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Extraordinary Large Red Shift of the n(Si)→3p(Si) Transition of Silylenes Caused by Trimethylsilyl and Trimethylgermyl Substituents [1]

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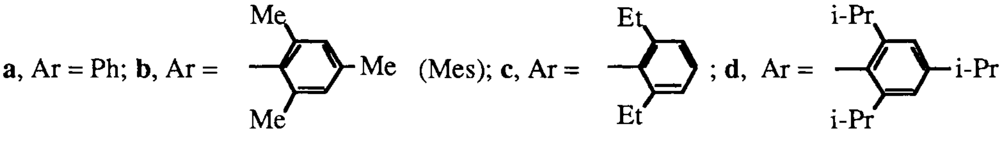
The n(Si)→3p(Si) absorption maxima of silylenes were shifted significantly red by introducing trimethylsilyl and trimethylgermyl substituents. The origin of the substituent effects will be attributed to the σ-electron donating ability of the trimethylmetal groups which lift the energy level of n(Si) orbital significantly.

One of the intriguing experimental targets in silylene chemistry is generation and characterization of ground-state triplet silylenes; no evidence for a triplet silylene has yet been obtained experimentally.[2] Since both the singlet-triplet energy separation and the n(Si)→3p(Si) transition energy in a silylene depend mainly on the relative energy levels between the occupied n(Si) and the vacant 3p(Si) orbitals, systematic studies of substituent effects on the absorption spectra would be informative in search of suitable ligands for ground state triplet silylenes. We have recently reported matrix isolation and absorption spectra of vinyl-substituted silylenes and found that a vinyl π ligand serves as a π acceptor to cause a significant red shift of the n(Si)→3p(Si) transition.[3] It is very interesting to investigate the absorption spectra of trialkylsilyl-substituted silylenes, because recent theoretical studies have shown significant decrease of the singlet-triplet separation as well as the n(Si)→3p(Si) transition energy by introducing electropositive silyl groups.[4] Whereas a number of silylsilylenes have been generated by photolysis and pyrolysis and detected by chemical trapping methods,[5-7] they have never been observed spectroscopically. We wish herein to report the first matrix isolation of trimethylsilyl- and trimethylgermyl-substituted silylenes and a related germylene:[8] Extraordinary large red shifts of the n(Si)→3p(Si) transition of silylenes have been found in these group-14 metal divalent species, in conformity with the theoretical calculations.

$$\underset{\mathbf{2}}{\mathrm{ArSi(SiMe_3)_3}} \xrightarrow[\text{3-MP, 77 K}]{h\nu\ (254\ \text{nm})} \underset{\mathbf{1}}{\mathrm{Ar\ddot{Si}SiMe_3}} + \mathrm{Me_3SiSiMe_3} \qquad (1)$$



As a typical example, a weak broad absorption band due to the n(Si)-3p(Si) transition of mesityl(trimethylsilyl)silylene (**1b**) was observed at 760 nm during photolysis of 2-mesityl-2-

(trimethylsilyl)hexamethyltrisilane (**2b**)[5] with a 125 W low pressure Hg arc lamp in 3-methylpentane (3-MP) at 77 K (Fig. 1). When the matrix was annealed for a few seconds, an intense band appeared at 390 nm accompanied by the disappearance of the 760 nm band. The new band would be assigned to the π-π^* transition of the corresponding disilenes formed by dimerization of **1b**.[9] In the presence of a Lewis base, the n(Si)→3p(Si) band of silylenes is known to be shifted blue by the formation of a silylene-base complex.[3,10] Actually, the absorption band due to the complex of **1b** was observed at 390 nm during the photolysis of **2b** in a 2-MeTHF matrix at 77 K.

Table 1. Absorption Maxima of Aryl(trimethylsilyl)silylenes and Related Silylenes and Germylenes in a 3-MP Matrix at 77 K

Silylene/Germylene	λ_{max}/nm	$\tilde{\nu}_{max}$/cm^{-1}	$\Delta\tilde{\nu}$/cm^{-1} a)
1a	660	15200	5200
1b	760	13200	6900
1c	570	17500	—
1d	570	17500	—
$\mathrm{Ph}\overset{\cdot\cdot}{\mathrm{Si}}\mathrm{GeMe_3}$	625	16000	4400
$\mathrm{Mes}\overset{\cdot\cdot}{\mathrm{Si}}\mathrm{GeMe_3}$	730	13700	6400
$\mathrm{Me_3Si{-}C{\equiv}C{-}}\overset{\cdot\cdot}{\mathrm{Si}}\mathrm{SiMe_3}$	660	15200	4800
$\mathrm{Ph}\overset{\cdot\cdot}{\mathrm{Ge}}\mathrm{SiMe_3}$	610	16400	6300
$\mathrm{Ph}\overset{\cdot\cdot}{\mathrm{Si}}\mathrm{Me}$ b)	490	20400	—
$\mathrm{Mes}\overset{\cdot\cdot}{\mathrm{Si}}\mathrm{Me}$ b)	497	20100	—
$\mathrm{Me_3Si{-}C{\equiv}C{-}}\overset{\cdot\cdot}{\mathrm{Si}}\mathrm{Me}$	500	20000	—
$\mathrm{Ph}\overset{\cdot\cdot}{\mathrm{Ge}}\mathrm{Me}$ c)	440	22700	—

a) $\Delta\tilde{\nu} = \tilde{\nu}_{max}(\mathrm{RMeM{:}}) - \tilde{\nu}_{max}(\mathrm{R(Me_3M')M{:}})$; M, M' = Si or Ge. b) Ref. 11. c) Ref. 12.

As shown in Table 1, absorption maxima for these silylsilylenes were shifted to unusually longer wave-lengths than those for the corresponding arylmethylsilylenes . The origin of the substituent effects will be attributed to the σ-electron donating ability of the trimethylsilyl group which lifts the energy level of n(Si) orbital significantly.

Unexpectedly, the λ_{max} values in a series of aryl(trimethylsilyl)silylenes **1a** - **1d** did not change uniformly with increasing the steric bulkiness of the aryl-substituents. Thus, the λ_{max} value of 760 nm for **1b** is the largest among all silylenes ever known, while the λ_{max} values for **1c** and **1d**, which bear more bulky 2,6-diethylphenyl and 2,4,6-triisopropylphenyl groups, were even smaller than that for **1a**. Tentative explanation for the stereoelectronic effects of the aromatic substituents is given as shown schematically in Fig. 2. Thus, we assume reasonably that in **1a**, the phenyl ring plane is mostly coplanar with the Si-Si bond, and therefore the vacant 3p(Si) orbital level is lowered due to the interaction with the phenyl pπ* orbitals as discussed in more detail in a previous paper;[3] the n(Si)-3p(Si) transition energy would be reduced by this interaction. The coplanar geometry will be maintained in **1b** but with the increase of the apex angle (θ) to avoid the steric hindrance between two substituents on silicon. As has been predicted theoretically,[4g] further red shift of the n(Si)-3p(Si) transition should be caused by the increase of θ. However, in **1c** and **1d**, the aryl groups are too large to hold the coplanarity by increasing θ; twisting of the aromatic groups will result in the decrease of pπ*-3p(Si) interaction and θ, and therefore, the increase of the n(Si)-3p(Si) transition energy.

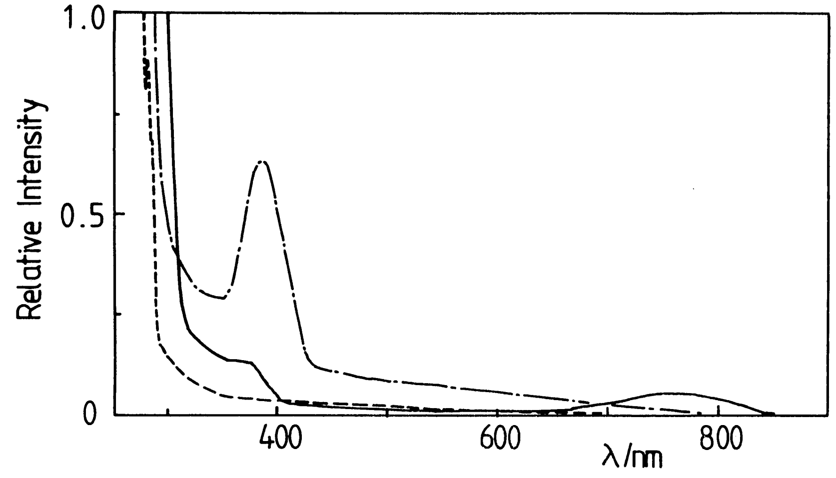
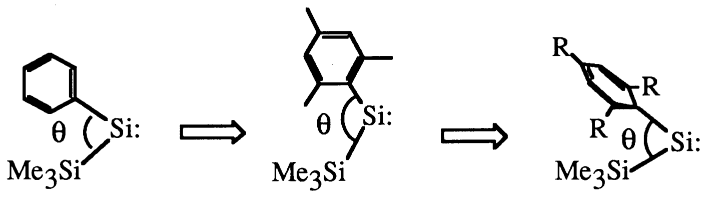


Fig. 1. UV spectra obtained during photolysis of **2a** in 3-MP: (a) before irradiation (-----), (b) after 45 min irradiation at 77 K (——), and (c) after annealing of the matrix for a few seconds (—·—).



	1a		**1b**		**1c, 1d**
Si-Si bond / aromatic ring :	coplanar	→	coplanar	→	perpendicular
apex angle (θ) :	small	→	large	→	small
λ_{max}:	660 nm	red shift →	760 nm	blue shift →	570 nm

Fig. 2. Schematic representation for the stereoelectronic effects of aromatic substituents on the absorption maxima of trimethylsilylsilylenes.

The extent of the red shift of the n(Si)-3p(Si) transition of phenyl- and mesitylsilylenes by introducing a trimethylgermyl group was a little smaller than that by a trimethylsilyl group. Whereas the origin is still open, it is noteworthy that the calculated singlet-triplet separations for (H_3Si)HSi:, (H_3Ge)HSi:, and (H_3Si)HGe: , which are 11, 12.6, and 14.4 kcal/mol, respectively, [4b,c] are quite parallel to the transition energies for

(Me3Si)PhSi:, (Me3Ge)PhSi:, and (Me3Si)PhGe:.

No signals due to a triplet silylene were observed by ESR during the photolysis of **2b** in a 3-MP matrix at 77 K. Whereas the silylene **1b** would be a singlet at the ground state, the present results together with the previous theoretical calculations[4a)] suggest that bis(trialkylsilyl)silylenes having bulky alkyl groups should be good candidates for ground-state triplet silylenes. We have failed however to generate bis(t-butyldimethylsilyl)silylene by the low-temperature photolysis of the corresponding cyclic trisilane,[13)] while the photolysis of the trisilane in solution at ambient temperatures gave the corresponding disilene quantitatively. Details will be reported elsewhere.

References

1) Chemistry of Organosilicon Compounds. 309.

2) For a review, see: Y. Apeloig, "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappoport, John Wiley & Sons, New York (1989), Part 1, Chap. 2.

3) M. Kira, T. Maruyama, and H. Sakurai, *Tetrahedron Lett.*, **23**, 243 (1992).

4) a) R. S. Grev, H. F. Schaefer III, and P. P. Gasper, *J. Am. Chem. Soc.*, **113**, 5638 (1991); b) R. S. Grev, H. F. Schaefer, and K. M. Baines, *ibid.*, **112**, 9458 (1990); c) R. S. Grev, *Adv. Organomet. Chem.*, **30**, 125 (1991); d) M. S. Gorden and D. Bartol, *J. Am. Chem. Soc.*, **109**, 5948 (1987); e) B. T. Luke, J. A. Pople, M.-B. Kroh-Jespersen, Y. Apeloig, M. Karni, J. Chandrasekhar, and P. v. R. Schleyer, *ibid.*, **108**, 270 (1986); f) M. B. Kroh-Jespersen, *ibid.*, **107**, 537 (1985); g) Y. Apeloig and M. Karni, *J. Chem. Soc., Chem. Commun.*, **1985**, 1048.

5) M. Ishikawa and M. Kumada, *Adv. Organomet. Chem.*, **19**, 51 (1981) and references cited therein.

6) Y. Nakadaira, T. Kobayashi, T. Otsuka, and H. Sakurai, *J. Am. Chem. Soc.*, **101**, 486 (1979); H. Sakurai, H. Sakaba, and Y. Nakadaira, *ibid.*, **104**, 6156 (1982); H. Sakurai, Y. Nakadaira, and H. Sakaba, *Organometallics,* **2**, 1484 (1983).

7) Y. -S. Chen, B. H. Cohen, and P. P. Gaspar, *J. Organomet. Chem.*, **195**, C1 (1981); Y. -S. Chen and P. P. Gaspar, *Organometallics*, **1**, 1410 (1982).

8) A preliminary account of this paper was presented at the XXV Silicon Symposium, Los Angels, April 1992, Paper No. 72P. Closely related results were presented by K. B. Banks, Y. Wang, and R. T. Conlin at the Symposium. Paper No. 7.

9) Recently, λ_{max} values for stable (E)- and (Z)-1,2-bis(2,4,6-triisopropyphenyl)-1,2-bis(trimethylsilyl)-disilenes have been reported to be 394 and 398 nm, respectively. R. S. Archibald, Y. van den Winkel, A. J. Millevolte, J. M. Desper, and R. West, *Organometallics*, **11**, 3276 (1992).

10) G. R. Gillette, G. H. Noren, and R. West, *Organometallics*, **6**, 2617 (1987); *ibid.*, **8**, 487 (1989); W. Ando, K. Hagiwara, and A. Sekiguchi, *ibid.*, **6**, 2270 (1987); W. Ando, K. Hagiwara, A. Sekiguchi, and A. Sakakibara, and H. Yoshida, *ibid.*, **7**, 558 (1988).

11) R. West, *Pure and Appl. Chem.*, **56**, 163 (1984).

12) W. Ando, H. Itoh, and T. Tsumuraya, *Organometallics*, **8**, 2759 (1989).

13) Photolysis of hexakis(triethylsilyl)cyclotrisilane has been reported to give tetrakis(triethylsilyl)disilene. The primary photo-products are assumed to be the disilene and bis(triethylsilyl)silylene which dimerizes to the disilene: H. Matsumoto, A. Sakamoto, and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, **1986**, 1768.

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