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BONDING STUDIES OF COMPOUNDS OF BORON AND THE GROUP IV ELEMENTS

XI*. PHOTOELECTRON SPECTRA OF STRAINED CYCLIC ORGANOSILICON COMPOUNDS

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SUMMARY

The He(I) photoelectron (PE) spectra of a series of silacyclobutanes $\mathrm{XX'\text{-}\overline{SiCH_2CH_2CHR}}$ and of a 1,3-disilacyclobutane $\mathrm{\overline{Me_2SiCH_2SiMe_2CH_2}}$ are reported and analysed. The ionisation potentials (IP's) of the uppermost ring molecular orbitals (MO's) (a_1 and b_1 within the C_{2v} point group) are definitively assigned on the basis of symmetry arguments, comparisons with simpler systems such as $\mathrm{SiX_4}$ and $\mathrm{(CH_2)}_n$, and extended Hückel theory (EHT) calculations, and comments are made on the origin of some of the other bands. The effects on these MO's of changes in the substituents X, X′, and R are discussed; they correlate well with the assignments and calculations. The effects of transannular interactions are assessed by comparisons with the spectrum of 1,1-dimethylsilacyclopentane.

INTRODUCTION

In alicyclic chemistry, the 3- and 4-membered cycloalkanes are regarded as "strained", from the standpoint both of their reactivity with regard to ring-opening (in many ways they have olefinic properties), and their standard enthalpies of formation (the strain-energy is variously estimated at 20–30 kcal/mole, depending on substituents[2]). Corresponding sila- and 1,3-disilacyclobutanes are similarly known to be highly reactive both to electrophiles such as $\mathrm{H_2SO_4}$ and nucleophiles such as PhLi[3]; these compounds are also readily polymerised in presence of catalytic amounts of certain transition metal complexes[4], and insertion products (*e.g.*, 2,2-dimethyl-1,1,1,1-tetracarbonyl-1-ferra-2-silacyclopentane from $\mathrm{\overline{Me_2SiCH_2CH_2CH_2}}$) have been isolated[5]. If transition-metal-promoted ring opening is a concerted process, then the symmetry properties of the ring MO's are relevant in the sense of Woodward–Hoffmann symmetry allowed pathways[6]; however, in the silacyclobutane/$\mathrm{Fe(CO)_9}$ reaction this is not relevant as only one bond of the ring is cleaved. Thermochemical studies on silacyclobutanes lend support to the proposition that these compounds

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* For Part X, see ref. 1.

have ring strain, although the strain energy appears to be less than for $(CH_2)_n$ ($n=3$ or 4)[7].

The high reactivity of sila- and 1,3-disilacyclobutanes towards electrophiles indicates the possibility of appropriate symmetry MO's of low IP's. Certainly, cyclopropane (ca. 10.7 eV)[8] and cyclobutane (ca. 11.0 eV)[9] have first IP's similar to that of ethylene (10.5 eV)[10], and lower than that of cyclopentane (11.4 eV)[11]. The total internal energies of the compounds and of appropriate transition states, and the consequent low activation energies for reaction, need not necessarily bear a simple relation to values of electronic energy levels. However, it appeared to be worthwhile to study the strained silicon compounds by PE spectroscopy and, with the aid of EHT calculations, to assign some of the MO's.

EXPERIMENTAL

The organisilicon heterocycles were prepared by standard methods[3,12] and checked for purity by IR, PMR, and GLC analysis. We thank Dow Corning Ltd., Barry, for a gift of $(MeO)_2\overline{SiCH_2CH_2CH_2}$. The compound $Me_2\overline{SiCH(Me)CH_2CH_2}$ (Found: C, 63.3; H, 12.2. C_6H_{14} calcd.: C, 63.1; H, 12.35%) was prepared (53% yield) by methylation of $Cl(Me)\overline{SiCH(Me)CH_2CH_2}$[13a] using MeMgI in diethyl ether; b.p. 61°/200 mmHg (lit.[13b] 102°/756 mmHg).

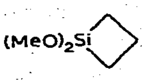
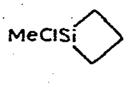
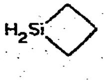
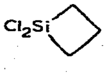
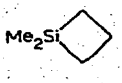
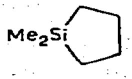
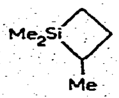
The He(I) PE spectra were obtained on a Perkin–Elmer PS16 instrument, with a modified inlet system to facilitate the study of air- and moisture-sensitive materials. The resolution (full width at half height) was of the order of 32 meV, as measured on the Argon doublet.

RESULTS AND DISCUSSION

The forms of the ring molecular orbitals of cyclobutane, silacyclobutane, and 1,3-disilacyclobutane are shown in Fig. 1 and the IP's (as well as ΔI, the difference in

TABLE 1

VERTICAL IONISATION POTENTIALS (eV) OF THE UPPERMOST RING ORBITALS OF SILACYCLOALKANES

Compound	a_1	b_1	$\Delta I(eV)$	*Compound*	a_1	b_1	$\Delta I(eV)$
	10.15	10.70	0.55		9.95	10.30	0.35
	10.05	10.60	0.55		10.50	10.70	0.20
	9.40	10.00	0.60		9.75	10.10	0.35
	9.20	9.65	0.45				

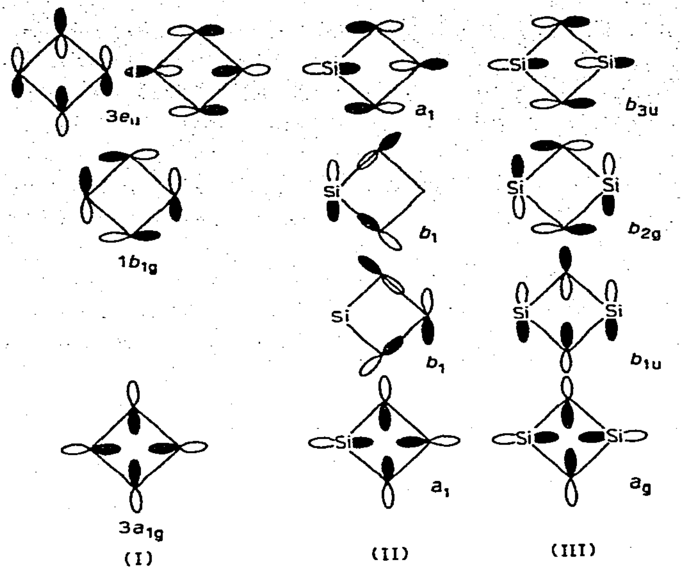


Fig. 1. Forms of ring molecular orbitals. (I) Cyclobutane; (II) Silacyclobutane; (III) 1,3-Disilacyclobutane.

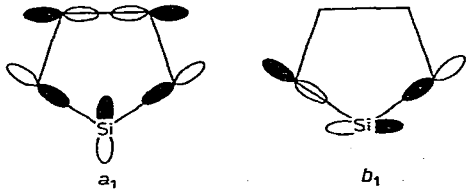


Fig. 1a. Form of the uppermost ring molecular orbitals: silacyclopentane.

their energies) of the two uppermost *ring* MO's of various silacyclobutanes are in Table 1. (These are not always the lowest IP's). We have omitted the MO's due to CH_2 moieties and the exocyclic $SiMe_2$. The relatively low energy band arising from the exocyclic $SiMe_2$ acts as an internal energy "marker", having approximately the same IP as in tetramethylsilane. For this reason, the methyl-substituted compounds form a cornerstone for our assignments. Our EHT calculations predict this band to come between the two b_1 ring orbitals; this is consistent with the finding that the IP corresponding to C–C (in Me_4C)[14] is at lower energy than C–Si (in Me_4Si)[1,15]. However for this reason the lower energy MO's are obscured and a complete assignment for all compounds is not possible. Complete assignments for the unsubstituted compounds, such as $H_2\overline{\text{SiCH}_2\text{CH}_2\text{CH}_2}$, with more theoretical discussion, form the subject of a future paper.

Substitution of silicon for carbon in a cyclobutane ring causes two major changes: (*i*) removal of the degeneracy of the $3e_u$ MO (Jahn–Teller split, 10.7 and 11.3 eV[9]), and (*ii*) a rise in energy of MO's gaining silicon character.

We shall first consider the case of 1,1-dimethylsilacyclobutane. One component of the cyclobutane $3e_u$ degenerate pair transforms directly into a_1, but the second forms a linear combination with the formerly $1b_{1g}$ MO, both transforming into b_1

symmetry in the silicon compound. This has the effect of confining the uppermost b_1 MO to the silicon half of the ring, and the lower one to the carbon half of the ring, Si–C bands generally being of higher energy than C–C (see above). IP's due to C–C bonds in aliphatic hydrocarbons are known to lie at higher energy than C–H. Hence, the energy ordering of the highest occupied MO's in $Me_2\overline{SiCH_2CH_2CH_2}$ is expected to follow the sequence: a_1 (ring) $>$ b_1 (Si–C ring) $>$ b_1 (Si–exocyclic Me_2) $>$ b_1 (C–C ring)

This is supported by the results of our EHT calculations.

Turning to the case of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, the $3e_u$ degenerate pair of $(CH_2)_4$ splits into b_{1u} and b_{3u} in the silicon compound, the energy

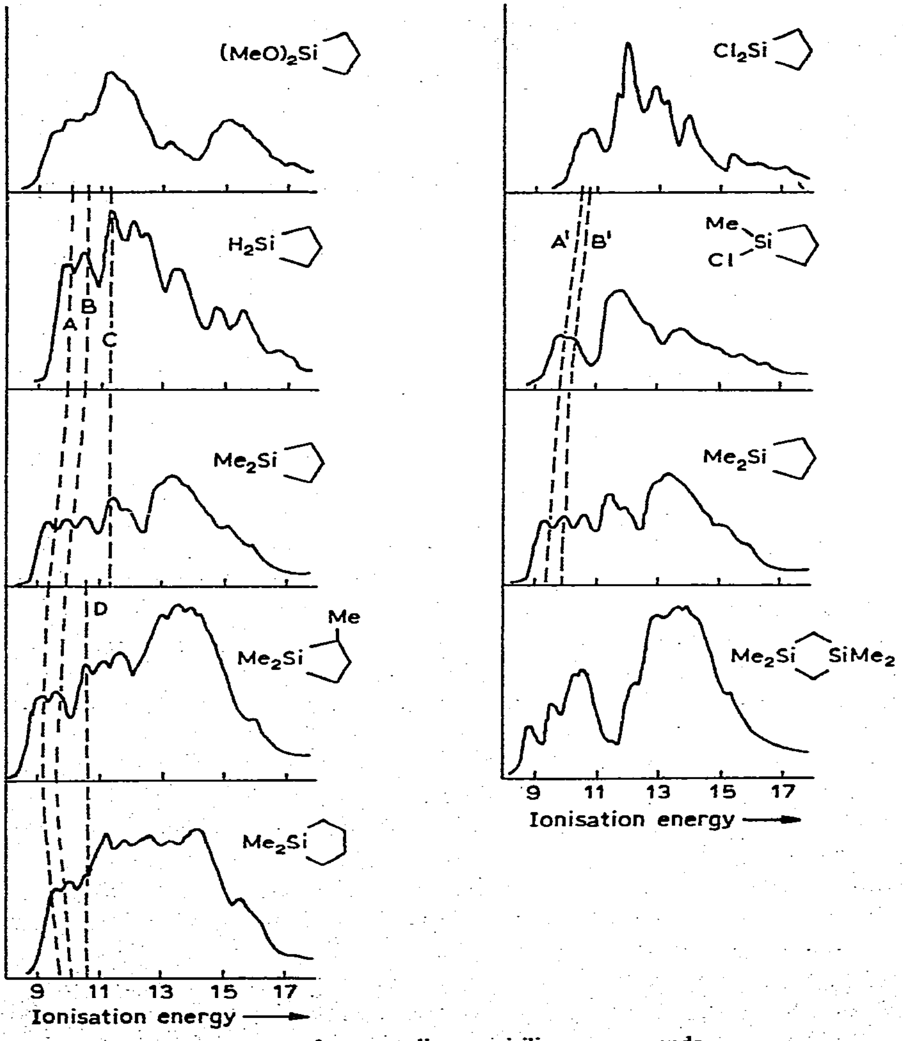


Fig. 2. Photoelectron spectra of some cyclic organisilicon compounds.

difference being due to different (see Fig. 1) anti-bonding transannular 1,3-interactions. The $1b_{1g}$ MO transforms directly into b_{2g}. All these MO's now have considerable silicon character and are consequently raised in energy. Our EHT calculations show the b_{3u} MO to be the highest occupied, then the b_{2g}, followed by b_{1u}, and finally the two exocylic $SiMe_2$ MO's. Although the EHT calculation predicts the lower two ring MO's to be very close in energy, and therefore the actual order may be in doubt, nevertheless the PE spectrum does show the presence of the expected five high energy MO's. The approximate relative intensities (as far as these can be estimated from overlapping bands) of the three bands is 1/1/3, and a splitting is apparent on the third band (see Fig. 2).

We now consider the substituted molecules (other than the 1,1-dimethyl derivative), the spectra of which are also shown in Fig. 2. Providing a reliable estimate is made of the position of any high energy bands due to the substituents, their effect on the ring MO's can be assessed. Since the position of the high energy band due to the exocyclic $SiMe_2$ group can be established from the PE spectrum of Me_4Si[1,15] (line D, Fig. 2), it seems reasonable to estimate positions of bands due to other substituents from similarly related acyclic compounds. In the simple, unsubstituted compound $H_2\overline{SiCH_2CH_2CH_2}$ a band at ca. 12 eV is expected, due to the exocyclic SiH_2 group, by comparison with the spectrum of SiH_4[16]. Experimentally, a band is found at 12.1 eV. This assignment, with support from EHT calculations, leads to the conclusion that the third band in the spectrum, centred at 11.45 eV, (line C, Fig. 2), corresponds to the b_1 (C–C ring) MO. If our MO model is correct, different substituents on the silicon atom should have little or no effect on the energy of this orbital. Inspection of the spectra of the 1,1-disubstituted compounds reveals that indeed this band does stay at a steady IP (11.5±0.05 eV). However, when an α-methyl group is introduced, the band shifts to higher energy. The inclusion of an overlapping C–C exocyclic band precludes a definitive assignment; nevertheless the absence of a band at ca. 11.5 eV provides confirmation for the b_1 (C–C ring) MO attribution.

The assignment of the two higher energy ring MO's is straightforward in the unsubstituted compound, the 1,1-dimethyl, and the 1,1,2-trimethyl compounds. However, in the case of the 1,1-dimethoxy compound, it appears that the highest occupied MO has oxygen character. This is apparent from a study of the PE spectra of $(EtO)_4Si$[15] and $(Me_3Si)_2O$[17]. In the latter, a band at 9.9 eV is well-separated from others due to two $SiMe_3$ groups, and we conclude that this is due to oxygen, although its exact nature (perhaps Si–O) is not yet defined. A band at 9.8 eV in $(EtO)_4Si$[15] confirms the hypothesis. Consequently, the second and third bands (Table 1) in the spectrum of 1,1-dimethoxysilacyclobutane are assigned to the two uppermost ring orbitals. Comparing the spectra of the dihydro, dimethyl, and dimethoxy compounds, it is evident that each of the various substituents has the same effect upon the two uppermost ring orbitals, and we draw attention to the constant separation, ΔI (Table 1), of 0.575±0.025 eV (Note, however, that the mean energy increases with increasing $+I$ effect of the substituent) (lines A and B, Fig. ..). For the 1,1,2-trimethyl-compound, ΔI is reduced to 0.40 eV; EHT calculations predict the same ordering as in the dimethyl compound, and hence the extra methyl group must affect one orbital more than the other. Furthermore, a similar effect is found in the 1-methyl, 1-chloro- and 1,1-dichloro compounds. Here the spectra are less complex, since the exocyclic band has moved to low energy*, and it is observed that the two uppermost ring orbitals converge with increasing Cl substitution (lines A′, B′, Fig. 2). That the stabilisation of the a_1 MO is constant across the series indicates that it is the b_1 which is partially destabilised by Cl substitution. This is a surprising result for the following reasons: (*i*) there is no convergence in the dimethoxy compound, which also has available "lone-pair" orbitals, (*ii*) some of the *p*-orbitals on chlorine transform as a_1+b_1, and therefore should interact with both MO's. It appears, therefore, that the effect of substituents on silicon on the two uppermost ring orbitals is not due solely to their inductive properties. This aspect is being further investigated.

The effect of transannular interactions in these systems may also be gauged by reference to the spectrum of 1,1-dimethylsilacyclopentane. Although this is complicated by the larger ring, the two high energy ring orbitals and the exocyclic $SiMe_2$ "marker" are readily distinguished. The a_1 ring orbital is stabilised by 0.3 eV, but the b_1 by only 0.1 eV. This is rationalised by reference to the MO scheme in Fig. 1a. The a_1 orbitals contains less transannular antibonding interactions than its four-membered counterpart, and the b_1 orbital, being less dependent on ring size, will be stabilised to a smaller amount via more positive bonding interaction.

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* Work on Me_nSiCl_{4-n} shows that chlorine substitution introduces no new bands in the region of the uppermost ring MO's[15].