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CYCLIC POLYSILANES

XII *. PHOTOELECTRON SPECTRA AND BONDING IN 1,2,3,4-TETRA-t-BUTYLTETRAMETHYLCYCLOTETRASILANE AND RELATED t-BUTYLSILICON COMPOUNDS

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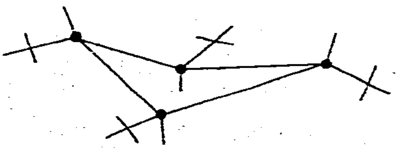
Summary

The photoelectron spectra of $[(CH_3)_3CSiCH_3]_4$ (I), $(CH_3)_3SiCl$ (II), $(CH_3)_3CSi(CH_3)_2Cl$ (III) and $[(CH_3)_3CSi(CH_3)_2]_2$ (IV), have been measured. These compounds show bands assigned to Si—C at 9.13 and 9.65 eV for I, 9.77 eV for III and 9.52 eV for IV. Ionizations due to Si—Si electrons appear at 8.52 eV for IV and at 7.42, 7.85 and 8.15 eV for I. The Si—Si level in IV is destabilized 0.17 eV relative to methylpolysilanes. The extremely low *IP*'s for I result in part from charge release from the t-butyl groups. However the major cause of the destabilization of the Si—Si level is the high degree of strain imposed on the internal Si bonding framework by the t-butyl substituents.

Introduction

The extremely low first ionization potential and high stability of $[(CH_3)_3CSiCH_3]_4$ (I) have been noted previously [1]. Here, we report the full photoelectron (PE) spectrum of I as well as those of $Si(CH_3)_3Cl$ (II), $(CH_3)_3CSi(CH_3)_2Cl$ (III) and $[(CH_3)_3CSi(CH_3)_2]_2$ (IV). Examination of these spectra, in conjunc-



(I)

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* For part XI see ref. 18.

tion with a molecular orbital (MO) study of $(CH_3)_3CSi(CH_3)_3$ (V), permits an analysis of the electronic structure of I.

Earlier interpretations of the nature of Si—Si bonding in alkylated polysilanes were based on the "Sandorfy C" model [2], originally developed for alkanes, in which linear combinations of sp^3 hybrid orbitals on carbon are taken to form σ MO's. Bock and Ensslin elaborated on this model with PE spectral studies on linear and cyclic permethylpolysilanes [3a]. In these spectra, there are intense, broad bands beginning at energies of ca. 10 eV and corresponding to ionizations from Si—C and C—H bonding orbitals. There are also bands at lower energy and these correspond to ionizations from MO's which are involved mainly in Si—Si bonding. The low energy bands may be curve-fit with one or more peaks, whose relative intensities are determined by the symmetry of the molecule being studied. The weighted average of the maxima of the first peaks in the PE spectra of $Si_2(CH_3)_6$, $Si_3(CH_3)_8$, $Si_4(CH_3)_{10}$, $Si_5(CH_3)_{10}$ and $Si_6(CH_3)_{12}$ is roughly 8.69 eV in each case.

Bock and Ensslin explained the results by using a simple model involving linear combinations of Si—Si bonding orbitals and the resultant σ-electron delocalization over the molecule. Orbital eigenvalues were obtained from the equation $E_n = \alpha_{\mathrm{SiSi}} + \lambda_n\beta_{\mathrm{SiSi}}$ in which α_{SiSi} is 8.69 eV. The predicted E_n are in excellent agreement with the observed ionization potentials. The model assumes that the Si—Si levels are well isolated from the Si—C and C—H MO's. Furthermore, vicinal interactions between silicons are considered to be much larger than geminal interactions.

Compound I differs from those studied by Bock and Ensslin in two ways. The molecule contains t-butyl groups, as well as methyl groups, and is highly strained [4]. The data listed in Table 1 indicate that the energy of the predominantly Si—Si level of a substituted disilane can vary considerably as the substituents on silicon are modified. However, as we shall see below, it is the structure of the silicon framework of I which is most important in causing the severe destabilization of the Si—Si MO's.

Experimental

The isomeric mixture of 1,2,3,4-tetra-t-butyltetramethylcyclotetrasilanes was prepared by the condensation of t-butylmethyldichlorosilane with sodium/potassium alloy as described earlier [18]. The all *trans* isomer I was separated by fractional crystallization from acetone and shown to be >95% pure by NMR spectroscopy.

All PE spectra were obtained on a Varian IEE-15 spectrometer. Argon was used as an internal standard. Repeated scans did not reveal any signs of sample decomposition.

Spectra for I were obtained at 88° C. Spectra for II and III were obtained at room temperature. For these compounds, assignments were made on a spectrum consisting of the time-averaged sum of 18 scans of a 1000 channel, 10 eV region. Spectra of IV were obtained at temperatures ranging between −180 and −100° C. Assignments were made on a spectrum consisting of the time-averaged sum of 7 scans of a 1000 channel, 10 eV region, and are in agreement with assignments made on a spectrum consisting of the time-averaged sum of

20 scans of a 500 channel, 10 eV region.

Each spectrum is a continuous plot of electron count rate versus binding energy. *IP*'s were deduced by use of the relation, $I = h\nu - E$. The vertical *IP* for a given orbital corresponds to the maximum count rate of the appropriate peak. The spectrometer provides a listing of the number of counts recorded at each data point, and this was used to make most of the assignments. The highest binding energy band in the spectrum of compound I was curve-fit using program GFIT [5]. All spectra were calibrated by assigning an *IP* of 15.76 eV to the data channel having the highest count rate for the transition to the $^2P_{3/2}$ state of argon. The spectra displayed in Fig. 1 are those produced by the spectrometer's recorder.

In the approximate Fenske—Hall calculations [6] carried out on V, Clementi's double-ζ Slater-type orbitals [7], curve-fit [8] to single-ζ form, were used as the basis functions for the carbon 1*s* and 2*s* orbitals, and for the silicon 1*s* through 3*s* orbitals. Carbon 2*p* and silicon 3*p* functions were left in double-ζ form. No 3*d* orbitals were placed on silicon. The hydrogen 1*s* exponent was

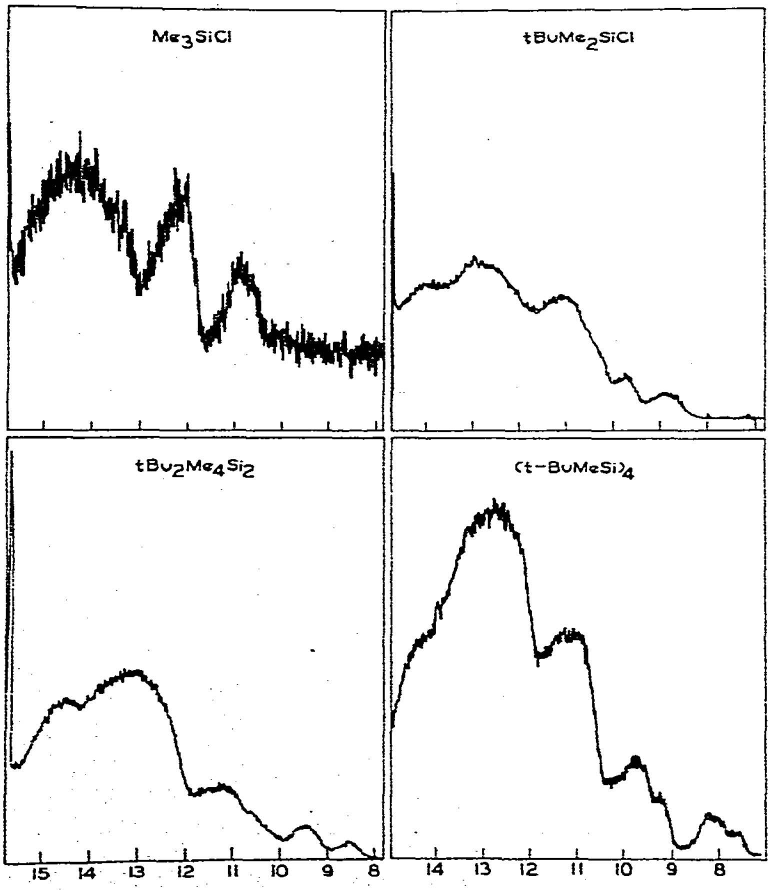

Fig. 1. PE spectra for $Si(CH_3)_3Cl$ (II), $(CH_3)_3CSi(CH_3)_2Cl$ (III), $[(CH_3)_3CSi(CH_3)_2]_2$ (IV), and $[(CH_3)_3CSiCH_3]_4$ (I). The spectra are plots of counts versus ionization potential (in eV).

chosen as 1.16 [9]. The silicon—carbon bond length was taken as 1.89 Å. The carbon—carbon bond length in the t-butyl group was taken as 1.54 Å. All carbon—hydrogen bond lengths were set at 1.09 Å. All angles employed were tetrahedral.

Results

The PE spectra of compounds I through IV are displayed in Fig. 1. Some of the vertical ionization potentials for these compounds are listed in Table 1, along with pertinent data from the PE spectra of $Si(CH_3)_4$ [3] and $SiCl_4$ [10].

The spectrum of compound II, $Si(CH_3)_3Cl$, (Fig. 1a) consists of three bands. The third band is extremely broad, and it probably contains several peaks corresponding to ionizations from C—H and Si—Cl levels. The other two bands have their maxima at 10.84 and 12.23 eV, respectively. The first band may be ascribed to ionizations from Si—C levels, while the second band correlates with ionizations from the lone pairs on chlorine. These assignments have been made on the basis of comparisons between the PE spectrum of II and the spectra of $Si(CH_3)_4$ and $SiCl_4$.

Two new features appear in the PE spectrum of III, $(CH_3)_3CSi(CH_3)_2Cl$, (Fig. 1b). The broad band between 11 and 15 eV exhibits more structure, and a new peak is evident, with its maximum at 9.77 eV. The extra structure at higher *IP* may be attributed to the addition of ionizations from the C—C levels of the t-butyl group to ionizations from the Cl lone pairs and from the Si—Cl and C—H levels. The new band is associated with ionization from the Si—C(t-Bu) level while the intermediate band (maximum at 10.71 eV) coresponds to ionizations from the Si—C(Me) levels.

The PE spectrum of IV, $[(CH_3)_3CSi(CH_3)_2]_2$, (Fig. 1c) contains a broad region between 11 and 15 eV, just as the spectrum of III does. In addition, the spectrum of IV, like the spectrum of III, contains two bands which may be ascribed to ionizations from the Si—C(t-Bu) and Si—C(Me) levels. The lowest energy band in the spectrum, with its maximum of 8.52 eV, is ascribed to ionization

TABLE 1

VERTICAL IONIZATION POTENTIALS OBTAINED FROM PE SPECTRA (eV)

Compound	Si—Si	Si—C(t-Bu)	Si—C(Me)	Cl lone pair	Ref.
$Si(CH_3)_4$			10.5		3a
$SiCl_4$				12.12	10
$Si(CH_3)_3Cl$			10.84	12.23	[a,b]
$(CH_3)_3CSi(CH_3)_2Cl$		9.77	10.71	12.09	[a]
$[(CH_3)_3CSi(CH_3)_2]_2$	8.52	9.52	10.8(sh)		[a]
$[(CH_3)_3CSiCH_3]_4$	7.42	9.13(sh)	[c]		[a]
	7.85	9.65			
	8.15				

[a] This work. [b] The Si—C(Me) and Cl lone pair *IP*'s were previously reported as 11.9 and 10.08 eV, respectively. We believe our assignment is correct, since it is consistent with assignments made for the other compounds studied here and with assignments reported for the PE spectra of some trimethylsilyl pseudohalides [16]. [c] Peak obscured by those arising from (C—C)(t-Bu) interactions.

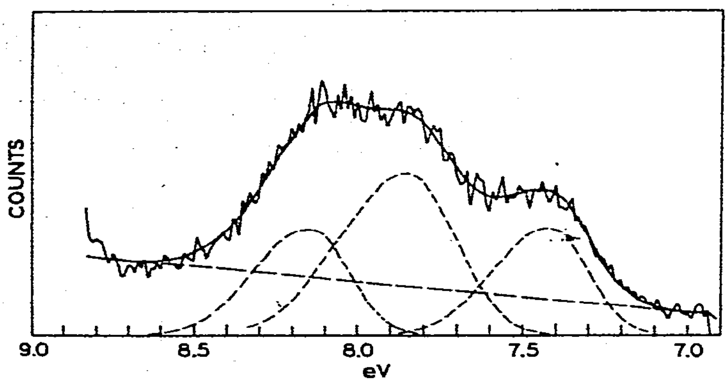

Fig. 2. Curve fit of lowest *IP* peak in the PE spectrum of $[(CH_3)_3CSiCH_3]_4$.

from the Si—Si level. This *IP* is 0.17 eV lower than that observed by Bock and Ensslin [3a] for the Si—Si level in $Si_2(CH_3)_6$.

The spectrum of I, $[(CH_3)_3CSiCH_3]_4$, (Fig. 1d) again contains a broad peak lying between 11 and 15 eV (this area contains peaks resulting from ionizations from the Si—C(Me) levels as well as from ionizations from C—C and C—H levels). In addition, the spectrum contains two bands at lower energies (between 9 and 11 eV and between 7 and 9 eV). The first of these has a maximum at 9.65 eV, as well as a shoulder with a local maximum at 9.13 eV. This band, containing at least two peaks, is associated with ionizations from the Si—C(t-Bu) levels. The second new band has been curve-fit [5] to three Gaussian peaks with relative intensities 1/2/1 (see Fig. 2) [11] *. These Gaussians have their maxima at 7.42, 7.85 and 8.15 eV, respectively. The weighted average of these values is 7.82 eV, which is 0.7 eV lower than the first *IP* of compound IV.

Discussion

Bock and Ensslin [3a] were successful in explaining the PE spectra of permethylated polysilanes with a model which assumed that the MO's which correspond to Si—Si interactions contain only insignificant contributions from the compounds' other orbitals. They were not as successful in applying their model to the study of polysilanes [3b], partly because the Si—H orbitals are not as well isolated from the Si—Si levels as Si—C orbitals are. Pitt and Bock had previously postulated a mixing of Si—Si sigma orbitals with the phenyl pi system in attempting to explain the relatively destabilized first *IP* of $C_6H_5Si_2(CH_3)_5$ [12]. In this study, it has been demonstrated that replacing a methyl group by a closely related alkyl group can also affect the *IP* of the Si—Si level in an alkylated disilane.

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* Compound I belongs to point group D_{2d}. Under the operations of this point group, the Si—Si bonds transform as a_1, b_1 and e, while the Si—C(t-Bu) bonds transform as a_1, b_2 and e. The Si—Si b_1 level cannot interact with the Si—C(t-Bu) levels, while the Si—Si a_1 and e levels are destabilized by interaction with the corresponding Si—C(t-Bu) levels. A $b_1 < e < a_1$ ordering would yield a 1/2/1 pattern in the PE spectrum, as is observed here. This is in contrast to the relative intensity pattern that might be expected from Hoffmann's treatment of C_4H_8.

TABLE 2

EIGENVALUES (*EiV*) AND PERCENT CHARACTERS OF SOME MOLECULAR ORBITALS OF $(CH_3)_3CSi(CH_3)_3$

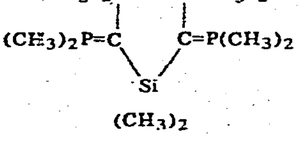
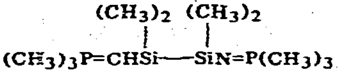
EiV (eV)	Character	
−13.66	$Si—C(CH_3)_3$	σ bond
−15.26	$Si—CH_3$	σ bond
−17.74	$C—(CH_3)_3$	σ bond

In addition, the spectra of compounds II, III and IV demonstrate that the levels representing Si—C(Me) and Si—C(t-Bu) interactions are energetically distinct. In order to gain insight into the reason for the separation of the Si—C levels, we performed Fenske—Hall MO calculations on compound V. These calculations place the Si—C(Me) level approximately 2 eV below the Si—C(t-Bu) level (see Table 2). The interaction between the Si and C(Me) levels is much stronger than that between the Si and C(t-Bu) levels. This situation arises because the Si—C(t-Bu) MO is destabilized by interaction with the C—C levels of the t-butyl group. Although the *IP*'s predicted by the calculation, via Koopmans' theorem [13], are undoubtedly larger than the actual *IP*'s of V, it is reasonable to assume that the bonding picture is qualitatively correct.

Despite the fact that the Si—C(t-Bu) levels are destabilized with respect to the Si—C(Me) levels, they are still well separated from the first band in the PE spectrum of I. Hence, these first peaks are still likely to represent ionizations from essentially pure Si—Si MO's. However, these peaks are not centered around 8.52 eV, as predicted by the Bock—Ensslin model (with α_{SiSi} adjusted appropriately) [3a,b]. The reasons for the increased destabilization of the Si—Si levels of I may be found in an examination of the compound's crystal structure [4]. The Si—Si bond length in I is somewhat longer than that in other polysilanes. Increasing the distance between silicons should destabilize the filled (bonding) Si—Si MO's In addition, the Si—Si—Si angle in I is unusually small (~87°), meaning

TABLE 3

IONIZATION POTENTIALS (eV) OF POLYSILANES

Compound	*IP*(Si—Si) (eV)	Ref.
$C_6H_5Si_2(CH_3)_5$	8.35	12
Si_2H_6	10.53	17
$(CH_3)_3P{=}CHSi_2(CH_3)_5$	8.63	14
	7.56	14
 $(CH_3)_3P{=}CHSi(CH_3)_2—Si(CH_3)_2N{=}P(CH_3)_3$	7.44	14

that geminal interactions should be larger there than they are in less strained polysilanes, such as those studied by Bock and Ensslin. Furthermore, the large dihedral angle in I (~37°) results in a silicon—silicon nonbonding distance of 3.27 Å. Interactions across the ring could also destabilize the Si—Si levels. The result of the combination of these effects is that I shows an *IP* lower than any previously reported for Si—Si levels.

Compound I is stable to oxidation over prolonged periods of time. Such behavior is extremely unusual for a compound with low *IP*'s, and contrasts sharply with the behavior of the compounds listed in Table 3. The phosphorus ylides, with their first *IP*'s ranging from 6.18 to 6.85 eV, are extremely sensitive towards oxygen and water and must be handled in an inert atmosphere [14]. Alkylpolysilanes with their first *IP*'s higher than 7.44 eV (the first *IP* of compound I) are also oxidized easily [15].

Consideration of the structure of compound I explains its anomalous stability. The bulk of the t-butyl groups makes the silicon skeleton inaccessible to attacking reagents. At the same time, the structural changes necessary to accommodate its bulky substituents cause the large destabilization of the compound's Si—Si MO's.

In future studies, we hope to pursue the relationship between electronic structure and strain by obtaining the PE spectra of $[Si(CH_3)_2]_4$ and other isomers of $[(CH_3)_3CSiCH_3]_4$ which have less favorable conformations than compound I.

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