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ENERGY LEVEL TRENDS IN 1,3,5,7-TETRASILAADAMANTANES ("CARBORUNDANES") AND RELATED MOLECULES FROM PHOTOELECTRON SPECTROSCOPY*

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SUMMARY

The photoelectron spectra of 1,3,5,7-tetrasilaadamantane and its tetrafluoro, -chloro and -methyl derivatives are presented and most of the bands out to 16 eV assigned by correlating them with those of other T_d molecules having known orbital sequences. Bands due to ionization from ring SiC, exocyclic SiC and SiH levels are well separated in the T_d molecules, but overlap strongly in the carbosilane $Si_7C_{16}H_{36}$ of C_{2v} symmetry whose PE spectrum is also reported. Despite the diffuseness of the spectra, fairly unambiguous estimates for transannular SiC–SiC and through-space CH–CH interaction parameters could be obtained. The energy level trends across the series appear to be dominated by the inductive effect of the substituents.

INTRODUCTION

Adamantane and molecules derived thereof continue to receive intense investigation[2]. The motivation for this interest is clearly to be found in the unique topology of the parent hydrocarbon: rigid and highly symmetrical carbon framework, absence of short H–H contacts, no eclipsed conformations, unable to undergo skeletal rearrangements, and with rearside attack at carbon impossible. Owing to these structural features, adamantanes have been extensively used as models for studying bridgehead reactivities[3] free from extraneous influences.

Since a detailed knowledge of the energy levels of adamantane and their symmetries is invaluable for assessing both experimental facts[3] and existing theories[4], we have recently been concerned with its photoelectron spectrum. In the present paper these studies[1] are extended to include the isostructural silicon analogue, 1,3,5,7-tetrasilaadamantane (I), and its tetrafluoro (II), tetrachloro (III) and tetramethyl (IV) derivatives. In addition, the spectrum of the carborundane $Si_7C_{16}H_{36}$, which consists of two 1,3,5,7-tetrasilaadamantane moieties connected[8] through C(2), C(4) and Si(3)

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* PE spectra of σ-bonded molecules, part V. For part IV see ref. 1.

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is reported.The isolation and synthesis of these novel organosilicon compounds, whose skeleton comprises only SiC bonds, has been described in a number of recent publications[5-8] from the Karlsruhe laboratory. The chemistry of these compounds is now under investigation, and it is hoped that the different reactivities towards ionic substitution, which have been observed on passing from cyclic and open-chain species to the cage structure[6-8], can be rationalised on the basis of the present and future PE data.

EXPERIMENTAL

1,3,5,7-Tetrachloro-1,3,5,7-tetrasilaadamantane (III) was isolated from the pyrolysis products[5] of Me_3SiCl. Treatment with $LiAlH_4$ yielded the unsubstituted compound[6], (I), and halogen exchange with ZnF_2 the tetrafluoro derivative[7], (II). The remaining two compounds, (IV), and $Si_7C_{16}H_{36}$, (V), were obtained[8] from the pyrolysis products of $SiMe_4$.

All PE spectra were measured with a Perkin–Elmer PS-18 photoelectron spectrometer equipped with a heated probe, and calibrated by use of rare gases and MeI as standards. The instrumental resolution varied between 18 and 27 meV for the Ar doublet (FWHM).

The presence of impurities and the possible occurrence of decomposition products in the ionisation chamber were monitored by comparing consecutive recordings of the same sample and by increasing the temperature of the probe. All details of the spectra proved to be well reproducible. Typical sample temperatures that gave between 10^3 and $4 \cdot 10^3$ counts per sec., were: (I) 58°, (II) 61°, (III) 112°, (IV) 25°, (V) 124°.

RESULTS AND DISCUSSION

Vertical IP's measured from the PE spectra (Fig. 1) are given in Table 1.

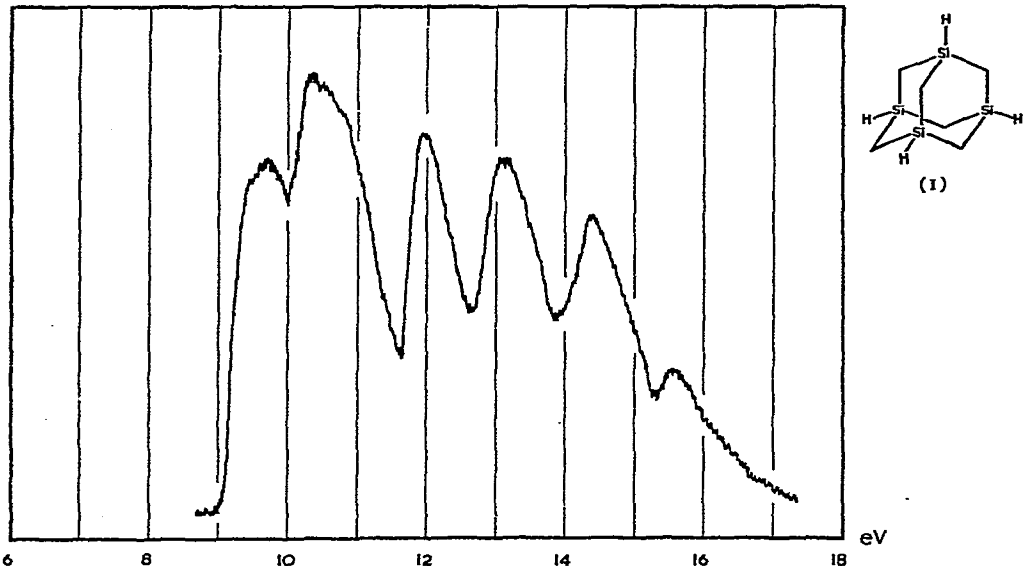
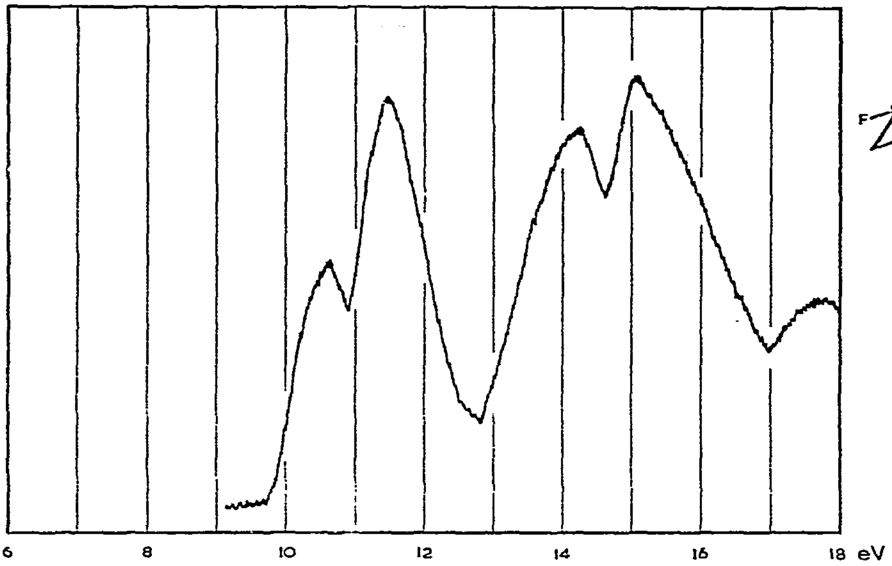
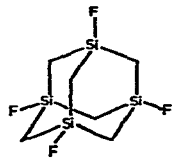
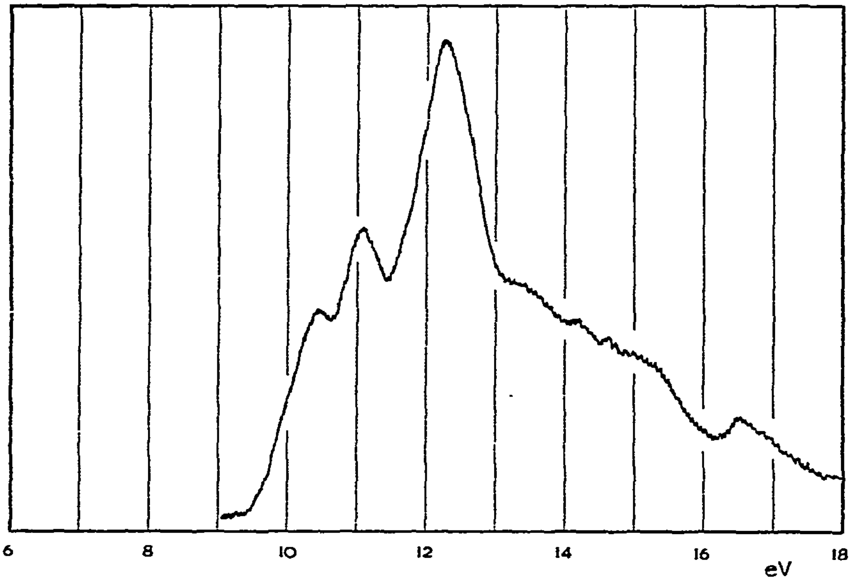


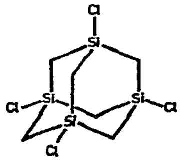
Fig. 1. He(I) Photoelectron spectra of the series (I)–(V). See also p. 111, 112.





(II)

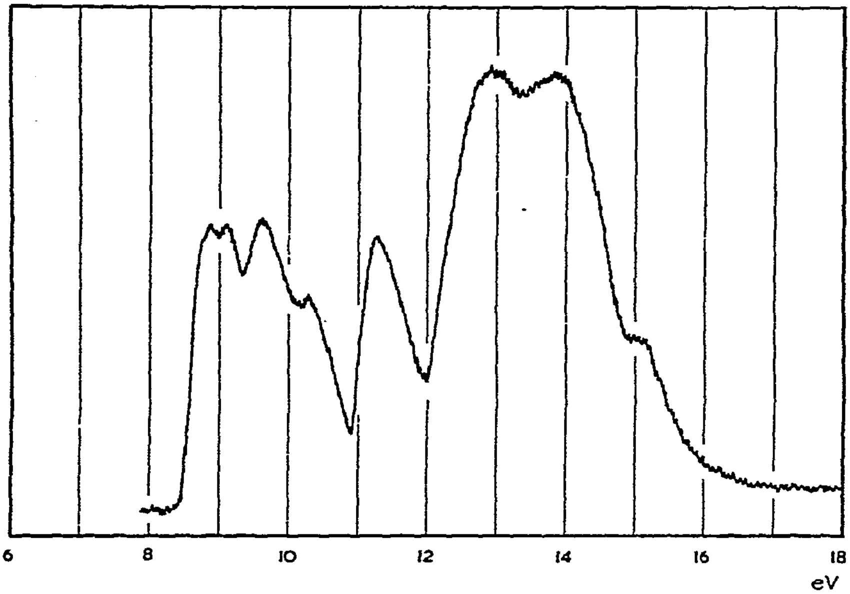


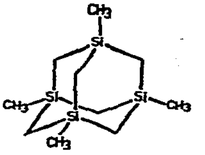


(III)

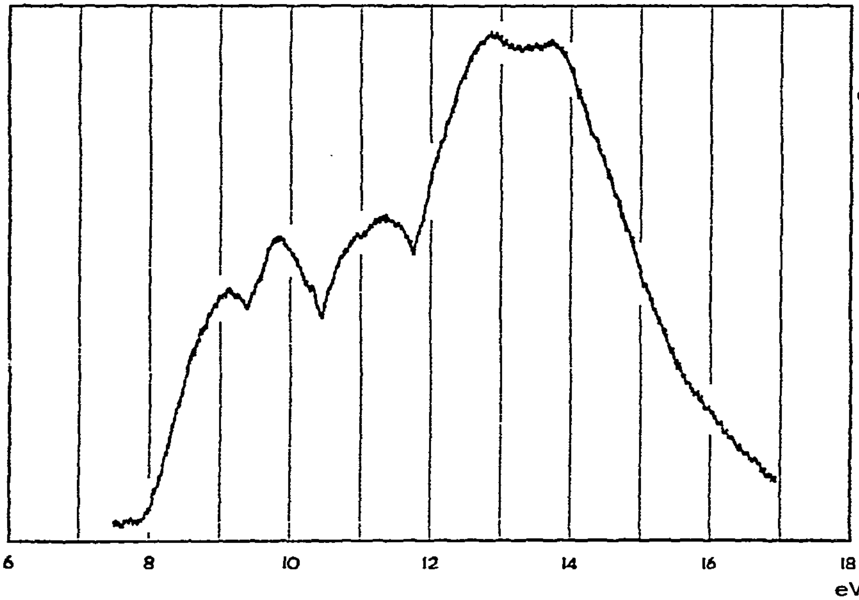
Adiabatic IP's for the first band, as determined from the onset of ionisation in the band wing, are also given. Although the IP's of adamantane have already been reported, they are presented in Table 1 again for comparative reasons.

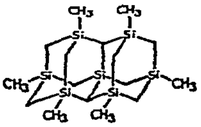
The main qualifications to Fig. 1 are as follows. The spectrum of (I) shows only a few bands, of which the second appears to accommodate two ionisation processes on account of its intensity and the shoulder at the high IE side. In (II), the low IE section is similar to that in (I), but the region beyond 15 eV becomes indecipherable due to a host of F lone-pair ionisations. Similarly in (III), bands arising from SiC and





(IV)





(V)

CH ionisation badly overlap with Cl lone-pair bands. The 8–12 eV region in the spectrum of (IV) is quite rich in detail, but the remainder is disappointingly amorphous. The spectrum of (V) is completely featureless in that the individual band components tend to merge into a continuum.

Thus, all five spectra are rather diffuse with no vibrational structure in any band. In the case of the Si-adamantane this is surprising at first sight since at least the 15.6 eV band originates from a non-degenerate level (*vide infra*). The corresponding

TABLE 1

IONISATION POTENTIALS IN EV FOR THE SERIES (I)–(V)

The values for adamantane[1] are included for comparison. All values ±0.05 eV, a = adiabatic, v = vertical, (sh) = shoulder.

Adamantane	*(I)*	*(II)*	*(III)*	*(IV)*	*(V)*
9.1 a	9.0 a	9.8 a	9.4 a	8.45 a	7.9 a
9.55 v	9.70 v	10.61 v	10.41 v	8.85 v	9.11 v
10.95 v	10.33 v	11.46 v	11.08 v	9.07 v	9.82 v
11.30 v	10.8 (sh)	14.29 v	12.23 v	9.60 v	11.30 v
13.00 v	11.93 v	15.09 v	13.3 (sh)	10.29 v	12.87 v
13.40 v	13.09 v	17.7 v	14.2 (sh)	11.25 v	13.70 v
14.85 v	14.38 v		15.3 (sh)	12.95 v	
16.96 a	15.59 v		16.50 (sh)	13.85 v	
18.45 v				15.0 (sh)	

transition in the C-adamantane, which occurs at 16.96 eV, is accompanied by strong excitation of a totally symmetric cage vibration with attendant quanta in the likewise totally symmetric CH_2 scissoring mode[1]. This contrasting behaviour is presumably due to the strongly reduced stretching and breathing modes in the silicon analogue, a view supported by the corresponding findings[9,10] in CMe_4 and $SiMe_4$ and by an approximate normal coordinate analysis that has recently been carried out for (IV)[11].

Before discussing the spectrum of the Si-adamantane in detail it will be useful to give a brief description of the bonding in the C-adamantane. Its ground state electronic configuration, as deduced from the He(I) PE spectrum, has been shown[1] to be $(7t_2)^6(2t_1)^6(3e)^4(1t_1)^6(6t_2)^6(5t_2)^6(5a_1)^2(4a_1)^2\ldots{}^1T_d$, where no ordering of the close-lying levels ($2t_1$, $3e$), ($1t_1$, $6t_2$) and ($5t_2$, $5a_1$) is implied. (The numbering scheme includes inner-shell MO's). $7t_2$, $2t_1$ and $3e$ are the principally CC-bonding levels, $1t_1$ and $5t_2$ are the respective out-of-phase and in-phase combinations of pseudo-π CH_2 group orbitals, while $6t_2$ and $5a_1$ concern essentially the tertiary CH bonds. That these CH_2 and CH levels are each split by several eV, has its origin in their through-space interaction. $5a_1$ gives rise to the 16.96 eV band and is hardly involved in bonding as evidenced by the prominent O–O vibrational component. The remaining CC and CH_2 levels are beyond the reach of the He(I) experiment.

The relative order of the three CC levels in adamantane is unusual and deserves comment. Were the number of nodes between neighbouring CC bonds in the molecular wave functions* the discriminating factor, we would expect three equidistant levels of order $2t_1 > 7t_2 > 3e$. The reversal of $2t_1$ and $7t_2$ has been rationalised[1] in terms of 1–3 transannular CC–CC interactions which are of opposite sign in these MO's. 1–4 interactions are of minor importance and will be neglected in the following argument.

On passing from the C- to the Si-adamantane, four major changes are expected to take place. (*i*) Owing to the lower electronegativity of Si compared to C, bands originating from CC levels suffer a shift to lower IP's whereas CH ionisations are hardly

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* These are considered to be linear combinations of the individual two-centre bonds.

affected. This contrasting behaviour of CC and CH levels upon Si substitution provides a diagnostically useful criterion for band assignments in hydrocarbons. (*ii*) Nearest neighbour and transannular CC–CC interactions are strongly overlap dependent. Since a SiC bond is longer than a CC bond, the overall separation of $7t_2$, $2t_1$ and $3e$ should decrease. (*iii*) Increasing the size of the cage increases at the same time the distances between the six CH_2 groups and thus diminishes their through-space interaction accordingly. In consequence $1t_1$ and $5t_2$ come closer together. (*iv*) Since SiH bonds ionise more readily than CH bonds, the centroid of $6t_2$ and $5a_1$ is expected to undergo a shift to higher energies, and the splitting of these MO's should similarly decrease to that between $1t_1$ and $5t_2$.

In accord with these qualitative arguments, the low-energy section in the spectrum of (I) shows two partly overlapping bands, of which the second exhibits a poorly defined shoulder at the high IE side. This argues for the following ordering of the SiC levels: $t_2 > t_1 > e$. That the first band remains almost stationary, indicates that the transannular interactions are more strongly reduced in (I) than the nearest neighbour interactions. The next band at 12 eV is assigned to t_2 symmetry and results from ionisation from a SiH orbital. It is followed by two bands that represent the t_1 and t_2 components of the through-space split CH_2 levels; their separation amounts to roughly two thirds of that found in adamantane. This latter band accommodates also the SiH bonding level of symmetry. Finally the weak peak at 15.6 eV corresponds to the 16.96 eV transition in adamantane.

On the whole, the spectrum of (I) is simpler and shows less band overlap than that of adamantane. The only disturbing feature in our interpretation is the low IE shift of the centroid of the two CH_2 levels. This shift could be due to the inductive effect of Si as has been observed to a similar extent on passing from CMe_4 to $SiMe_4$.

The spectrum of (II) is of particular interest, in that previous work on the effect of fluorine substitution has been largely confined to planar molecules where the MO's can be classified with respect to the plane of symmetry[12]. Since such a distinction cannot be made in a molecule such as (II), which is spherical in shape, one would expect an indiscriminate shift of all bands to higher IP's. This appears to be the case. We note from Fig. 1 that the high IE shift amounts to roughly 1 eV for both SiC and CH_2 ionisations, and that the transannular and through-space splittings are essentially unaltered, as expected. Owing to the fact that ionisation from the SiF bonds, which assume the role of the four SiH bonds in (I), occurs beyond 15 eV, there is now a window between the bands resulting from SiC and CH_2 ionisation.

Substitution of the four H atoms in (I) by chlorine causes a similar albeit less pronounced trend of the main structural features to higher IP's. As with (II), the t_1 and e (SiC) ionisations apparently coincide so that the second band gains considerably in intensity relative to that in (I). The splitting between the t_2 and (t_1, e) SiC levels appears to be slightly reduced. This could indicate that an interpretation of the spectrum of (III) on the basis of semi-localised SiC and CH wave functions is oversimplified, and that their interaction with the SiCl bonds and Cl lone-pairs has to be taken into consideration. Ionisation from the Cl lone-pair orbitals, which transform as $e+t_1+t_2$ in a T_d molecule, appears as an intense, rather broad band at 12.2 eV. That through-space or spin-orbit (SO) interactions can account for the diffuseness of this band, seems unlikely in view of the large Cl–Cl distance of ca. 6 Å and the small SO coupling constants of Cl and Si (Cl^+ 0.10 eV, Si^+ 0.024 eV). An explanation in terms of vibronic interactions (all lone-pair MO's are degenerate) and/or delocalisation over the SiC framework (*vide supra*; the levels in question bunch close together) appears more satisfactory. The higher IE section of the spectrum, arising from the CH_2 and SiCl levels (which transform as t_2+a_1) is too diffuse to deserve any discussion.

The low IE band system in the spectrum of (IV) is strikingly different from that of all previous spectra, in that the three SiC ionisations are now clearly distinguishable. The low IE shift of *all* three band components relative to (I) is however not readily explained in terms of interaction with the exocyclic SiC bonds, since this effect should operate specifically on the t_2 component. This difficulty* is not disposed of by invoking interaction with CH_3 orbitals of correct symmetry. (The matrix elements in question can be rigorously derived in an "equivalent orbital" basis and turn out to be small.) We therefore conclude that the influence of the methyl substituents is predominantly inductive in nature. The remainder of the spectrum is easy to analyse: the 11.2 eV band represents the t_2 and a_1 components of the exocyclic SiC levels, and the split band extending from 12 to 15 eV concerns again the through-space split CH_2 levels (t_1+t_2 components) and the (presumably unsplit) pseudo-π CH_3 orbitals with components $e+t_1+t_2$. Both the position and the shape of this band are reminiscent of the second $SiMe_4$ band[10]. The ill-defined shoulder at 15 eV is analogous to the 15.6 eV band in (I).

The spectrum of (V) is too diffuse to be amenable to a detailed analysis. This lack of structure is clearly a consequence of the large number of close-lying levels which are all non-degenerate in C_{2v} symmetry. However, on looking more closely at Fig. 1 we note that the bands in the spectrum of (V) bear a striking one-to-one correspondence to those of (IV); this we take to indicate that they can still be classified as arising from SiC ring levels (8–10.4 eV region), exocyclic SiC levels (10.4–11.8 eV) and CH, CH_2 and CH_3 levels (11.8–ca. 15 eV). Bands correlating with the a_1 band in (IV) are conceivably obscured by the host of ionisations expected to fall within this particular region.

Corroborative evidence for the transannular effects deduced from the PE spectra is provided by the above mentioned study[11] of the IR and Raman spectra of (IV). Whereas the stretching force constant of the exocyclic SiC bonds (2.95 mdyn/Å) is "normal", *i.e.*, similar to that found in $SiMe_4$, the force constant of the inner SiC bonds is considerably smaller: 2.65 mdyn/Å.

CONCLUSIONS

Cage molecules with T_d symmetry provide an excellent vehicle for the study of molecular strain via PE spectroscopy: both the ordering and the separation of the bands correlating with the upper ring MO's are the result of a delicate balance between nearest neighbour and transannular interactions; these in turn depend sensitively on the size of the cage, that is, on the CX bond length (X = Si, C). On passing from the C- to the Si-adamantane, the partial relief of strain is reflected in a sizeable decrease of the splitting between these levels. Bands originating from the through-space split CH_2 orbitals undergo similar gradations on passing down the series. It would be interesting

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* The incipient splitting in the 9 eV band, which is present in all our expanded recordings, poses another problem that remains to be solved. A Jahn–Teller effect appears unlikely considering the size of the molecule.

to see whether these trends continue in the thus far unknown germanium and tin analogues. Attempts to synthesize these molecules are in progress.

The observed energy level trends across the series (I)–(IV) due to substituents could be satisfactorily related to inductive effects. Chlorine is found to behave much like fluorine, that is, it stabilises all levels indiscriminately though to a lesser extent than fluorine. Methyl groups have the opposite effect.

We have nowhere required the empty *d*-orbitals of Si to rationalise the bonding in these molecules. It is clear that the degeneracy of *e.g.*, the chlorine lone-pair components $e+t_1+t_2$ in (III) would be lifted if the Si (3*d*) levels would take part in the bonding. The lack of any splitting in the corresponding band once more emphasises[13] that p_π–d_π interactions in tetravalent Si compounds are too weak to be detected by PE spectroscopy. There have been several attempts in the recent literature to deduce evidence for *d*-orbital effects from a comparison of the first IE's of corresponding carbon and silicon compounds, *e.g.*, CCl_4 and $SiCl_4$. The present data provide yet another demonstration that such a procedure is totally unwarranted in view of the fact that through-space and/or transannular interactions—which are usually both antibonding in the uppermost level—are generally stronger in the carbon analogue, due to the shorter bond lengths involving carbon. In consequence the gradations of the first IE's within a homologous series does not necessarily conform to the electronegativity scale.

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