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Bis(diisopropylamino)silylene and Its Dimer

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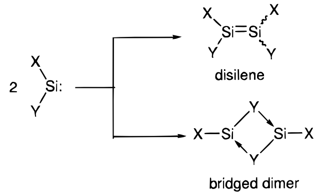
Recent theoretical calculations have shown that the structure of silylene dimers depends strongly on the substituents; while simple H_2Si: dimerizes to give a stable disilene, $H_2Si{=}SiH_2$, dimers of several heteroatom substituted silylenes (X, Y = NH_2, OH, F, etc.) are bridged by the heteroatoms as shown in Scheme 1.[1]

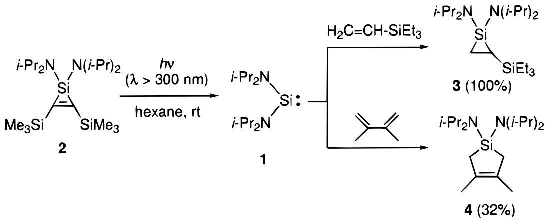
Diaminosilylene [$(H_2N)_2Si$:] is particularly interesting because the theoretical calculations at the HF/6-31G* level have shown that diaminosilylene has no energy minimum at the disilene geometry, while a local minimum is observed at the corresponding bridged dimer geometry.[1f] Whereas a number of diaminosilylenes have been generated and even isolated,[2] there has been no spectroscopic evidence for the dimer structures reported so far.[3] In this paper, we have found that bis(diisopropylamino)silylene (**1**) generated photochemically is rather stable at room temperature in solution and gives the dimer at low temperature. In contrast to the theoretical prediction,[1f] the dimer is not compatible with the bridged structure but with the disilene, as evidenced by UV−vis spectroscopy.

Photochemical generation of **1** is confirmed by several trapping experiments. Exhaustive irradiation of hexane solutions of 3,3-bis(diisopropylamino)-1,2-bis(trimethylsilyl)-3-silacyclopropene (**2**)[4] (ca. 2×10^{-2} M) at room temperature with a 500-W high-pressure mercury arc lamp in the presence of triethylvinylsilane and 2,3-dimethyl-1,3-butadiene gave **3**[4] and **4**[5] in 100 and 32% yields, respectively (Scheme 2).[6]

Scheme 1



Scheme 2



The following observations indicate that **1** generated photochemically is stable enough to be observed by NMR and UV−vis spectroscopies in solution at room temperature. During irradiation of **2** in toluene-*d*$_8$ in a sealed tube with a 500-W high-pressure mercury arc lamp at 25 °C, a set of signals assignable to **1** appeared at 1.29 (a doublet) and 3.60 ppm (a septet) with the intensity ratio of 6:1 together with signals due to bis(trimethylsilyl)acetylene in the ^{1}H NMR spectrum;[7] the yield of **1** determined NMR spectroscopically was 90% under the consumption of 48% of **2**. While the new signals were rather persistent at 25 °C, the disappearance of the signals together with the increase of the signal intensity of **2** was observed upon heating of the mixture to 75 °C, being indicative of readdition of **1** to bis(trimethylsilyl)acetylene.[8] When a similar photolysis of a 3-methylpentane (3-MP) solution of **2** was monitored at room temperature by UV−vis spectroscopy, a new band appeared at 335 nm (band I) as shown in Figure 1. The band maximum is reasonably assigned as n → p transition of **1** because the n → p transition of a related cyclic diaminosilylene has been observed at 344 (sh) nm.[2h] Whereas the absorption bands of these diaminosilylenes are unusually blue-shifted from that of dimethylsilylene (453 nm),[9] the effective intramolecular interaction between lone-pair orbitals on nitrogens and a vacant silicon 3p orbital to raise the latter level is responsible for the blue shift, as demonstrated both theoretically and experimentally;[10] typically, λ_{max} of Mes(Me_2N)Si: (405 nm) has been found at a 92-nm shorter wavelength than that of Mes(H)Si: (λ_{max} 497 nm).[10c,11]

As shown in Figure 1, a new band emerged at 439 nm (band II) when a 3-MP solution of **1** prepared by photolysis of **2** at room temperature was cooled to 77 K. With lowering temperatures, the absorbance of band II increased, and the maximum of

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[1] (a) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, *109*, 5303. (b) Malrieu, J.-P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916. (c) Trinquier, G.; Barthelat, J.-C. *J. Am. Chem. Soc.* **1990**, *112*, 9121. (d) Spoliti, M.; Ramondo, F.; Bencivenni, L.; Kolandaaivel, P.; Kumaresan, R. *J. Mol. Struct.* **1993**, *283*, 73. (e) Maxka, J.; Apeloig, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 737. (f) Apeloig, Y.; Müller, T. *J. Am. Chem. Soc.* **1995**, *117*, 5363.

[2] For isolated diaminosilylenes and their reactions, see: (a) Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Meltzler, N. *J. Am. Chem. Soc.* **1994**, *116*, 2691. (b) Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33. (c) Arduengo, A. J., III; Bock, H.; Chen, H.; Denk, M.; Dixon, D. A.; Green, J. C.; Herrmann, W. A.; Jones, N. L.; Wagner, M.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 6641. (d) Denk, M.; Hayashi, R. K.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 10813. (e) Denk, M.; Green, J. C.; Metzler, N.; Wagner, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2405. (f) Metzler, N.; Denk, M. *Chem. Commun.* **1996**, 2657. (g) West, R.; Denk, M. *Pure Appl. Chem.*, **1996**, *68*, 785. (h) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. J. Chem. Soc., *Chem. Commun*. **1995**, 1931. (i) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. *J. Organomet. Chem.* **1996**, *521*, 211. (j) Drost, D.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1997**, 1845. For other transient or relatively unstable diaminosilylenes, see: (k) Veith, M.; Lisowsky, R.; Köppe, R.; and Schnöckel, H. *Chem. Ber.* **1992**, *125*, 1375. (l) Huppmann, F.; Maringgele, W.; Kottke, T.; Meller, A. *J. Organomet. Chem.*, **1992**, *434*, 35. (m) Huppmann, F.; Noltemeyer, M.; Meller, A. *J. Organomet. Chem.*, **1994**, *483*, 217.

[3] Possible dimerization of a stable cyclic diaminosilylene is discussed.[1f,2e.]

[4] Sakamoto, K.; Tsutsui, S.; Sakurai, H.; Kira, M. *Bull. Chem. Soc. Jpn*. **1997**, *70*, 253.

[5] **4**: a colorless oil; ^{1}H NMR ($CDCl_3$, δ) 1.12 (d, $J = 6.8$ Hz, 24 H), 1.61 (s, 4 H), 1.79 (s, 6 H), 3.38 (sept, $J = 6.8$ Hz, 4 H); ^{13}C NMR ($CDCl_3$, δ) 19.7, 24.4, 28.7, 44.8, 130.1; ^{29}Si NMR ($CDCl_3$, δ) −2.2; HRMS calcd for $C_{18}H_{36}N_2Si$ 310.2804, found 310.2795.

[6] Generation of silylenes by the photolysis of the corresponding 3-silacyclopropenes has been reported: (a) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Am. Chem. Soc.* **1977**, *99*, 245. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879.

[7] The ^{1}H NMR spectra before and after irradiation of **2** in toluene-*d*$_8$ are shown in the Supporting Information. Despite a number of experiments, we have failed to measure the ^{13}C and ^{29}Si NMR spectrum of **1** due to the low concentration. Concentration of the solution of **1** lead to its decomposition even at 0 °C. Similar thermal instability is reported for a cyclic diaminosilylene [:Si(N(*t*-Bu)$CH_2)_2$].[2e,g] Very recently, interesting reactions of the diaminosilylene with the corresponding diaminogermylene were reported: Schäfer, A.; Saak, W.; Weidenbruch, M.; Marsman, H.; Henkel, H. *Chem. Ber./Recl.* **1997**, *130*, 1733.

[8] The yield of **2** regenerated by recombination is estimated to be 14% by NMR spectroscopy. In addition, when 2,3-dimethyl-1,3-butadiene was introduced in the dark after irradiation of a solution of **2** at room temperature, **4** was formed in 10% yield. These trapping experiments give the definitive evidence for the existence of **1** at room temperature in solution, while the yields are rather low due to the competitive decomposition.[7]

[9] Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 5427.

[10] Theoretical studies: (a) Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1048. (b) Apeloig, Y.; Karni, M., West, R.; Welsh, K. *J. Am. Chem. Soc.* **1994**, *116*, 9719. Experimental studies: (c) Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R.; Michl, *J. Silicon, Germanium, Tin, Lead Compd.* **1986**, *9*, 75. (d) Gillette, G. R.; Noren, G.; West, R. *Organometallics* **1990**, *9*, 2925.

S0002-7863(98)00008-0 CCC: $15.00

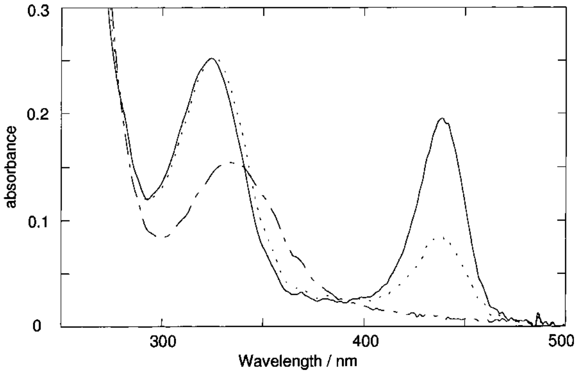
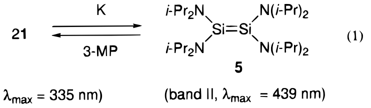


Figure 1. Temperature-dependent UV spectra of 3-MP solution of **1**, prepared by irradiation of **2** at 292 K (—•—), at 107 K (- - -), and at 77 K (— — —).

band I shifted from 335 nm at 292 K to 325 nm at 77 K; the spectral change was reversible between 77 and 292 K. The ratio of the absorbance of band I (A_{I}) to that of band II (A_{II}) was not independent of A_{I} at a constant temperature.[13] Instead, A_{II} was proportional to A_{I}^2, being indicative that diaminosilylene **1** is equilibrated in solution with a dimer of **1** which is responsible for band II (eq 1). Although the absolute equilibrium constant



$$2\,\mathbf{1} \underset{\text{3-MP}}{\overset{K}{\rightleftarrows}} (i\text{-Pr}_2\text{N})_2\text{Si}{=}\text{Si}(\text{N}(i\text{-Pr})_2)_2 \quad \mathbf{5} \qquad (1)$$

in 3-MP (K) cannot be determined by our experiments, the equilibrium constant in a 95/5 mixture of 3-MP and 2-methyltetrahydrofuran (2-MeTHF) (K') was found to be rather smaller than K ($K'/K = 0.6$ at 77 K), suggesting significant stabilization of **1** by a polar solvent.[14] While reversible thermal dissociation of disilenes to the corresponding silylenes has been reported by Okazaki et al.,[17] the present results afford the first direct spectroscopic observation of the reversible equilibrium between silylene and disilene.

On the basis of the following arguments, the dimer structure is not compatible with the bridged dimer but with the corresponding disilene **5**. Thus, the amino-bridged silylene dimer should be colorless because a known amino-bridged dimer of bis(dimethylamino)stannylene is colorless ($\lambda < 400$ nm).[18] While the maximum of band II is red-shifted considerably from the reported value for tetramethyldisilene (344 nm),[19] successive dialkylamino substitution to the disilene has been shown to cause significant red shift of the maximum; the $\lambda_{\max}$ values found for (diethylamino)trimethyldisilene[20a] and 1,1-bis(diethylamino)-2,2-dimethyldisilene[20b] are 395 and 417 nm in 3-MP at 77 K, respectively. Extrapolation of the substituent effects suggests that the value of 439 nm is reasonable as the maximum of a tetrakis(dialkylamino)disilene.

The absorbance of band I should decrease along with the formation of the dimer at lower temperatures, but in reality, it even increases accompanying the significant blue shift and narrowing of the bandwidth, as shown in Figure 1. The temperature dependence of the feature of band I would be related to the conformational change around Si−N bonds depending on temperatures. Thus, with lowering temperatures, overlap between nitrogen lone-pair orbitals and a vacant 3p(Si) orbital will increase in average due to the decrease of the amplitude of the torsion around the Si−N bonds, which in turn causes the blue shift (vide supra) and the band narrowing. Related behavior has been observed for the UV−vis spectra of aryloxysilylenes by West et al.[10d] Since the $\pi \rightarrow \pi^*$ transition of **5** is allowed but the n → p transition of **1** is forbidden, the actual contribution of **5** in the silylene−disilene equilibrium will be smaller than that anticipated by the apparent ratio of the absorbances between the bands I and II. Therefore, the decrease of the absorbance of band I by dimerization of **1** will be compensated for by the narrowing of the bandwidth and possible increase of the oscillator strength of the n → p transition of **1**, while at present, there is no supporting evidence for the latter rationalization. The UV−vis spectral behavior of **1** in solution implies also that the major component in the equilibrium is **1** even at 77 K and no dimers other than **5** such as the bridged dimer contribute to the equilibrium.

The present spectroscopic study suggests that the bridged dimer would be the transition state for the scrambling of the amino substituents found previously[4] or the transient species which exists only at higher temperatures (>80 °C).

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Supporting Information Available: Experimental details of spectroscopic studies of **1** and 1,1-bis(diethylamino)dimethyldisilene (9 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(11) A reviewer has pointed out the possibility that the new species observed by ^{1}H NMR is an oligomer of **1** such as the cyclic trimer, $[(i\text{-Pr}_2\text{N})_2\text{Si}]_3$, which is invisible in the UV spectra. The possibility will be rationalized if the cyclotrisilane is in equilibrium with a small amount of **1** (the ratio of the trimer with **1** > 95/5); a cyclotrisilane has been known to decompose at 40 °C to give the corresponding silylene and disilene.[12] However, a UV−vis spectrum obtained after exhaustive photolysis of **2** (5.0×10^{-4} M) in 3-MP at room temperature showed that the absorbance of the band due to **1** was 0.50. The result means that the absorption coefficient (ϵ) of **1** should be at least 18 000, if the yield of **1** is less than 5%. The estimated ϵ value is far larger than that expected for a forbidden n → p transition of a silylene. On the other hand, according to our assignment, the ϵ value of **1** is estimated reasonably as >950.

(12) Belzner, J.; Ihmels, H.; Kneisel, B. O.; Gould, R. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 305. See also: Weidenbruch, M. *Comments Inorg. Chem*. **1986**, *5*, 247.

(13) Experimental details of the concentration dependence of the ratio of A_{I} and A_{II} are given in the Supporting Information.

(14) The band due to the dimer (band II) is not observed even at 77 K when **1** was generated in 100% 2-MeTHF. Apparently, 2-MeTHF stabilizes silylene **1** more than the dimer. The origin of the solvent effects cannot be attributed, however, to the well-established complexation of silylenes with Lewis bases because the complexation should cause significant blue shift of the n → p transition;[15] in reality, the absorption maximum of **1** and its temperature dependence in both 3-MP/2-MeTHF (95/5) and 2-MeTHF solutions were the same as those in 3-MP. Intermolecular complexation of **1** with 2-MeTHF would be hampered because of the low Lewis acidity of **1** due to the effective intramolecular electron donation by the amino substituents. Complexation of **1** with precursor **2** is also implausible because the nucleophilicity of **2** is expected to be similar to that of 2-MeTHF on the basis of the low basicity of silyl-substituted amines in general[16] and severe steric bulkiness of the isopropyl substituents in **2**. The observed solvent effect on K is explained by the effective solvation to rather polar silylene **1** due to the contribution of the ylide structure.

(15) (a) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1987**, *6*, 2617. (b) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1989**, *8*, 487. (c) Pearsall, M.-A.; West, R. *J. Am. Chem. Soc.* **1988**, *110*, 7228. (d) Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270. (e) Ando, W.; Sekiguchi, A.; Hagiwara, K.; Sakakibara, A.; Yoshida, H. *Organometallics* **1988**, *7*, 558. (f) Kira, M.; Maruyama, T.; Sakurai, H. *Heteroat. Chem.* **1994**, *5*, 305.

(16) Bassindale, A. R.; Taylor, P. G. in *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: NY, 1989; Part I, Chapter 12.

(17) (a) Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.*, **1993**, *115*, 10428. (b) Suzuki, H.; Tokitoh, N.; Okazaki, R. *Bull. Chem. Soc. Jpn.*, **1995**, *68*, 2471.

(18) (a) Foley, P.; Zeldin, M. *Inorg. Chem.* **1975**, *14*, 2264. (b) Corvan, P. J.; Zuckerman, J. J. *Inorg. Chim. Acta* **1979**, *34*, L255. (c) Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1984**, *23*, 413.

(19) (a) Sekiguchi, A.; Maruki, I.; Ebata, K.; Kabuto, C.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1991**, 341. (b) Sekiguchi, A.; Maruki, I.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 11460.

(20) (a) Yoshida, M.; Sakamoto, K.; Sakurai, H. *Abstract of 67th Annual Meeting of Chem. Soc. Jpn.*, **1994**, 1H126. (b) Sakamoto, K.; Tsutsui, S.; Kira, M., unpublished results. 1,1-Bis(diethylamino)dimethyldisilene was generated by the photolysis of the corresponding 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes in 3-MP matrix at 77 K. Experimental details are given in the Supporting Information.