

THE ELECTRONIC ABSORPTION AND IONIZATION POTENTIALS OF CARBOSILANES. THE QUESTION OF 1,3(*d-d*) INTERACTION IN THE EXCITED STATE

C. G. PITT, M. S. HABERCOM,

Chemistry and Life Sciences Laboratory, Research Triangle Institute, Research Triangle Park, North Carolina 27709 (U.S.A.)

M. M. BURSEY AND P. F. ROGERSON*

Venable Chemical Laboratory, University of North Carolina, Chapel Hill, North Carolina 27514 (U.S.A.)

(Received July 19th, 1968)

SUMMARY

The electronic absorption spectra of carbosilanes containing the $\begin{array}{c} | & & | \\ -\text{Si}-\text{C}-\text{Si}- \\ | & & | \end{array}$ group have been measured. The cyclic carbosilanes $(\text{Me}_2\text{SiCH}_2)_n$, $n=2, 3, 4$, and 2,2,6,6-tetramethyl-2,4,6-trisilasp[3.3]cycloheptane exhibit large bathochromic shifts relative to analogous acyclic carbosilanes. Electron impact-ionization potential measurements demonstrate the shifts are primarily a manifestation of ground state destabilization, rather than excited state stabilization originating from 1,3(*d-d*) interaction. The spectra of Si-phenylated carbosilanes confirm this conclusion.

INTRODUCTION

The UV absorption maxima of mercaptals are strikingly shifted to the red when compared with alkyl sulfides¹. This bathochromic shift has been attributed in part to 1,3(*d-d*) interaction of the unoccupied *d*-orbitals of the geminal sulfur atoms, which results in stabilization of the excited state of the transition². A similar 1,3-interaction, involving sulfur 3*d*-orbitals and carbon 2*p*- π orbitals, has been invoked² to explain the anomalous UV absorption spectra of allyl and benzyl sulfides³, β -mercapto-ketones^{1a} and β -mercapto-esters^{1a, **}. There is now a growing body of evidence which suggests that the 3*d*-orbitals of silicon may also interact with non-adjacent functional groups. Examples of systems in which such intramolecular interaction has been postulated include α -halomethylsilanes (nuclear quadrupole resonance⁵, dipole moment and boiling point data⁶, hydrogen bonding studies⁵, and deviation from linear free energy correlations^{5,7}) α -Oxamethylsilanes, α -aminomethylsilanes (basicity studies⁸), β -silylketones (UV⁹ and IR spectral data¹⁰), and benzyl- and allylsilanes (hydrogen bonding studies⁵ and spectral data^{11,12}). Molecular orbital calculations for α -chloromethylsilane indicate that the interaction in this molecule is best described by a 1,3 (C \rightarrow Si) bond of σ rather than π -symmetry⁵, and it seems reasonable by

* N.S.F. Trainee

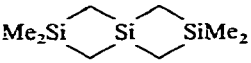

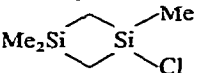
** For a summary of the UV absorption spectra see ref. 4.

analogy to suppose that 1,3-interaction in α -amino- and α -oxamethylsilanes will also have σ -symmetry. The UV absorption spectra of allyl- and benzylsilanes can be interpreted in terms of $1,3(p-d)_\sigma$ or $1,3(p-d)_\pi$ bonding, both of which are consistent with the observed red shift; however, Shorygin, *et al.*¹², have advanced a different explanation based on the interaction of the σ -electrons of the Si-CH₂ bond with the π -electrons of the multiple bond. In a study designed to assess the importance of 1,3 interaction of d orbitals in organosilicon compounds, we have measured the UV absorption and the ionization potentials of geminal carbodisilanes (Si-C-Si), which may be considered the silicon analogs of mercaptals (S-C-S).

RESULTS AND DISCUSSION

The long wavelength maximum associated with the σ -electrons of the Si-C bond, for example in tetramethylsilane, occurs at $\sim 160 \text{ m}\mu$ ¹³, and consequently the perturbation of this transition cannot be studied except by vacuum UV techniques. Thus the failure of XSiMe₂-CH₂-SiMe₂X (X = Cl or H) to absorb in the UV ($\epsilon^{195} 0$) does not rule out 1,3-interaction of the silicon atoms. However, a comparison of 1-(trimethylsilylmethyl)heptamethyltrisilane (I), which absorbs at $217.7 \text{ m}\mu$ ($\epsilon 7550$), with octamethyltrisilane ($216.3 \text{ m}\mu$, $\epsilon 8200$) and with decamethyltetrasilane ($234.8 \text{ m}\mu$, $\epsilon 16600$)¹⁴ demonstrates that the α -trimethylsilylmethyl group does not significantly perturb the trisilane chromophore. Although the lowest excited state of polysilanes is not proven to be $3d$ in character, it is known^{14,15} to interact strongly with orbitals of π -symmetry (*e.g.* phenyl, vinyl); thus the failure to observe any shift in (I) can be regarded as evidence against appreciable $1,3(d-d)$ interaction. Since this negative result might be attributed to the slightly larger Si-Si internuclear

TABLE I
THE UV ABSORPTION MAXIMA AND IONIZATION POTENTIALS OF CARBOSILANES

Compound	λ_{max} (m μ)	ϵ	IP (eV)
Me ₄ Si	$\sim 160^a$		9.8 ^b
HMe ₂ SiCH ₂ SiMe ₂ H	Transparent	$\epsilon^{195} 0$	
ClMe ₂ SiCH ₂ SiMe ₂ Cl	Transparent	$\epsilon^{195} 0$	
<i>n</i> -Me ₇ Si ₃ -Me	216.3	8180	
<i>n</i> -Me ₇ Si ₃ -CH ₂ -SiMe ₃	217.7	7550	
<i>n</i> -Me ₇ Si ₃ -SiMe ₃	234.8	16,600	
(Me ₂ Si-CH ₂) ₄	End absorption	$\epsilon^{195} 150$	9.21 ± 0.04
(Me ₂ Si-CH ₂) ₃	End absorption	$\epsilon^{195} 1580$	9.39 ± 0.03
(Me ₂ Si-CH ₂) ₂	198.0	5430	8.56 ± 0.07
	211.8	7750	7.78 ± 0.06
	End absorption	$\epsilon^{195} 850$	8.83 ± 0.07
	End absorption	$\epsilon^{195} 2300$	

^a Ref. 13. ^b Ref. 16.

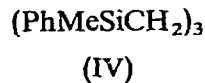
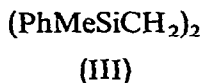
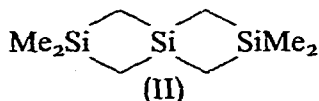
distances or to steric hindrance in acyclic derivatives, when compared to sulfur analogs, the absorption spectra of the series of cyclic carbosilanes, $(\text{Me}_2\text{SiCH}_2)_m$ were determined. In contrast to the acyclic derivatives, these cycles do absorb in the UV (Table 2), the extent depending markedly on the ring size. The very large bathochromic shift of the absorption maxima (≈ 1.75 eV relative to tetramethylsilane) observed for the 1,3-disilacyclobutane cannot be accredited simply to intramolecular Si-Si interaction, for 1,1-dimethylsilacyclobutane also absorbs in the UV (ϵ^{195} 850). This suggests that ring strain, *i.e.* abnormal hybridization, can contribute in part to the red shift of the cyclic carbosilanes.

TABLE 2
THE UV ABSORPTION MAXIMA OF PHENYLATED CYCLIC CARBOSILANES

Compound	λ_{max} (m μ)	ϵ
$(\text{PhMeSi-CH}_2)_3$	259.7, 217.0, 213.2	880, 31400, 3150
	260.3, 220.0	295, 8500
	260.2, 220.2	680, 19200
	260.3, 219.7	270, 10050
PhSiMe_3	259.0, 218.7 (sh), 214.5, 211.0, 207.5 (sh)	270, 6790 8870, 9460, 8960
$(\text{ViMeSi-CH}_2)_2$	End absorption	ϵ^{195} 17500

To differentiate between these two alternative explanations of the bathochromic shifts, we have measured the electron impact-ionization potentials of the cyclic carbosilanes. Such measurements provide a reasonable estimate of the ground state energies of the electronic transitions in so far as they represent a Franck-Condon removal of an electron from each system. They may be compared with the Frank-Condon electronic transitions, then, to provide a fair approximation of the contribution of ground-state energies in these transitions. The results, shown in Table 1, clearly demonstrate that the destabilization of the ground state is largely, if not solely, responsible for the red shifts relative to acyclic carbosilanes. For larger rings, the *EI-IP's* approach the value reported for tetramethylsilane¹⁶. A regular change is not observed, probably because of the increasing "delocalization" of the σ -electrons with the lengthening of the silicon-carbon skeleton (*cf.* 6-membered *vs.* 8-membered ring). This effect may also explain why the *IP* of 1,1,3,3-tetramethyl-1,3-disilacyclobutane is lower than that of 1,1-dimethylsilacyclobutane, despite the fact that the latter should be more strained from a consideration of bond lengths, and its chemical reactivity¹⁷.

The absorption maxima of the spirane (II) occurs at 211.8 m μ (ϵ 7750). This bathochromic shift of 13.8 m μ (0.41 eV), relative to the 1,3-disilacyclobutane ring, is clearly shown by the *IP* determination to originate from ground state destabilization rather than extended excited state interaction across three silicon atoms.

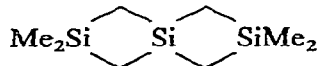


Further confirmation of the absence of $d-d$ interaction in the excited state is obtained from the spectra of the Si-phenylated carbosilanes (Table 2). Thus although the absorption maxima of both the primary and secondary bands of these derivatives are shifted to the red relative to phenyltrimethylsilane, the phenyl groups of (III) and (IV) are electronically remote. Likewise, the extinction coefficients of the absorption maxima in all phenylated derivatives are directly proportional to the number of Si-C₆H₅ groups in the molecule. This is in marked contrast to the absorption spectra of phenylated disilanes^{14,15}. Furthermore, a similar bathochromic shift of both bands is exhibited by 1-phenyl-1,3-dimethylsilacyclobutane. All of these facts indicate that neither 1,3($d-d$) interaction nor delocalization of the σ -electrons in banana bonds, as proposed for cyclopropanes, is responsible for the observed electronic properties. Rehybridization of the $3sp^3$ (and d) orbitals of the silicon atom in the strained rings may be sufficient to explain the enhanced perturbation of the phenyl absorption bands.

Finally, we note that (trimethylsilyl)methyl methyl sulfide exhibits a plateau at 202.5 $m\mu$ (ϵ 1900) indicating that if there is any significant 1,3-interaction of the d -orbitals of Si and S, the anticipated bathochromic shift is more than nullified by a concomitant 1,3($p-d$) σ bond.

2,2,6,6-Tetramethyl-2,4,6-trisilaspiro[3.3]cycloheptane (II)

This compound was prepared from the reaction of magnesium with silicon tetrachloride and bis(chloromethyl)dimethylsilane, by a modification of the procedure of Kriner¹⁸. The IR spectrum is similar to that of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, showing strong absorption at 940 cm^{-1} assigned to the Si-CH₂Si wag¹⁸. The NMR spectrum shows signals at 17.5 Hz, 8 H (CH₂) and 16 Hz, 12 H (CH₃) and, when compared with the spectra of other carbosilanes, suggests that substituents exocyclic to the disilacyclobutane ring undergo a downfield shift of approximately 17 Hz as a result of the anisotropy of the ring system:

	Si-CH ₃ (Hz)	Si-CH ₂ Si (Hz)
(Me ₂ Si-CH ₂) ₃	+ 3	-19
(Me ₂ Si-CH ₂) ₂	+18	+ 2.5
	+16	+17.5

EXPERIMENTAL

UV absorption spectra were determined in dry spectral grade iso-octane using a Cary 14 spectrometer. NMR spectra were obtained with a Varian A-60 spectrometer and are reported downfield from tetramethylsilane (internal standard). IR spectra were determined using a Perkin-Elmer Model 221 spectrometer. GLPC analyses were performed with an F & M Model 300 instrument using a 6 ft column of 2% SE 52 on Chromosorb G. The purity of all compounds was confirmed by GLPC

and, when appropriate, by refractive index. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Ionization potentials were measured on a Hitachi RMU 6E mass spectrometer, modified by the incorporation of a digital voltmeter readable to ± 0.01 volt (United Systems Corporation, Dayton, Ohio), with reduced trap current (*ca.* 2 μ A) and repeller voltage (< 0.5 volt). Extensive experimentation indicated that the accuracy of Kiser's single-point method¹⁹ was similar to the accuracy of methods requiring the recording of complete ionization efficiency curves, such as the semi-logarithmic method²⁰. The single-point method, or the energy compensation technique, was used for the determination of all values. Xenon was used as a calibration standard. Benzene and anthracene were also introduced at the same time as the silane to serve as secondary standards. The three standards were used to construct a correlation line in a plot of observed values *vs.* literature* electron-impact data. The least-squares value of the silane ionization potential was then determined from this plot. Data were obtained at least in sextuplicate, were repeated on different days, and were occasionally confirmed by simultaneous measurement of two samples in admixture with the standards. The error figures quoted for the ionization potentials are standard deviations of all determinations and are within the 0.1 eV often quoted as the limit of accuracy of the electron impact method; in our opinion, they do not reflect an improvement in accuracy for electron-impact methods in general.

1-Chloro-1,3,3-trimethyl-1,3-disilacyclobutane, 1-phenyl-1,3,3-trimethyl-1,3-disilacyclobutane, and $(\text{Me}_2\text{SiCH}_2)_n$, $n=2$ and 3 were prepared by the method of Kriner¹⁸. Bis(chlorodimethylsilyl)methane was prepared by the procedure of Greber and Degler²¹. 1-Phenyl-1,3-dimethyl-1-silacyclobutane was prepared by the method of Weyenberg *et al.*²². Samples of 1,3-divinyl-1,3-dimethyl-1,3-disilacyclobutane, $(\text{PhMeSiCH}_2)_n$, $n=2$ and 3, all of which were *cis-trans* isomer mixtures, and $(\text{Me}_2\text{SiCH}_2)_4$ were kindly supplied by Prof. W. A. Kriner. 1,1-Dimethyl-1-silacyclobutane was kindly donated by Drs. W. H. Atwell and D. R. Weyenberg, and (trimethylsilyl)methyl methyl sulfide by Professor H. Sakurai.

[1-(Trimethylsilyl)methyl]heptamethyltrisilane (I)

To a solution of (trimethylsilyl)methyl lithium, from (trimethylsilyl)methyl chloride (2.50 g, 0.0204 mole), lithium wire (0.280 g, 0.0403 g-atom) and dry, olefin free petroleum ether (25 ml), was added n-heptamethyltrisilanyl chloride (1.20 g, 0.00534 mole). The mixture was stirred and refluxed overnight. After filtration, the filtrate was washed with 10% aqueous hydrochloric acid and water, and dried over anhydrous magnesium sulfate. Concentration gave the crude product ($\approx 80\%$ purity) as a yellow oil (1.41 g), which was purified by preparative GLPC (SE52). n_D^{25} 1.4728, $v_{\text{max}}^{\text{film}}$ 1055 (Si-CH₂-Si). The NMR spectrum (CCl₄, TMS) showed singlets at -16.5 Hz (Si-CH₂-Si) and at 1,2,4 and 6.5 Hz (Si-CH₃). (Found: C, 47.51; H, 11.74. C₁₁H₃₂Si₄ calcd.: C, 47.75; H, 11.67%.)

Bis(dimethylsilyl)methane

Bis(chlorodimethylsilyl)methane (5.08 g, 34.8 mmole) was added cautiously to a stirred suspension of lithium aluminum hydride (0.73 g, 26.2 mmole) in ether (25

* Average values of recent literature data are as follows: Xe, 12.12; C₁₄H₁₀, 7.41; C₆H₆, 9.23 eV.

ml). After stirring overnight, the mixture was hydrolyzed with 30% aqueous hydrochloric acid, and the product was extracted with ether. After drying over magnesium sulfate, fractional distillation afforded 0.86 g of the desired product, b.p. 55° (160 mm); n_D^{22} 1.4134, Reported²³ for bis(dimethylsilyl)methane, b.p. 103°, n_D^{20} 1.4140.

2,2,6,6-Tetramethyl-2,4,6-trisilaspiro[3.3]cycloheptane (II)

One ml of a solution of bis(chloromethyl)dimethylsilane (6.00 g, 38.2 mmoles) in dry tetrahydrofuran (THF 6 ml) was added to a stirred mixture of silicon tetrachloride (3.24 g, 19.1 mmole), magnesium turnings (2.23 g, 0.0918 g-atom) in dry THF (5 ml). Reaction commenced on warming, and the remainder of the bis(chloromethyl)dimethylsilane, diluted with THF (20 ml), was added dropwise with external cooling. As the reaction mixture became more viscous, more THF (25 ml) was added. After stirring for 5 h, the mixture was poured into water (25 ml) and filtered to remove unchanged magnesium and a polymeric solid. The filtrate was extracted with ether, and the ether extracts were dried over magnesium sulfate. Concentration and distillation at 0.75 mm gave 0.3 g of (II) of approximately 90% purity, b.p. 33–36°. Purification was accomplished by preparative GLPC (SE 52). v_{\max}^{film} 2960 m, 2900 w, 1350 w, 1250 m, 940 s, 835 s, 770 m, 680 m and 670 (sh) cm^{-1} . The NMR spectrum (CCl_4 , TMS) showed signals at 17.5 Hz, 8 H (Si-CH₂) and 16 Hz, 11.4 H (Si-CH₃).

Because of the difficulty of obtaining the pure product by preparative GLPC in sufficient amount for combustion analysis, high resolution mass spectral analysis was carried out. (Found: mol. wt., 200.0867. $\text{C}_8\text{H}_{20}\text{Si}_3$ calcd.: mol. wt., 200.0873.)

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Professor W. A. KRINER (St. Josephs College), Drs. W. H. ATWELL and D. R. WEYENBERG (Dow Corning Corporation), Professor H. SAKURAI (Kyoto University) and the General Electric Corporation, all of whom very generously supplied compounds for this study. The mass spectral analysis of (II) was performed by the Dow Corning Corporation.

REFERENCES

- (a) E. A. FEHNEL AND M. CARMACK, *J. Amer. Chem. Soc.*, 71 (1949) 84;
(b) D. C. NICHOLSON, E. ROTHSTEIN, R. W. SAVILLE AND R. WHITELEY, *J. Chem. Soc.*, (1953) 4019.
- H. H. JAFFE AND M. ORCHIN, *Theory and Application of Ultraviolet Spectra*, Wiley, New York, 1962, pp. 474–481; S. OAE, W. TAGAKI AND A. OHNO, *Tetrahedron*, 20 (1964) 437.
- H. P. KOCH, *J. Chem. Soc.*, (1949) 387.
- C. C. PRICE AND S. OAE, *Sulfur Bonding*, Ronald Press, New York, 1962.
- R. H. BANEY, G. A. L. GANT, J. LIPOWITZ AND J. W. MENTELE, *3rd International Symposium on Organometallic Chemistry, Munich, Germany, 1967, Abstracts*, 56.
- H. FREISER, R. CHARLES, J. SPEIER AND M. EAGLE, *J. Amer. Chem. Soc.*, 73 (1951) 5229.
- O. STEWARD AND O. R. PIERCE, *J. Amer. Chem. Soc.*, 83 (1961) 1916, 4932.
- E. W. ABEL, D. A. ARMITAGE AND S. P. TYFIELD, *J. Chem. Soc., A*, (1967) 554; J. T. WANG AND C. H. VAN DYKE, *Inorg. Chem.*, 6 (1967) 1741.
- W. K. MUSKER AND R. W. ASHBY, *J. Org. Chem.*, 31 (1966) 4237.
- W. K. MUSKER AND G. L. LARSON, *J. Organometal. Chem.*, 6 (1966) 627.
- A. D. PETROV, YU. P. EGGROV, V. F. MIRONOV, G. I. NIKISHIN AND A. A. BURGARKOVA, *Izv., Akad. Nauk. SSSR, Otd. Khim. Nauk*, (1956) 50; (1963) 1525; YU. P. EGOROV, L. A. LEITES, N. G. TOLSTIKOVA AND E. A. SHERNYSHEV, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1961) 445.

- 12 V. A. PETUKHOV, V. F. MIRONOV AND P. P. SHORYGIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1964) 2203.
- 13 P. P. SHORYGIN, V. A. PETUKHOV, O. M. NAFEDOV, S. P. KOLESNIKOV AND V. I. SHIRYAEV, *Teor. i Experm.-Khim., Akad. Nauk Ukr. SSR*, 2 (1966) 190.
- 14 H. GILMAN, W. H. ATWELL AND G. L. SCHWEBKE, *J. Organometal. Chem.*, 2 (1964) 369.
- 15 D. N. HAGUE AND R. H. PRINCE, *J. Chem. Soc.*, (1965) 4690; *Proc. Chem. Soc.*, (1962) 300; H. GILMAN, W. H. ATWELL AND G. L. SCHWEBKE, *Chem. Ind. (London)*, (1964) 1063; H. SAKURAI, K. TOMINAGA AND M. KUMADA, *Bull. Chem. Soc. Jap.*, 39 (1966) 1279; H. SAKURAI, H. YAMAMORI AND M. KUMADA, *Bull. Chem. Soc. Jap.*, 38 (1965) 2024; H. SAKURAI AND M. KUMADA, *Bull. Chem. Soc. Jap.*, 37 (1964) 1894; *Chem. Commun.*, (1968) 198.
- 16 B. G. HOBROCK AND R. W. KISER, *J. Phys. Chem.*, 65 (1961) 2186.
- 17 D. SEYFERTH, R. DAMRAUR AND S. S. WASHBURNE, *J. Amer. Chem. Soc.*, 89 (1967) 1538.
- 18 W. A. KRINER, *J. Org. Chem.*, 29 (1964) 1601.
- 19 R. W. KISER AND E. J. GALLEGOS, *J. Phys. Chem.*, 66 (1962) 947.
- 20 F. P. LOSSING, A. W. TICKNER AND W. A. BRYCE, *J. Chem. Phys.*, 19 (1951) 1254.
- 21 G. GREBER AND G. DEGLER, *Makromol. Chem.*, 52 (1962) 174.
- 22 D. R. WEYENBERG AND L. E. NELSON, *J. Org. Chem.*, 30 (1965) 2618.
- 23 A. V. TOPCHIEV, N. S. NAMETKIN AND L. S. POVAROV, *Dokl. Akad. Nauk SSSR*, 109 (1956) 332.

J. Organometal. Chem., 15 (1968) 359-365