-derivative was prepared by treating the dichloride with SbF_3 in the presence of a catalytic amount of $SbCl_5$. Compounds were purified by vacuum fractionation; identity and purity were established using i.r. and n.m.r. spectroscopy. Cyclopentene was a commercial sample. 4,4-Dichlorocyclopentene was prepared by thermal rearrangement at 220 °C of 1,1-dichloro-2-vinylcyclopropane in a sealed tube (4 h).[5] It was purified by vacuum fractionation and its identity confirmed by mass and ^{13}C n.m.r. spectroscopy.

He(I) (21.22 eV) photoelectron (p.e.) spectra were recorded using a modified Perkin-Elmer PS16 spectrometer; samples were admitted from a vacuum manifold through a needle valve. Instrumental resolution was between 25 and 30 meV.† The p.e. spectra of cyclopentene, 4,4-dichlorocyclopentene, 1-silacyclopent-3-ene, 1,1-dichloro-1-silacyclopent-3-ene, and 1,1-difluoro-1-silacyclopent-3-ene are illustrated



Photoelectron spectra of (*a*) cyclopentene, (*b*) 4,4-dichlorocyclopentene: (*c*) silacyclopent-3-ene, (*d*) 1,1-dichloro-1-silacyclopent-3-ene, and (*e*) 1,1-difluoro-silacyclopent-3-ene

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† 1 eV ≈ 1.60 × 10^{-19} J.

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[5] A. D. Ketley, A. J. Berlin, E. Gorman, and L. P. Fisher, *J. Org. Chem.*, 1966, **31**, 305.

in the Figure. The vertical ionisation potentials are collected in the Table.

DISCUSSION

The spectrum of cyclopentene contained one band of low binding energy, clearly separated from all the others, at 9.17 eV. We take this to be essentially the CC π-bonding level; the extent of involvement of other orbitals, notably CH_2 bonding levels antisymmetric to the plane of the ring, is unknown but may be expected to be small. As the ring is not strictly planar,[6] the σ–π distinction is not absolute, but may be expected to be valid to a reasonable level of approximation.

Vertical ionisation potentials (eV)

$C_4H_6(CH_2)$	$C_4H_6(SiH_2)$	$C_4H_6(SiF_2)$	$C_4H_6(SiCl_2)$	$C_4H_6(CCl_2)$	Assignment
9.17	9.21	9.62	9.63	9.78	CC π bonding
	10.47	10.75	10.49		SiC σ bonding
			11.82	11.0, 11.5	Cl $3p$ lone pairs
11—15	11—15	12—15	12—15	12—15	σ bonding (np)
15.5	15.5	15.5	15.5	15.5	σ bonding (np)

The first band in the spectrum of 1-silacyclopent-3-ene may also be assigned to the CC π-bonding level; it is fairly well separated from the rest of the spectrum. The SiH_2 bonding levels, one of which is of ' π ' symmetry relative to the plane of the ring, may be involved to some extent; this interaction, if significant, should decrease the binding energy of the π-bonding level. The observed binding energy, 9.21 eV, is not significantly different from that for cyclopentene, suggesting that little mixing occurs. Equally, there is no evidence of any stabilisation of the π-bonding electrons by transannular interaction with Si $3d$ orbitals. It is possible that both effects operate, cancelling each other, but the evidence certainly does not require this.

Any transannular interactions may be expected to be more noticeable in halogenated compounds because of the contraction of d orbitals induced by the inductive effect of the halogens. An increase in binding energy of the first band, to *ca.* 9.6 eV, was indeed observed for the $SiCl_2$ and SiF_2 derivatives. However, the observed binding energy for the CCl_2 derivative, 9.8 eV, shows clearly that this increase cannot be attributed to d-orbital effects such as ' β π-bonding ', which are not likely to occur for a carbon compound. It seems likely to arise from the direct inductive effect of the halogen atoms and from changes in hyperconjugative interactions of the ring π level with MX_2 σ-bonding orbitals.

An interesting feature of the spectra of the two dichlorides is that, whereas the Cl lone pairs ($3p$) in the $SiCl_2$ group give rise to a single intense band, 0.7 eV broad, at 11.8 eV, the corresponding levels in the CCl_2 group are split into two groups giving peaks at 11.0 and 11.5 eV. The latter peak was further split into two distinct maxima, separated by over 0.2 eV. The greater complexity in this case shows the stronger interaction that occurs between the Cl $3p$ lone pairs in the CCl_2 group, because of the closer mutual proximity of the two Cl atoms.

Conclusion.—The detailed comparison of precisely comparable compounds (the CH_2 and SiH_2 pair, and the CCl_2 and $SiCl_2$ pair) has shown clearly that in the silicon compounds ' β π-bonding ' need not be invoked to explain the p.e. spectrum. This reinforces the findings that the dimethylsilicon analogue shows no such effect,[4] and our experimental evidence [7] that the suggested anomalies [8] in ring geometry in these components do not in fact exist.

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[6] J. Laane and R. C. Lord, *J. Chem. Phys.*, 1968, **48**, 1508.

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