Photochemical Formation of 9-Silaanthracenes in Rigid Glass

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UV photolysis of 9,10-dihydro-9-silaanthracenes in 3-methylpentane glass at 77 K results in the formation of 9-silaanthracenes and diphenylmethyl-type radicals; by use of a triplet quencher, it was confirmed that these were produced *via* the lowest triplet state.

A number of compounds containing silicon–carbon or silicon–silicon double bonds have recently been reported. However, few silaaromatic compounds have been prepared apart from silabenzene,[1] disilabenzene,[2] and 9-silaanthracenes,[3] which were prepared by Maier *et al.* using the pyrolysis technique. 9-Silaanthracenes have been produced by flash pyrolysis of 9,10-dihydro-9-silaanthracenes around 1000 °C followed by a successive matrix isolation of product at 15 K.[3] However, there has been no report on the photochemical formation of these compounds. In this communication we report an observation of UV–VIS absorption and fluorescence spectra of 9-silaanthracenes produced by UV photolysis of 9,10-dihydro-9-silaanthracenes.

Photochemical formation of 9-silaanthracenes was examined for 9,10-dihydro-9-silaanthracenes in rigid glass at 77 K with irradiation either by a 100 W low-pressure mercury lamp (253.7 nm) or by the output of the fourth harmonic of a Nd^{3+} : YAG laser (266 nm, Quanta-Ray GCR-130, Spectra Physics). 9-Phenyl- and 9-methyl-9,10-dihydro-9-silaanthracene were synthesized according to the literature[4,5] and their structures were confirmed by comparison of their NMR and MS spectra with those of authentic samples. The differential absorption spectrum before and after the photolysis of 9-phenyl-9,10-dihydro-9-silaanthracene **1** is shown in Fig. 1(*a*). Absorption peaks can be seen at 510, 472, 454, 407 and 385 nm. As these are similar to the spectrum of 9-phenyl-9-silaanthracene **2** produced in an Ar matrix at 15 K,[3] these absorption peaks are ascribed to the presence of **2**. The intense absorption peaks observed at 361, 342, 329 and 305 nm are attributed to diphenylmethyl-type carbon-centred radicals **3**.[6,7] This classification was confirmed by UV photolysis of **1** in ethanol glass at 77 K: absorption bands attributed to **2** disappeared and only the latter absorption peaks remained. This also indicates that **2** and/or its precursor reacts with ethanol even at 77 K, unlike **3**. All the absorption bands attributed to **2** and **3** were thermally bleached when the irradiated sample was warmed to room temperature.

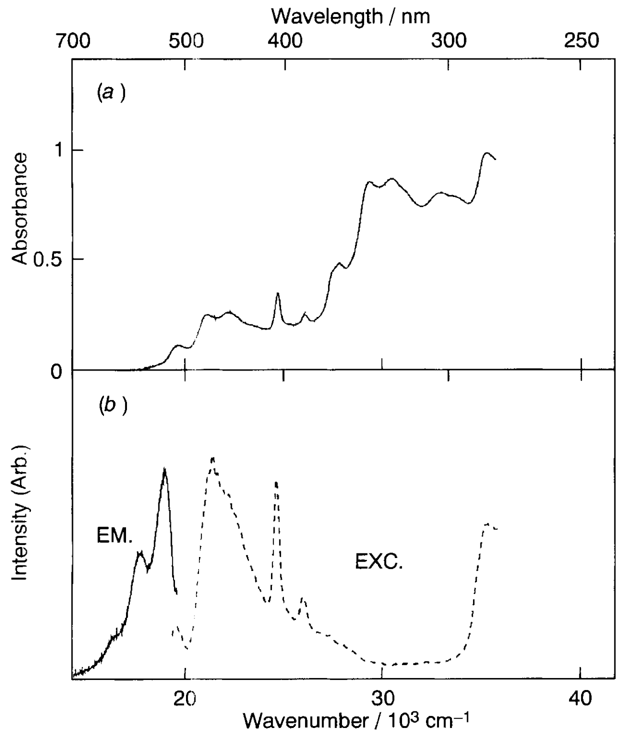
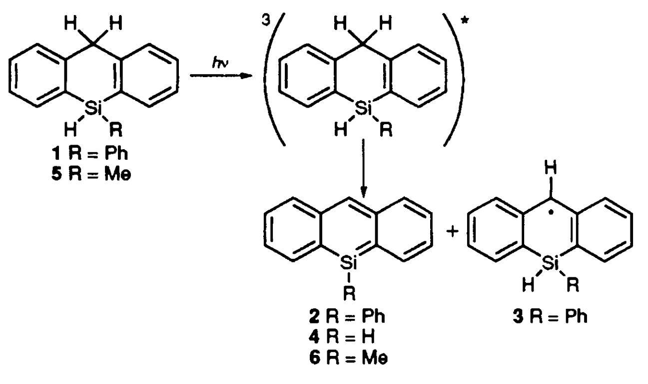


Fig. 1 (*a*) Differential absorption spectrum before and after the photolysis and (*b*) fluorescence spectrum observed after the photolysis of 9-phenyl-9,10-dihydro-9-silaanthracene in 3-methylpentane at 77 K. The fluorescence emission (full line) and excitation spectra (broken line) were observed by excitation at 407 nm and monitoring at 528 nm, respectively.

The above assignment was confirmed by the fluorescence spectrum of **2** recorded on a Hitachi M850 fluorescence spectrophotometer as shown in Fig. 1(*b*). By excitation of the 407 nm absorption band, an emission spectrum was observed with peaks at 528 and 565 nm. The excitation spectrum measured by monitoring the fluorescence intensity at the 528 nm emission band shows peaks at 513, 470, 450 (shoulder), 407, 385, 366 and 283 nm. These correspond to the absorption peaks attributed to **2** and there is no band which correlates to those of **3**. The minor differences in peak wavelength and relative peak intensity between the absorption and fluorescence spectra may be due to superimposition of the weak absorption bands of **3** and silylene, for which the absorption maximum is expected to be 490 nm.[8] Vibrational progression characteristic of anthracene derivatives is observed in the 407, 385 and 366 nm peaks. The vibrational spacings indicated by these peaks are 1400 cm^{-1}, being highly similar to those of anthracene derivatives.

The electronic excited states of 9-silaanthracene **4** have been calculated by the CNDO/S-CI method[9,10] using the structure determined by the MNDO PM3 method[11] for **4** and the results are given in Table 1. The first, third and seventh excited singlet states correlate to the ^1L_a, ^1L_b and ^1B_b bands, respectively, of anthracene, and the red shift of these bands is indicated in **4**. The 513 and 407 nm absorption peaks are assigned to the 0–0 band of the first and third electronic transitions, respectively. The 283 nm peak is ascribed to the seventh band.

UV photolysis of 9-methyl-9,10-dihydro-9-silaanthracene **5** in 3-methylpentane glass at 77 K gave absorption and fluorescence spectra similar to those obtained for **1**. These spectra are attributed to 9-methyl-9-silaanthracene **6**. The assignment of the bands is also shown in Table 1.



Scheme 1

Table 1 Calculated results and assignment of electronic states for 9-silaanthracenes

	Calculated			Observed							
	Energy			**4**[a]		**2**[b]		**2**[a]		**6**[b]	
	/10^3 cm^{-1}	/nm	f-value	/10^3 cm^{-1}	/nm	/10^3 cm^{-1}	/nm	/10^3 cm^{-1}	/nm	/10^3 cm^{-1}	/nm
1	22.8	438	0.247	20.2	494	19.5	513	20.0	500	19.5	513
2	22.9	436	0.034	—	—	—	—	—	—	—	—
3	25.8	387	0.188	25.0	400	24.6	407	24.8	404	24.6	406
4	33.3	300	0.000	—	—	—	—	—	—	—	—
5	34.6	289	0.030	—	—	—	—	—	—	—	—
6	35.4	282	0.030	—	—	—	—	—	—	—	—
7	36.0	277	0.994	—	—	35.1	285	—	—	—	—

[a] Ref. 3; in Ar matrix at 15 K. [b] This work; fluorescence excitation spectrum in 3-methylpentane at 77 K.

To study the reaction path by which **2** is prepared, UV photolysis of **1** was carried out in the presence of a quantity of the triplet quencher, 2,3-dimethyl-1,3-butadiene (0.3 mmol dm^{-3}), sufficient to completely quench the phosphorescence of **1**. After photolysis, the absorption bands of **2** and **3** were not observed, indicating that the photochemical reaction proceeds *via* the lowest triplet state. Studies on the mechanistic details of the photochemical formation of 9-silaanthracenes are now in progress.

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