Photophysical and Photochemical Processes of 9,10-Dihydro-9-silaphenanthrene Derivatives: Photochemical Formation and Electronic Structure of 9-Silaphenanthrenes

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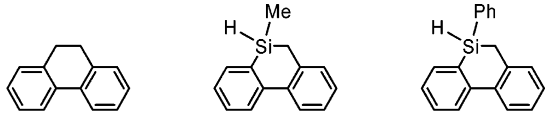
Photophysical and photochemical processes of 9-methyl- and 9-phenyl-9,10-dihydro-9-silaphenanthrene derivatives have been studied at room temperature and 77 K in comparison with the carbon analogue, 9,10-dihydrophenanthrene. These 9,10-dihydro-9-silaphenanthrene derivatives show smaller fluorescence quantum yield and remarkably larger Stokes shifts than those of the carbon analogue. In contrast, their phosphorescence quantum yields are two times larger than those of the carbon analogue, although the absolute value is not so large (∼0.1). Reaction products and intermediates produced by the 266 nm light photolysis have been studied, and it has been confirmed that 9-methyl- and 9-phenyl-9-silaphenanthrenes have been photochemically formed in methylcyclohexane at 77 K, in addition to the formation of radical cations of 9,10-dihydro-9-silaphenanthrene derivatives and the carbon-centered radical: 9-hydro-9-silaphenanthrenyl radical.

Introduction

Recently much attention has been paid for organic electroluminescent (EL) materials. Organosilicon compounds such as poly(silafluorene) are considered to be a useful candidate for EL materials,[1,2] and it is important to study luminescence properties of these organosilicon compounds. We have studied photophysical and photochemical properties of organosilicon compounds such as benzylsilane derivatives,[3,4] 9,10-dihydro-9-silaanthracene derivatives,[5,6] and poly(methylphenylsilane) functionalized with azobenzene groups.[7,8] For some 9,10-dihydro-9-silaanthracene derivatives, fluorescence and phosphorescence quantum efficiencies were determined to be ca. 0.1 and 0.4, respectively.[5] We also confirmed the photochemical formation of 9-phenyl-9-silaanthracene in the photolysis of 9-phenyl-9,10-dihydro-9-silaanthracene in 3-methylpentane at 77 K by comparing the electronic spectrum with that of 9-phenyl-9-silaanthracene formed by means of the flash vacuum thermolysis by van den Winkel and Maier et al.[9] The formation of 9-silaanthracene derivative has been supported by the UV absorption spectrum reported by Tokitoh et al. for the 9-silaanthracene derivative kinetically stabilized by the bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl] phenyl (Tbt) group, on the silicon atom.[10−15]

Formation of 9-silaphenanthrene has recently been deduced from the isolation of trapping products formed in the thermal retro-ene elimination of several 9-substituted-9,10-dihydro-9-silaphenanthrenes by two of us, Oba and Nishiyama.[16] To the best of our knowledge, however, there has been no report on their photophysical and photochemical properties of 9-substituted-9,10-dihydro-9-silaphenanthrenes. In this study we have investigated whether the 9-silaphenanthrenes are produced or not by the UV light-irradiation of 9-substituted-9,10-dihydro-9-silaphenanthrenes shown in Chart 1 by comparing the electronic spectrum with that of 9-silaphenanthrenes prepared in the same manner as that of silaaromatic compounds such as 2-silanaphthalene, silabenzene, and 9-silaanthracene derivatives.[10−15]

CHART 1



1 **2** **3**

Experimental Section

Materials. 9,10-Dihydrophenanthrene (**1**) (GR. Tokyo Chem. Ind. Co.) was purified by repeated recrystallization from cyclohexane. 9-Methyl-9,10-dihydro-9-silaphenanthrene (**2**) and 9-phenyl-9,10-dihydro-9-silaphenanthrene (**3**) were synthesized according to the procedure reported elsewhere.[16] Biphenyl (UP. Tokyo Chem. Ind. Co.) was used as a standard to estimate emission quantum yield. Methylcyclohexane (>99% Wako Pure Chem. Ind. Ltd.), methanol (GR. Tokyo Chem. Ind. Co.), ethanol (GR.Tokyo Chem. Ind. Co.), and 2-chlorobutane (GR. Tokyo Chem. Ind. Co.) were used as received. All samples were fully bubbled with high-purity Ar gas just before use.

Absorption spectra were recorded on a Hitachi U3300 spectrophotometer. Fluorescence emission and excitation spectra were measured by using a Hitachi M850 or F4500 fluorescence spectrometer with band-pass of 2.5 or 5 nm for both emission and excitation. Fluorescence and phosphorescence quantum

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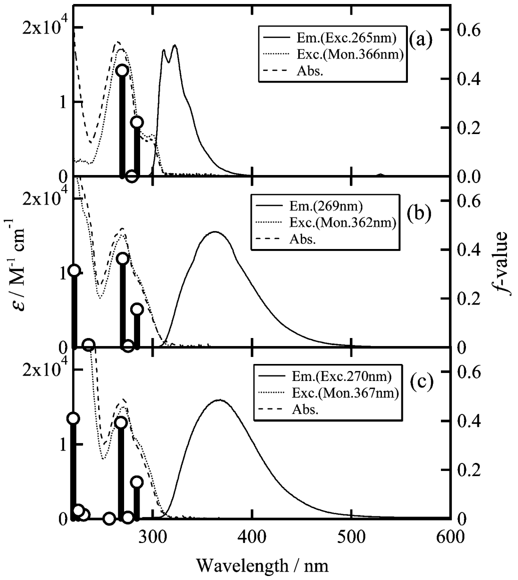


Figure 1. Absorption (broken line), emission (full line), and excitation (dotted line) spectra of 9,10-dihydrophenanthrene (a), 9-methyl-9,10-dihydro-9-silaphenanthrene (b), and 9-phenyl-9,10-dihydro-9-silaphenanthrene (c) in methylcyclohexane at room temperature. Calculated electronic transitions are shown by the stick spectra.

yields were determined relative to those of biphenyl in methylcyclohexane at room temperature and at 77 K. Fluorescence lifetimes were measured by using an Edinburgh Analytical Instruments FL900CDT Spectrometer system (H_2 pulser, pulse width 0.8 ns, 10^8 photons/pulse, repetition rate 40 kHz).[3] Phosphorescence decay was recorded on a Hitachi F4500 fluorescence spectrometer with band path of 2.5 nm and response time of 0.01 s. Nanosecond laser photolysis was studied by using a Unisoku TSP601H nanosecond laser photolysis system by flowing the sample solution using 266-nm light of an Nd^{3+}:YAG laser (output of fourth harmonic, 2 mJ/pulse, pulse width 8 ns, 10 Hz).[3] Steady-state photolysis was carried out at 77 K using 266-nm light of an Nd^{3+}:YAG laser (1800 pulses). Products formed in the photolyses in methanol/ethanol 1:1(vol/vol) mixed solution at 77 K were analyzed by use of a gas chromatography mass spectrometry (GC-MS) spectrometer (Hewlett-Packard GC5890 Series II, methyl silicone capillary column, and JEOL JMS-AX-500 and DA7000 data systems).

The PM3 calculations were carried out to obtain optimized molecular structures of the ground and excited states of 9,10-dihydro-9-silaphenanthrene and possible reaction intermediates,[17] and CNDO/S-CI calculations were performed to study the electronic spectra for the optimized structure[18] with appropriate parameters for the silicon atom.[19]

Results and Discussion

Photophysical Processes of 9,10-Dihydro-9-silaphenanthrene Derivatives at Room Temperature. Parts a−c of Figure 1 show the absorption (broken line), emission (full line), and excitation spectra (dotted line) of 9,10-dihydrophenanthrene (**1**), 9-methyl-9,10-dihydro-9-silaphenanthrene (**2**), and 9-phenyl-9,10-dihydro-9-silaphenanthrene (**3**) in methylcyclohexane (MCH) at room temperature. These absorption spectra are similar to each other, and the molar absorption coefficients of the absorption maxima of **1** (at around 265 nm), **2** (269 nm), and **3** (270 nm) were determined to be ca. 18 000, 15 700, and 16 100 M^{-1} cm^{-1}, respectively. These spectra are reasonably explained by the calculated electronic spectra (stick spectra). It is noted that a weak absorption peak was observed at 303 nm for **1**, while a shoulder was observed around 300 nm for both **2** and **3**. It is understood that these 9,10-dihydrophenanthrene derivatives have electronic structures similar to each other and the perturbation given by the introduction of a silicon atom is rather small. On the excitation of the absorption maxima, fluorescence spectra were determined as shown by the full line in Figure 1. The fluorescence spectrum of **1** shows peaks around 307 and 322 nm with small Stokes shifts, while those of **2** and **3** are broad and show maxima at 362 and 367 nm with remarkably large Stokes shifts, respectively. This indicates that the conformational changes on going from the ground to the fluorescing state in **2** and **3** are much larger than that of **1** and C−C(methylene)−Si−C linkages are much flexible than the C−C(methylene)−C(methylene)−C linkage. Thus, it is expected that the photophysical and photochemical properties of the fluorescing states of **2** and **3** are different from that of **1**.

TABLE 1: Photophysical Parameters of 9,10-Dihydro-9-silaphenanthrene Derivatives in Methylcyclohexane at Room Temperature

	1	2	3
Φ_f	0.57	0.03	0.02
τ_f (ns)	5.9 ± 0.5	0.6 ± 0.4	0.4 ± 0.4
τ_f^0 (ns)	10.3	20	20
k_f (10^7 s^{-1})	9.7	5.0	5.0
k_f^{nr} (10^7 s^{-1})	7.3	160	240

Fluorescence quantum yields (Φ_f) of **1**, **2**, and **3** were determined relative to that of biphenyl ($\Phi_f = 0.14$)[20] to be 0.57, 0.03, and 0.02 at room temperature. Φ_f(**1**) is in good agreement with the reported value (Φ_f(**1**) = 0.55) determined in cyclohexane at room temperature.[21] Remarkable reduction in Φ_f is admitted for **2** and **3** compared with that of **1**, indicating that nonradiative deactivation is much more efficient in **2** and **3** than that of **1**.

Fluorescence decay profiles of these compounds were determined by means of the single photon counting technique in MCH at room temperature by monitoring the fluorescence at the maxima upon excitation of the absorption maxima. The fluorescence decay curve of **1** was analyzed by a single-exponential function, and its lifetime (τ_f) was determined to be 5.9 ± 0.5 ns, in agreement with the value (6.6 ns) reported for **1** in cyclohexane at room temperature.[21] The fluorescence decay curves of **2** and **3** were also analyzed by single-exponential functions with lifetimes of 0.6 ± 0.4 and 0.4 ± 0.4 ns, respectively. Radiative lifetime ($\tau_f^0 = \tau_f/\Phi_f$) of **1** was estimated to be 10.3 ns, and radiative (k_f) and nonradiative decay rate constants ($k_f^{nr} = k_f(1/\Phi_f - 1)$) of **1** were estimated to be 9.7 and 7.3 × 10^7 s^{-1}, respectively. Radiative lifetimes of **2** and **3** were determined to be both 20 ns, and radiative and nonradiative decay rate constants were estimated to be 5.0 and 160 × 10^7 s^{-1} for **2** and 5.0 and 240 × 10^7 s^{-1} for **3**, respectively. These photophysical parameters are summarized in Table 1.

Photophysical Processes of 9,10-Dihydro-9-silaphenanthrene Derivatives at 77 K. Parts a−c of Figure 2 show the absorption, emission, and excitation spectra of **1**, **2**, and **3** in MCH at 77 K. These absorption spectra (broken line) are similar to those observed at room temperature. Fluorescence spectra (full line) observed upon excitation of the absorption maxima at 77 K are also similar to those at room temperature, but the wavelength of the fluorescence maximum is shifted to the shorter wavelength by 10 nm in **2** and by 5 nm in **3** compared with that at room temperature. These spectral shifts may be interpreted by the dual fluorescence, which is evidenced by the analysis of the fluorescence decay curves as shown below.

Fluorescence quantum yields (Φ_f) of **1**, **2**, and **3** were also determined at 77 K relative to that of biphenyl ($\Phi_f = 0.14$)[22] in

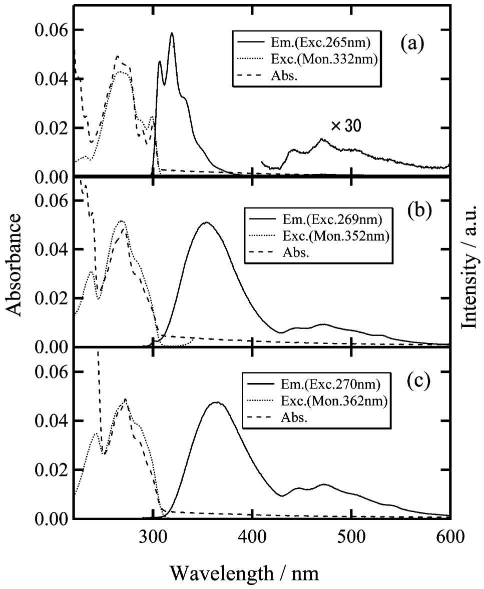


Figure 2. Absorption (broken line), emission (full line), and excitation (dotted line) spectra of 9,10-dihydrophenanthrene (a), 9-methyl-9,10-dihydro-9-silaphenanthrene (b), and 9-phenyl-9,10-dihydro-9-silaphenanthrene (c) in methylcyclohexane at 77 K.

MCH to be 0.66, 0.28, and 0.23, respectively. Remarkable increases in $\Phi_f(\mathbf{2})$ and $\Phi_f(\mathbf{3})$ at 77 K compared with those at room temperature are noticeable. This indicates that nonradiative deactivation of the fluorescing state becomes less efficient in **2** and **3** at 77 K than at room temperature. Fluorescence decay profiles of these compounds were determined in MCH at 77 K by means of the single photon counting technique with monitoring wavelengths of 323, 352, and 364 nm and excitation wavelengths of 280, 270, and 270 nm for **1**, **2**, and **3**, respectively. The fluorescence decay curve of **1** was analyzed by a single-exponential function, and its lifetime (τ_f) was determined to be 5.2 ± 0.5 ns, being comparable to that at room temperature. The fluorescence decay curves of **2** and **3** at 77 K were analyzed by double-exponential functions with lifetimes of 2.6 ± 0.2 ns (emission intensity of 34%) and 4.5 ± 0.3 ns (66%) for **2** and 2.7 ± 0.3 ns (39%) and 5.8 ± 0.5 ns (61%) for **3**. These results may indicate that there are double minima in the potential curve of the lowest excited singlet state with a small barrier between them, which is overcome at room temperature to give single-exponential decay.

Radiative lifetimes of **1** were estimated to be 7.9 ns at 77 K, and the radiative and nonradiative decay rate constants of **1** were estimated to be 12.7 and 6.5 × 10^7 s^{-1}, respectively. As mentioned above, the fluorescence spectra observed for **2** and **3** at 77 K consist of two components with rather close lifetimes to each other. Therefore it is difficult to resolve the fluorescence spectra into a long and short lifetime components. We estimated the lower and upper limits of the decay rate constants by considering two limited cases where the emission intensity is due to only the long or short lifetime component. Radiative decay rate constants of **2** and **3** at 77 K were estimated to be in the range of (∼9−16) and (∼12−25) × 10^7 s^{-1}, respectively, and nonradiative decay rate constants were in the range of (∼16−30) and (∼13−28) × 10^7 s^{-1}. These radiative decay rate constants of **2** and **3** at 77 K are comparable with those at room temperature, while nonradiative decay rate constants are smaller by one order than those at room temperature. Thus it is understood that the increase of nonradiative decay rate is responsible for the short fluorescence lifetimes of **2** and **3** at room temperature and for the decrease in fluorescence quantum yield. All photophysical parameters determined at 77 K are summarized in Table 2.

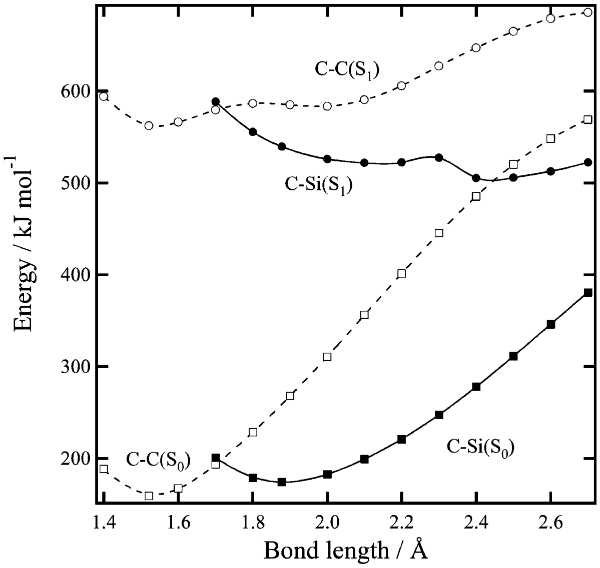


Figure 3. Potential-energy curves calculated for the ground (S_0) and excited (S_1) states of 9,10-dihydrophenanthrene (broken line) and 9,10-dihydro-9-silaphenanthrene (full line).

TABLE 2: Photophysical Parameters of 9,10-Dihydro-9-silaphenanthrene Derivatives in Methylcyclohexane at 77 K

	1	2	3
Φ_f	0.66	0.28	0.23
τ_f (ns)	5.2 ± 0.5	2.6 ± 0.2 (34%) 4.5 ± 0.3 (66%)	2.7 ± 0.3 (39%) 5.8 ± 0.5 (61%)
τ_f^0 (ns)	7.9	9−16	12−25
k_f (10^7 s^{-1})	12.7	6−11	4−8
k_f^{nr} (10^7 s^{-1})	6.5	16−30	13−28
Φ_p	0.04	0.08	0.11
τ_p (s)	3.0 ± 0.2	1.1 ± 0.2	0.8 ± 0.2
k_p (s^{-1})	0.04	0.10	0.18
k_p^{nr} (s^{-1})	0.29	0.81	1.1

To study the large Stokes shift observed for **2** and **3** and the dual fluorescence at 77 K, we examined the structural change in the excited state by use of the PM3 calculation. Figure 3 shows the potential-energy curves of the ground (S_0) and excited singlet (S_1) states calculated for a model compound, 9,10-dihydro-9-silaphenanthrene, as a function of the bond length between C(methylene) and Si (or C(methylene)) atoms. All other bond lengths and angles were varied to obtain the optimized structure. A stable structure was predicted at ca. 1.54 Å of the C(methylene)−C(methylene) bond length for both the S_0 and S_1 states of **1**. For 9,10-dihydro-9-silaphenanthrene, a normal bond length of ca. 1.90 Å was predicted for the C−Si single bond in the S_0 state, while for the S_1 state a shallow minimum and a deeper minimum were predicted at around 2.1 and 2.4 Å, respectively, with a barrier of 5 kJ mol^{-1}. As a result, it is expected that the C−Si bond length changes from ca. 1.90 Å in the S_0 state to longer bond lengths (2.1 or 2.4 Å) in the S_1 state of 9,10-dihydro-9-silaphenanthrene. Thus the large Stokes shifts observed for **2** and **3** may be explained by the elongation of the C(methylene)−Si bond in the lowest excited singlet state. It is noticed that the fluorescence band maxima of **2** and **3** are shifted to longer wavelength by 5−10 nm on going from 77 K to room temperature, suggesting that the larger structural change induced by the C(methylene)−Si bond elongation takes place at room temperature.

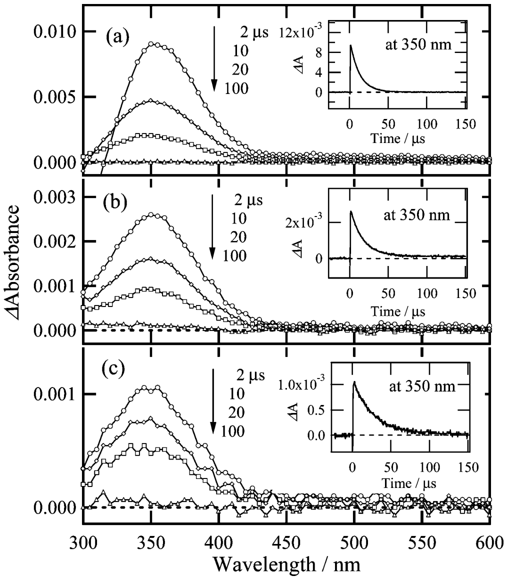


Figure 4. Transient absorption spectra observed upon nanosecond laser flash photolysis in cyclohexane for 9,10-dihydrophenanthrene (a), 9-methyl-9,10-dihydro-9-silaphenanthrene (b), and 9-phenyl-9,10-dihydro-9-silaphenanthrene (c) at room temperature. Insets are decay curves determined at 350 nm.

As shown in Figure 2, structured phosphorescence spectra of **1**, **2**, and **3** were observed in the wavelength region longer than 420 nm and are similar to each other in contrast to the fluorescence spectra. Phosphorescence quantum yields (Φ_p) of **1**, **2**, and **3** were measured relative to biphenyl ($\Phi_p = 0.24$)[22] in MCH at 77 K and were estimated to be 0.04, 0.08, and 0.11, respectively. Phosphorescence decay profiles of these compounds were determined by monitoring the emission at 480 nm upon excitation at 260 nm. Phosphorescence lifetimes (τ_p) of **1**, **2**, and **3** were determined to be 3.0 ± 0.2, 1.1 ± 0.2, and 0.8 ± 0.2 s in MCH at 77 K, respectively. By assumption that $\Phi_{isc} = 1 - \Phi_f$, radiative ($k_p = 1/\tau_p^0 = \Phi_p/(\tau_p\Phi_{isc})$) and nonradiative decay rate constants ($k_p^{nr} = 1/\tau_p - 1/\tau_p^0$) for the triplet state were estimated to be 0.04 and 0.29 s^{-1} for **1**, 0.10 and 0.81 s^{-1} for **2**, and 0.18 and 1.1 s^{-1} for **3**, respectively, by assumption that Φ_{isc} is evaluated by $1 - \Phi_f$. These parameters are summarized in Table 2.

Photolysis of 9,10-Dihydro-9-silaphenanthrene Derivatives: Nanosecond Laser Flash Photolysis. Nanosecond laser flash photolysis of **2** and **3** were studied by irradiation with 266-nm light pulse in comparison with **1**. Parts a−c of Figure 4 show nanosecond transient absorption spectra of **1**, **2**, and **3** in Ar-saturated cyclohexane solution at room temperature. A broad absorption band was observed around 350 nm for all compounds. By the analysis of the absorption decay curves determined at 350 nm bands (shown in insets), the lifetimes were estimated to be 12, 16, and 26 μs for **1**, **2**, and **3**, respectively. Since these absorption spectra are similar to each other and also similar to the triplet−triplet absorption spectrum of **1** reported by Heinzelmann and Labhart,[23] these spectra are ascribable to their triplet−triplet absorption. No spectral evidence was obtained for photochemical products or intermediates in the nanosecond transient absorption spectra other than the triplet state. Upon the 266-nm photolysis of these samples at 77 K, similar transient absorption spectra were observed. Therefore it is confirmed that only triplet species are produced upon the nanosecond laser flash photolysis for these samples.

Steady-State Photolysis of 9,10-Dihydro-9-silaphenanthrene Derivatives at 77 K. Photolysis of samples **1**, **2**, and **3** by irradiation with the pulsed laser light of 266 nm (1800 shots) were carried out in 2-chlorobutane and in MCH glass at 77 K. Parts a−c of Figure 5 show the difference absorption spectra of **1**, **2**, and **3** before and after the photolysis in 2-chlorobutane. For **1**, two intense absorption bands were observed with maxima around 670 and 400 nm, being in good agreement with the absorption spectrum of its radical cations produced by ^{60}Co γ-ray irradiation with dose of 10 kGy (10 kGy/h × 1 h). This spectrum is also very similar to that reported by Shida.[24] Similar absorption spectra were observed for **2** and **3** with absorption maxima around 670 and 400 nm, and these spectra are ascribable to their radical cations. Absorbance ratio of the 400-nm band to the 670-nm band is about 3.1, 2.7, and 1.9 for the radical cations of **1**, **2**, and **3**. Parts a−c of Figure 6 show the difference absorption spectra of **1**, **2**, and **3** before and after the photolysis in MCH. Similar to the absorption spectra in 2-chlorobutane, a

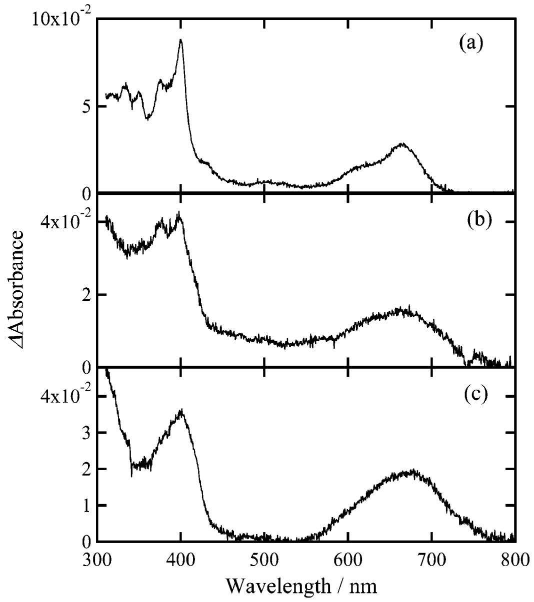


Figure 5. Difference absorption spectra before and after the photolysis of 9,10-dihydrophenanthrene (a), 9-methyl-9,10-dihydro-9-silaphenanthrene (b), and 9-phenyl-9,10-dihydro-9-silaphenanthrene (c) in 2-chlorobutane at 77 K.

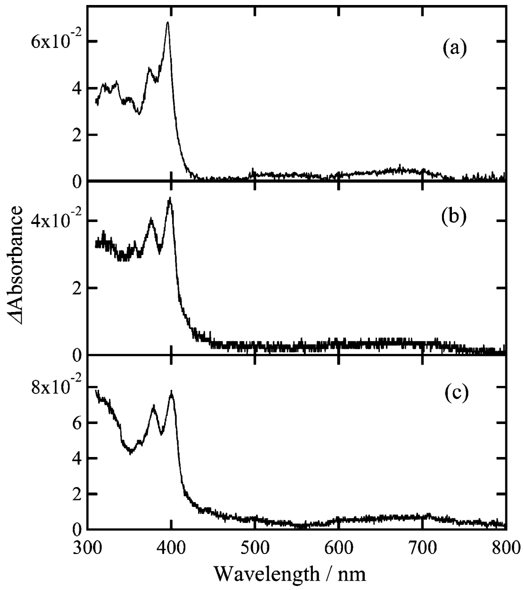


Figure 6. Difference absorption spectra before and after the photolysis of 9,10-dihydrophenanthrene (a), 9,10-dihydro-9-methyl-9-silaphenanthrene (b), and 9-phenyl-9,10-dihydro-9-silaphenanthrene (c) in methylcyclohexane at 77 K.

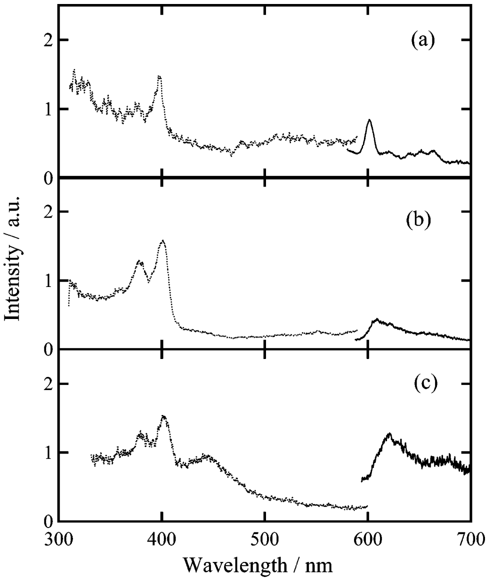


Figure 7. Fluorescence spectra around the 600-nm region (full line, excitation wavelength = 400 nm) and excitation spectra (dotted line, monitored at the fluorescence peak around 600 nm) after the photolysis of 9,10-dihydrophenanthrene (a), 9-methyl-9,10-dihydro-9-silaphenanthrene (b), and 9-phenyl-9,10-dihydro-9-silaphenanthrene (c).

weak and broad absorption band was commonly observed in the visible region with maximum around 670 nm, and also an intense and sharp band was around 400 nm. This indicates that the radical cations are also produced by the photolysis in MCH at 77 K. However, the absorbance ratio of the 400-nm band to the 670-nm band are about 9 for all samples, suggesting that at least an additional absorption band ascribable to reaction product or intermediate is overlapping with that of the radical cations in the 400-nm region. These 400- and 670-nm absorption bands disappeared when the photolyzed solutions were warmed to room temperature, indicating that the additional absorption band is ascribable to unstable species at room temperature. It should be noted that these intermediates and unstable products are considered to be formed by multiphoton process, because no such absorption band was observed in the nanosecond transient absorption spectra.

We studied the photolysis of 9,10-dihydro-9-silaanthracene derivatives at 77 K and confirmed the formation of 9-silaanthracene, 9,10-dihydro-9-silaanthracene-9,9-diyl (silylene-type species), and 9-hydro-9-silaanthracenyl radical (carbon-centered radical at the 10th carbon) by studying the absorption and fluorescence spectra.[5] This carbon-centered radical is the benzyl-type radical that shows an intense absorption band in near-UV region and a very weak band in the visible region, and exhibits a fluorescence band in the visible region.

To examine the emitting species produced upon the photolysis in MCH at 77 K, fluorescence spectra were measured and the results are shown in Figures 7 and 8. On the excitation of the 400-nm absorption of **1**, a fluorescence band was observed around 600 nm as shown in Figure 7a (full line). By monitoring the 600-nm emission, an excitation spectrum was observed with maxima around 400 and 375 nm (dotted line), being in agreement with the absorption spectrum of Figure 6a. This spectral pattern with a long-wavelength emission and an intense short-wavelength absorption in the near UV region is characteristic of the benzyl-type radicals. Therefore the 610-nm emission and the absorption with peaks around 400 and 375 nm can be ascribed to the carbon-centered radicals at the 10 position: the 9-hydro-9-phenanthrenyl radical.

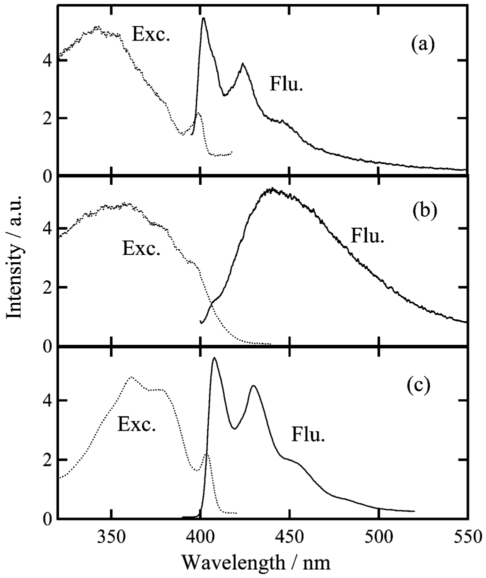


Figure 8. Fluorescence spectra in the region of 400−550 nm (full line, excitation wavelength = 380 nm) and excitation spectra (dotted line) monitored at wavelength 423 and 440 nm observed after the photolysis of 9-methyl-9,10-dihydro-9- silaphenanthrene (a) and 9-phenyl-9,10-dihydro-9-silaphenanthrene (b), respectively, and fluorescence and excitation spectra of 9-Tbt-9-silaphenanthrene observed by excitation at 360 nm and monitored at 430 nm (c).

Similar weak fluorescence and excitation spectra were also observed for **2** and **3** photolyzed in MCH at 77 K as shown in parts b and c of Figure 7, respectively. The excitation spectrum determined by monitoring the fluorescence at 610 nm corresponds well to the absorption spectrum in the region 370−400 nm. According to the spectral resemblance of the 400-nm absorption band of **2** and **3** to that of **1**, the 400-nm bands shown in parts b and c of Figure 6 are ascribable to the carbon-centered radicals: 9-hydro-9-silaphenanthrenyl radicals. Since we could not find out the 400-nm absorption band due to the carbon-centered radicals in the transient absorption spectra, these radicals are considered to be produced by a multiphoton process via the triplet state as mentioned above. It is noted here that the 450-nm excitation band observed for **3** may be attributed to unknown silylene species judging from its wavelength.

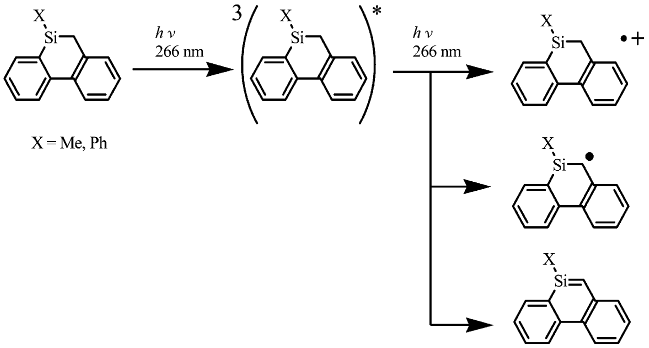
Another fluorescence band was observed upon excitation with the 380-nm light for **2** and **3** photolyzed in MCH at 77 K. For **2**, two distinct fluorescence peaks were observed at 402 and 423 nm as shown in Figure 8a (full line). The excitation spectrum observed by monitoring the fluorescence at 423 nm shows a peak at 399 nm and also an intense and broad peak at around 340 nm (Figure 8a, dotted line). Figure 8c shows the fluorescence (full line, excitation wavelength 360 nm) and excitation spectrum (dotted line, monitor wavelength 430 nm) of 9-Tbt-9-silaphenanthrene synthesized by Shinohara and Tokitoh.[15] Fluorescence peaks were observed at around 407 and 430 nm, and excitation peaks were at around 403 and 360 nm. These spectra are similar to those observed for **2**, and therefore the spectra of Figure 8a are reasonably ascribed to 9-methyl-9-silaphenanthrene. The fluorescence decay curve of 9-methyl-9-silaphenanthrene observed at the 423-nm emission peak was determined by means of the single photon counting technique by exciting the 399-nm band. The decay curve was analyzed by sum of two single-exponential functions with lifetimes of 6.3 ns (intensity ratio 86%) and 2.0 ns (14%). This result is very similar to that of 9-Tbt-9-silaphenanthrene; the fluorescence lifetimes are 6.9 ns (94%) and 2.4 ns (6%). These results also support the above assignment of the fluorescence in the region

TABLE 3: Calculated Results of Electronic Absorption Spectra of 9-Silaphenanthrene and Phenanthrene

		transition energy, eV (nm)		oscillator strength, calcd
		calcd	obsd (λ_{max})	
9-silaphenanthrene	Ψ_I	3.65 (340)	3.10 (400)	0.150
	Ψ_{II}	3.71 (334)	3.64 (340)	0.292
phenathrene	Ψ_I	3.84 (323)	3.58 (346)	0.001 (^1L_b)[a]
	Ψ_{II}	4.39 (282)	4.23 (293)	0.188 (^1L_a)[a]

[a] Reference 27.

SCHEME 1



400−550 nm to 9-methyl-9-silaphenanthrene. As a result it can be pointed out that 9-silaphenanthrenes exhibit dual fluorescence. This dual fluorescence may be attributed to the closely lying first two electronic transitions predicted by the MO calculation for 9-silaphenanthrene as shown in Table 3.

If 9-methyl-9-silaphenanthrene is produced upon the photolysis at 77 K, it may be trapped by methanol or ethanol to give 9-methoxy- or 9-ethoxy-9,10-dihydro-9-silaphenanthrenes. By investigation of the photoproducts formed upon the photolysis of **2** in methanol/ethanol (1:1 vol/vol) mixed solution at 77 K, the alcohol-trapped products, *m*/*z* 240 of methoxy derivative and *m*/*z* 254 of ethoxy derivative, were detected by means of GC-MS analysis. This result also supports the photochemical formation of 9-methyl-9-silaphenanthrene at 77 K.

The fluorescence spectrum of **3** photolyzed in MCH at 77 K is shown in Figure 8b. When the 380-nm absorption band was excited, a fluorescence spectrum was observed in the region of 400−550 nm with a maximum around 440 nm as shown in Figure 8b (full line). Excitation spectrum determined by monitoring the emission at 440 nm shows a maximum at 360 nm with several shoulders around 400 nm (dotted line). Although the excitation spectrum seems to be different from those of 9-methyl- and 9-Tbt-9-silaphenanthrene, this difference is reasonably explained by the spectral overlapping of the intense second absorption band to the weak first absorption band, induced by the large red shift of the second band. Fluorescence decay curve was determined at 430 nm by means of the single photon counting technique by exciting the 400-nm band. The decay curve was analyzed by sum of two single-exponential functions with lifetimes of 5.0 ns (intensity ratio 32%) and 1.6 ns (68%). These fluorescence lifetimes correspond well with those of **2**, although the intensity ratio is reversed. The reverse in intensity ratio supports the band overlapping mentioned above.

Electronic Structure of 9-Silaphenanthrenes. The spectral characteristics of 9-silaphenanthrenes are explained by their electronic structure. The carbon analogue, phenanthrene, shows a weak structured absorption band ($\epsilon_{max} \approx 250$ M cm^{-1}) in the region of 300−350 nm and intense absorption peaks at around 290 nm ($\epsilon_{max} \approx 15\,000$ M^{-1}cm^{-1}) and 260 nm ($\epsilon_{max} \approx 67\,000$ M^{-1}cm^{-1}). These absorption bands are assigned to the ^1L_b, ^1L_a, and ^1B_a (^1B_b) transitions, respectively.[25−27] Calculated results obtained by CNDO/S-CI calculation for 9-silaphenanthrene are shown in Table 3 in comparison with those of phenanthrene. According to the results, the first two transitions are represented in terms of four singly excited electronic configurations: $\Phi_{(LUMO\leftarrow HOMO)}$, $\Phi_{(LUMO\leftarrow HOMO\leftarrow HOMO-1)}$, $\Phi_{(LUMO+1\leftarrow HOMO)}$, and $\Phi_{(LUMO+1\leftarrow HOMO-1)}$, where HOMO is the highest-occupied molecular orbital and LUMO is the lowest-unoccupied molecular orbital, as follows

$$\Psi_I(^1L_b) = 0.702\Phi_{(LUMO+1\leftarrow HOMO)} - 0.661\Phi_{(LUMO\leftarrow HOMO-1)} + \cdots$$

$$\Psi_{II}(^1L_a) = 0.881\Phi_{(LUMO\leftarrow HOMO)} + 0.450\Phi_{(LUMO+1\leftarrow HOMO-1)} + \cdots$$

These transitions are polarized along the molecular short- and long-axis, respectively.

The first two electronic transitions of 9-silaphenanthrene are calculated to be both located at about 340 nm and also represented in terms of four electronic configurations

$$\Psi_I(\text{9-silaphenanthrene}) = 0.546\Phi_{(LUMO+1\leftarrow HOMO)} - 0.592\Phi_{(LUMO\leftarrow HOMO-1)} - 0.521\Phi_{(LUMO\leftarrow HOMO)} + \cdots$$

$$\Psi_{II}(\text{9-silaphenanthrene}) = -0.806\Phi_{(LUMO\leftarrow HOMO)} + 0.439\Phi_{(LUMO+1\leftarrow HOMO-1)} + \cdots$$

It is understood that the configuration $\Phi_{(LUMO\leftarrow HOMO)}$ contributes to Ψ_I by a weight of about 25% different from the case of phenanthrene (negligibly small contribution). Although the silicon atom substitution induces reduction of symmetry of these molecular orbitals, rather high correlation of the charge density of molecular orbitals between 9-silaphenanthrene and phenanthrene was confirmed by expanding molecular orbitals of 9-silaphenanthrene in terms of those of phenanthrene

$$\phi_{HOMO}(\text{9-silaphenanthrene}) = 0.971\phi_{HOMO}(\text{phenanthrene}) + \cdots$$

$$\phi_{HOMO-1}(\text{9-silaphenanthrene}) = 0.978\phi_{HOMO-1}(\text{phenanthrene}) + \cdots$$

$$\phi_{LUMO}(\text{9-silaphenanthrene}) = 0.893\phi_{LUMO}(\text{phenanthrene}) + \cdots$$

$$\phi_{LUMO+1}(\text{9-silaphenanthrene}) = 0.953\phi_{LUMO+1}(\text{phenanthrene}) + \cdots$$

CNDO/S-CI calculation predicts that the energy of HOMO increases by 0.37 eV compared with that of phenanthrene upon introduction of Si atom at the 9 position, whereas that of LUMO decreases by 0.55 eV as shown in Figure 9, in contrast to very small change in energy of HOMO−1 (0.04 eV) and LUMO+1 (0.01 eV).

These data indicate that both the first and the second transition bands are expected to be shifted to the longer wavelength, especially with larger shift in the second transition, and as a result these two transitions are expected to be more closely lying than in the case of phenanthrene. Actually, as can be understood from Figure 8a the absorption maxima of these two transition

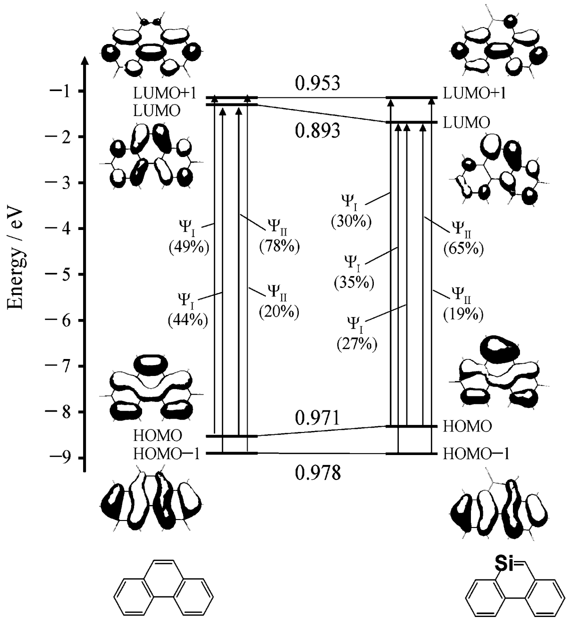


Figure 9. Correlation diagram of molecular orbitals between phenanthrene and 9-silaphenanthrene. Figures along the connecting lines are the contribution weight of the correlating MOs. Ψ_I and Ψ_{II} are the first and second transitions. The percentage in the parentheses is the contribution weight of the singly excited configuration obtained by the configuration interaction calculation.

bands are shifted to red and located at around 399 and 340 nm, respectively. Furthermore, it is expected for 9-phenyl-9-silaphenanthrene that the second transition band is largely shifted to red to give band overlapping with the first transition band.

Summary

Photophysical processes of 9-methyl- and 9-phenyl-9,10-dihydro-9-silaphenanthrene derivatives have been studied at room temperature and 77 K in comparison with the carbon analogue, 9,10-dihydrophenanthrene. Reaction products and intermediates produced upon the 266-nm photolysis have been studied, and it has been confirmed that 9-methyl- and 9-phenyl-9-silaphenanthrenes have been photochemically formed in methylcyclohexane at 77 K in addition to the formation of radical cations of 9,10-dihydro-9-silaphenanthrene derivatives and 9-hydro-9-methyl-9-silaphenanthrenyl radicals (carbon-centered radical). These intermediates and unstable products were all formed by multiphoton processes.

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