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Photophysical and photochemical processes of 9,10-dihydro-9-silaanthracenes: photochemical generation and electronic structure of 9-phenyl-9-silaanthracene

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Abstract

Photophysical processes of 9,10-dihydro-9-silaanthracene (**1**) and its 9-phenyl derivative (**2**) have been studied in 3-methylpentane at 77 K. Photolyses of these compounds have been carried out at 77 K and reaction intermediates have been studied. Carbon-centered radicals and silylenes have been observed for **1**, while for **2**, formation of carbon-centered radicals and 9-phenyl-9-silaanthracene has been confirmed by use of UV–vis absorption spectrum, fluorescence spectrum, fluorescence polarization and results of semi-empirical MO calculations. The electronic structure of 9-silaanthracene has been discussed in comparison with that of anthracene. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Dihydro-9-silaanthracene; 9-Phenyl-9-silaanthracene; Photophysical process; Photolysis; Electronic structure

1. Introduction

The long-standing interest in isolating and characterizing unsaturated silicon compounds has increased dramatically in the past 30 years [1,2]. Silaaromatic compounds are usually unstable at room temperature because of their high reactivity compared with the corresponding carbon analogues. A number of experimental and theoretical papers dealing with aromaticity in silaaromatic compounds have appeared recently, e.g. in 1977 Barton and Banasiak isolated methylsilabenzene for the first time [3]. This was followed by the first unambiguous evidence for the existence of silabenzene, reported by Barton and Burns in 1978 [4]. Maier et al. have generated silabenzene and 1,4-disilabenzene [5] by thermolysis and measured their absorption spectra in an Ar matrix at 10 K. Recently, Tokitoh et al. isolated 2-silanaphthalene which is stabilized kinetically by the bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl group on silicon atom [6]. Their method is considered to be promising and may be available for preparation of other stable silaaromatic compounds. To the best of our knowledge, however, there has been no report on the preparation of stable silaanthracene. Maier et al. reported the generation of 9-silaanthracenes by use of the flash vacuum thermolysis technique at 15 K [7]. Since anthracene is produced by the photolysis of 9,10-dihydroanthracene even at 77 K, it is expected that 9-silaanthracenes are produced upon the photolyses of 9,10-dihydro-9-silaanthracenes under similar conditions. There has been, however, no report on the photochemical generation of 9-silaanthracenes.

We have reported preliminary results of the photolyses of 9,10-dihydro-9-silaanthracenes in 3-methylpenatane glass at 77 K and the formation of 9-phenyl-9-silaanthracene [8]. In this paper, photophysical processes of 9,10-dihydro-9-silaanthracene (**1**) and 9-phenyl-9,10-dihydro-9-silaanthracene (**2**) have been studied. Photolysis of these compounds has been examined in 3-methylpentane and ethanol glass at 77 K with

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our attentions focussed on the reaction intermediates. Electronic structure of 9-silaanthracene has also been studied in comparison with that of anthracene.

2. Experimental

9,10-Dihydro-9-silaanthracene (**1**), 9-phenyl-9,10-dihydro-9-silaanthracene (**2**), and 9,9-di(trimethylsilyl)-9,10-dihydro-9-silaanthracene (**3**) were prepared according to the procedure reported [9,10]. Toluene (S.G. Tokyo Chemical Industry Co.) was used after confirming its purity by fluorescence measurement. 2,3-Dimethyl-1,3-butadiene (98%, Aldrich Chemical Co.) and ethanol (S.S.G. Wako Pure Industries Ltd.) were used as received. 3-Methylpentane (GR. Wako Pure Industries Ltd.) was purified by distillation over $LiAlH_4$ under an Ar atmosphere. 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 using a Hitachi M850 fluorescence spectrometer with band pass of 3 or 5 nm for both emission and excitation. Fluorescence lifetimes were measured by using an Edinburgh Analytical Instruments FI900CDL spectrometer system (H_2 pulser, pulse width 0.8 ns, 10^8 photons/pulse, repetition rate 40 kHz) [11]. Phosphorescence decay was recorded on a Hitachi M850 fluorescence spectrometer. Steady-state photolysis was carried out at 77 K using light output of fourth harmonics from an Nd^{3+}:YAG laser (266 nm, Quanta-Ray GCR130, Spectra Physics).

Semiempirical MO calculations by the PM3 method [12] were carried out to obtain optimized molecular structures of the ground state of 9-silaanthracene and carbon-centered radicals produced from 9,10-dihydro-9-silaanthracenes. Structures of the 9,10-dihydro-9-silaanthracene-9,9-diyl in the ground and the first excited singlet states were also calculated. CNDO/S-CI calculations were performed to study the electronic spectra of the reaction intermediates with the optimized geometry [13].

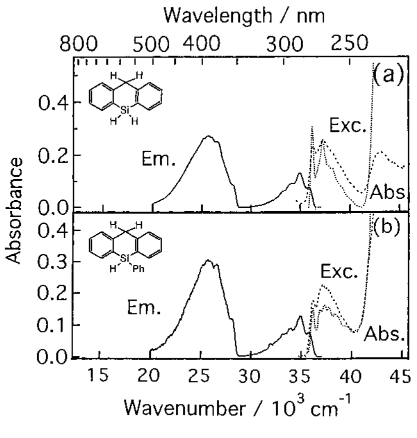


Fig. 1. Absorption (dotted line), emission (full line) and excitation (broken line) spectra of 9,10-dihydro-9-silaanthracene (a) and 9-phenyl-9,10-dihydro-9-silaanthracene (b) in 3-methylpentane at 77 K.

Polarization degree, P, was determined for 9-phenyl-9-silaanthracene by use of the equation: $P = (I_{\parallel} - fI_{\perp})/(I_{\parallel} + fI_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ are emission intensities when the electric vectors of the emission are parallel and perpendicular to that of the excitation light, respectively, and f is a correction factor for the polarized light of the apparatus used.

3. Results and discussion

3.1. Photophysical processes of 9,10-dihydro-9-silaanthracenes

Fig. 1a shows the absorption spectrum (dotted line), fluorescence emission (full line) and excitation spectra (broken line) of **1** in 3-methylpentane (3MP) at 77 K. The absorption band around 270 nm with molar absorption coefficient of ca. 950 M^{-1} cm^{-1} is attributable to the $^1L_b \leftarrow {}^1A$ transition commonly observed for the compounds containing a phenyl group. Upon excitation at the 260-nm band, fluorescence emission of **1** was observed with several peaks around 280 nm and a phosphorescence spectrum was observed in the region longer than 350 nm with intensity stronger than the fluorescence. When the fluorescence was monitored at 300 nm, the excitation spectrum was observed with peaks at 268 and 275 nm, being in good agreement with the absorption spectrum. When the phosphorescence emission was monitored at 400 nm, essentially the same excitation spectrum was observed. These spectra resemble those of toluene. Fig. 1b shows the absorption (dotted line), fluorescence emission (excited at 260 nm; full line), and excitation spectra (monitored at 300 nm; broken line) of **2** in 3MP at 77 K. These spectra resemble those of **1**. In ethanol (EtOH), absorption, emission and excitation spectra of **1** and **2** were also measured at 77 K and no significant difference was observed from those in 3MP.

To clarify photophysical properties of **1** and **2**, fluorescence and phosphorescence quantum yields (Φ) were determined relative to those of toluene, and their lifetimes (τ_f) were measured. Relative fluorescence quantum yields of **1** and **2** in 3MP at 77 K were determined to be 0.29 ± 0.05 and 0.28 ± 0.05, respectively. Since the fluorescence quantum yield of toluene is reported to be 0.29 [14], Φ_f (**1**) and Φ_f (**2**) are both estimated to be 0.08. Fluorescence decay profiles of these compounds were determined in 3MP at 77 K by use of the single photon counting method by monitoring the emission at 300 nm and by excitation at 267 nm. Fluorescence lifetimes (τ_f) of **1**, **2** and toluene were

Table 1
Photophysical parameters in 3-methylpentane at 77 K

Sample	**1**	**2**	Toluene
$\Phi_f^{sam}/\Phi_f^{tol}$ [a]	0.29 ± 0.05	0.28 ± 0.05	1.00
Φ_f	0.08	0.08	0.29 [b]
τ_f (ns)	9.6 ± 1.0	8.0 ± 1.0	66 ± 2
τ_f^0 (ns)	114	99	228
$k_f^0/10^6$ (s^{-1})	8.8	10.1	4.4
$k_f^{nr}/10^7$ (s^{-1})	9.6	11.5	1.1
$\Phi_p^{sam}/\Phi_p^{tol}$ [a]	1.4 ± 0.2	1.6 ± 0.3	1.0
Φ_p	0.41	0.46	0.26 [b]
τ_p (s)	2.0 ± 0.1	1.1 ± 0.1	4.3 ± 0.1
τ_p^0 (s)	4.9	2.4	11
k_p^0 (s^{-1})	0.20	0.42	0.091
k_p^{nr} (s^{-1})	0.30	0.49	0.14

[a] Φ^{sam} and Φ^{tol} are quantum yields of sample and toluene, respectively.

[b] Ref. [14].

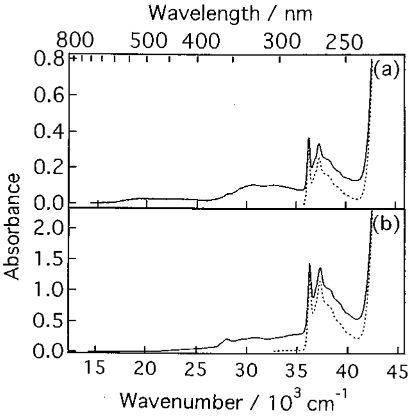


Fig. 2. Absorption spectra of 9,10-dihydro-9-silaanthracene before (dotted line) and after (full line) the photolysis in 3-methylpentane (a) and in ethanol (b) at 77 K.

determined to be 9.6 ± 1.0, 8.0 ± 1.0, and 66 ± 2 ns in 3MP at 77 K, respectively.

Radiative lifetimes of fluorescence (τ_f^0) of **1**, **2** and toluene were estimated to be 114, 99 and 228 ns, respectively, by the equation $\tau_f^0 = \tau_f/\Phi_f$. Radiative decay rates (k_f^0) are therefore determined to be 8.8×10^6, 10.1×10^6 and 4.4×10^6 s^{-1} for **1**, **2** and toluene, respectively. Non-radiative decay rates (k_f^{nr}) of **1**, **2** and toluene are estimated to be 9.6×10^7, 11.5×10^7 and 1.1×10^7 s^{-1}, respectively, by the equation $k_f^{nr} = k_f^0(1/\Phi_f - 1)$. All photophysical parameters described above are summarized in Table 1.

The quantum yields of intersystem crossing are also estimated by the following assumption (Ermolev's rule) valid for anthracene: $\Phi_{isc} = 1 - \Phi_f$, and are determined to be 0.92 for both **1** and **2** [15]. The phosphorescence quantum yields of **1** and **2** are determined, relative to that of toluene, to be 1.4 ± 0.2 and 1.6 ± 0.3, respectively. Since Φ_p of toluene was reported to be 0.26 [14], Φ_p of **1** and **2** are estimated to be 0.41 and 0.46, respectively. Phosphorescence decay profiles of these compounds were determined by monitoring the emission at 400 nm upon excitation at 260 nm. Phosphorescence lifetimes (τ_p) of **1**, **2** and toluene were determined to be 2.0 ± 0.1, 1.1 ± 0.1 and 4.3 ± 0.1 s in 3MP at 77 K, respectively. Radiative lifetimes of phosphorescence (τ_p^0) were determined by the equation $\tau_p^0 = \tau_p\Phi_{isc}/\Phi_p$. The values of τ_p^0 of **1** and **2** are 4.9 and 2.4 s, respectively, and are smaller than that of toluene, $\tau_p^0 = 11$ s. Radiative decay rates, k_p^0, are also estimated to be 0.20 and 0.42 s^{-1} for **1** and **2**, respectively. They are 2.0 and 4.2 times greater than that of toluene ($k_p^0 = 0.091$). Values of k_p^{nr} of **1** and **2** are estimated to be 0.30 and 0.49 s^{-1}, respectively, by the equation $k_p^{nr} = 1/\tau_p - 1/\tau_p^0$. All photophysical parameters described above are also summarized in Table 1.

3.2. Photolysis of 9,10-dihydro-9-silaanthracenes at 77 K

Upon photolysis of 9,10-dihydroanthracene at 77 K, anthracene and the carbon-centered radical are produced. The latter shows a prominent absorption band around 355 nm and a fluorescence band in the region of 500–600 nm with a fluorescence lifetime of ca. 280 ns. It is interesting to study whether similar reactions take place for 9,10-dihydro-9-silaanthracenes to give silaanthracenes and the carbon-centered radicals.

Sample **1** was photolyzed in 3MP and in EtOH at 77 K by irradiation with 266-nm light. Fig. 2 shows the absorption spectra of **1** before (dotted line) and after (full line) the photolysis in 3MP (a) and EtOH (b). There is an absorption band in the region 300–360 nm in both 3MP and EtOH. In addition to this band, a broad and weak band was observed around 500 nm in 3MP but not in EtOH. When the 355-nm peak was excited, fluorescence emission spectra were observed with peaks at 538 and 586 nm in both 3MP and EtOH as shown in Fig. 3. Excitation spectrum (broken line) observed by monitoring the fluorescence at 586 nm shows a peak at 355 nm and weak bands in the visible region. The 355-nm band in EtOH becomes slightly broad compared with that in 3MP.

It is noticed that the fluorescence spectrum resembles that of carbon-centered radicals produced by the photolysis of 9,10-dihydroanthracene. A CNDO/S-CI calculation was carried out to study the electronic spectrum of the carbon-centered radical. The calculated results shown in Fig. 3c explain well the observed excitation spectrum. The fluorescence decay profile was measured by monitoring the emission at 586 nm, and the lifetime was determined to be 350 ns, being comparable with that of the diphenylmethyl radical (430 ns) produced from diphenylmethane [16]. These observations suggest that the carbon-centered radical is pro-

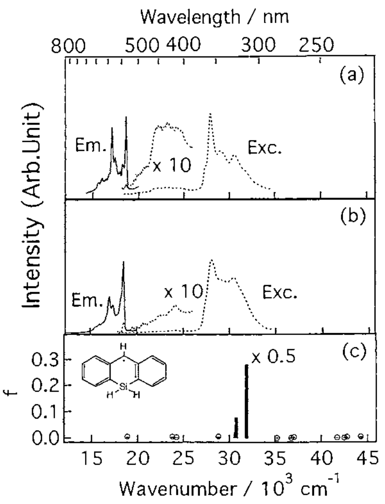


Fig. 3. Fluorescence emission (full line) and excitation spectra (broken line) of 9,10-di-hydro-9-silaanthracene photolyzed in 3-methylpentane (a) and in ethanol (b), and the calculated electronic spectrum of the carbon-centered radical (c).

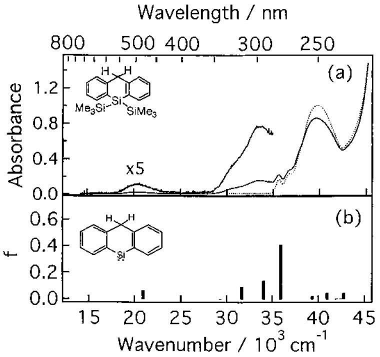


Fig. 4. Absorption spectra of 9,9-di(trimethylsilyl)-9,10-dihydro-9-silaanthracene (a) before (dotted line) and after (full line) the photolysis in 3-methylpentane at 77 K and the calculated electronic spectrum of the silylene (b).

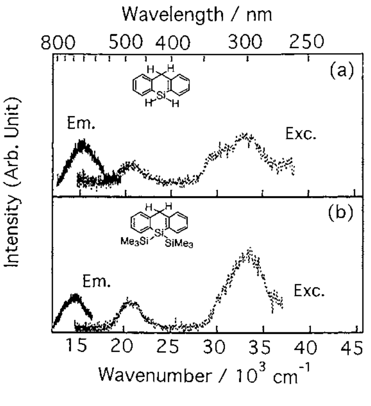
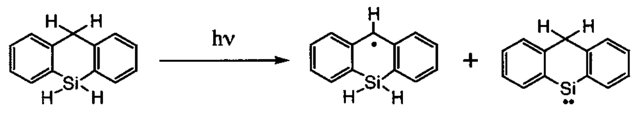


Fig. 5. Fluorescence emission (full line) and excitation spectra (broken line) of the silylene produced upon the photolysis of 9,10-dihydro-9-silaanthracene (a) and 9,9-di(tri-methylsilyl)-9,10-dihydro-9-silaanthracene (b) in 3-methylpentane at 77 K.

duced upon the photolysis of **1**. Photolysis in the presence of a triplet quencher was studied by adding a sufficient amount of 2,3-dimethyl-1,3-butadiene (more than 0.5 M) to the system so that all phosphorescence was quenched [17]. By irradiation with 266-nm light, any absorption band attributable to the carbon-centered radical was not observed in both 3MP and EtOH. This result indicates that carbon-centered radicals are produced via the lowest triplet state.

Gaspar et al. studied the laser flash photolysis of 9,9-di(trimethylsilyl)-9,10-dihydro-9-silaanthracene (**3**) and reported that the transient absorption band of the 9,10-dihydro-9-silaanthracene-9,9-diyl (to be abbreviated as the silylene) was observed with a peak at 490 nm [18]. Photolysis of **3** was carried out in 3MP at 77 K and the resulting absorption spectrum is shown in Fig. 4a. The absorption bands attributable to the silylene were observed around 300 and 500 nm. These bands have the corresponding bands in the spectrum observed after the photolysis of **1** shown in Fig. 2a. The calculated electronic spectrum of the silylene shown in Fig. 4b explain well the observed spectrum. Fluorescence emission of the silylene was also measured for both **1** and **3** as shown in Fig. 5a and b, respectively. They resemble each other, i.e. the broad emission band around 700 nm and excitation bands around 300 and 500 nm are ascribed to the silylene produced from both **1** and **3**. A large Stokes shift was observed in the spectra of the silylene (ca. 5000 cm^{-1}). This Stokes shift is explained by the change in angle of C–Si–C upon electronic transition. The angles, C–Si–C, in the optimized molecular structure of the silylene in S_0 and S_1 states calculated by the PM3 method are 102 and 117°, respectively. This conformational change induced by the transition from S_0 to S_1 state may be responsible for the large Stokes shift. Similar large Stokes shift was observed for dimethylsilylene, where the angles of Me–Si–Me in S_0 and S_1 states are 98 and 121°, respectively [19]. These absorption bands attributable to the silylene disappear in EtOH glass, being consistent with the fact that silylenes are trapped by EtOH by insertion reaction. Thus primary photochemical processes of **1** are summarized in Scheme 1.

Sample **2** was also photolyzed in 3MP and in EtOH at 77 K. The absorption spectra observed before and after the photolysis in 3MP and EtOH are shown in Fig. 6a and b, respectively. The spectrum of Fig. 6b (full line) resembles that of **1**, photolyzed in EtOH as shown in Fig. 2b and therefore, the 360-nm band is ascribed to the carbon-centered radical. While the spectrum is observed after the photolysis in 3MP, additional absorption bands were observed in the visible region (peaked at 511 and 407 nm) as shown in Fig. 6a. When the 360-nm peak was excited, a fluorescence emission spectrum was observed in the region 530–600 nm with peaks at 586 and 538 nm as in the case of **1**



Scheme 1.

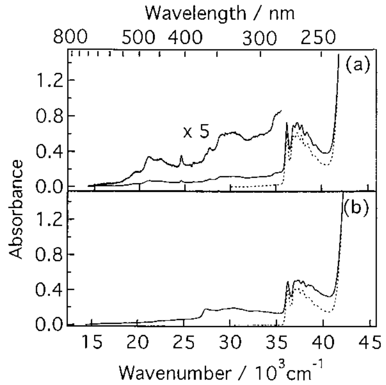


Fig. 6. Absorption spectra of 9-phenyl-9,10-dihydro-9-silaanthracene before (dotted line) and after the photolysis in 3-methylpentane (a) and in ethanol (b) at 77 K.

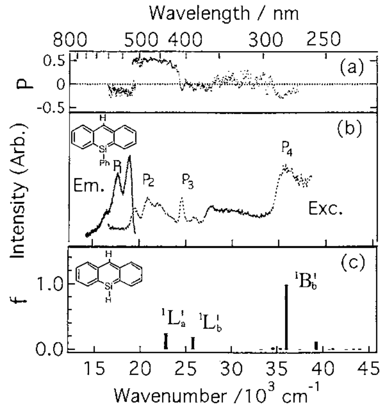
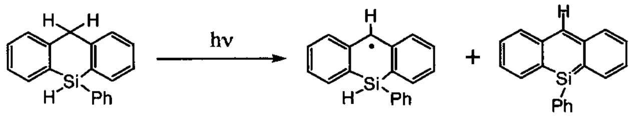


Fig. 7. Polarization degree (a) of fluorescence emission (full line) and excitation spectra (broken line) at 77 K (b) in comparison with the calculated electronic spectrum of 9-silaanthracene (c). Excitation and monitoring wavelengths were 280 and 530 nm, respectively.



Scheme 2.

(Fig. 3a). The emission is ascribable to the carbon-centered radical. Excitation spectrum, observed by monitoring the 586-nm emission band, is similar to that of **1**. Fluorescence lifetime was determined to be 370 ns similar to that (350 ns) of the carbon-centered radical produced form **1**. These observations support the formation of the carbon-centered radical.

By excitation of the additional absorption band at 280 nm, observed in the photolysis of **2** in 3MP glass, the emission was observed with peaks at 528 and 565 nm as shown in Fig. 7b by the full line. The excitation spectrum was also measured by monitoring the 530-nm emission and is shown by the dotted line in Fig. 7b. There are peaks at 512, 475, 407, 386 and ca. 280 nm, which correspond to the absorption bands peaked at 511, 476, 407, 385 and 285 nm, respectively. This excitation spectrum is very similar to the absorption spectrum of 9-phenyl-9-silaanthracene determined by van den Winkel et al. by the flash vacuum thermolysis technique [7]. Thus the photochemical generation of 9-phenyl-9-silaanthracene is confirmed.

The calculated absorption spectrum of 9-silaanthracene, shown in Fig. 7c, explains the excitation spectrum of 9-silaanthacene. Three prominent bands in the region 420–520, 407 and 280 nm can be assigned to the first ($^1L'_a$), third ($^1L'_b$) and seventh ($^1B'_b$) transition bands of 9-phenyl-9-silaanthracene. It is noted that the broad excitation band around 360 nm is ascribed to the carbon-centered radical.

Polarization measurements were carried out to confirm the above assignments of electronic transitions for 9-phenyl-9-silaanthracene. The polarization degree of fluorescence emission and excitation spectra were determined by excitation at 280 nm and by monitoring the fluorescence at 530 nm, respectively, and the results are shown in Fig. 7a. It is understood that polarization direction of the 280-nm band (denoted as P_4) is parallel to that of 407 nm (P_3) and perpendicular to the band in the region 420–520 nm (P_2). By comparison with the calculated results, P_2, P_3 and P_4 are, respectively attributable to the $^1L'_a$, $^1L'_b$, and $^1B'_b$ bands of which transition moments are polarized parallel to the molecular long-axis, short-axis and short-axis, respectively. Therefore these bands can be correlated with three absorption (excitation) bands, ^1L_a, ^1L_b and ^1B_b bands, of anthracene, respectively. As a result, it is understood that the electronic structure of 9-silaanthracene is similar to that of anthracene. Fluorescence lifetime of 9-phenyl-9-silaanthracene was determined to be 10 ns which is comparable with that of 9-phenylanthracene (6.5 ns) [20].

To clarify the mechanism of the generation of 9-phenyl-9-silaanthracene, the photolysis of **2** was also studied in the presence of the triplet quencher, 2,3-dimethyl-1,3-butadiene. Neither the carbon-centered radical nor 9-phenyl-9-silaanthracene was observed, indicating that these species are produced via the lowest triplet state. This is the same as the photolysis of **1**. Excitation light power dependence of the 407 nm absorption was examined and the formation of 9-phenyl-9-silaanthracene was found to be a three-photon process. The primary photochemical process of **2** is summarized in Scheme 2.

3.3. Electronic structure of 9-silaanthracene

In order to clarify the electronic structure of 9-silaanthracene, its electronic states have been studied by MO calculations. The symmetry of 9-silaanthracene belongs to the point group C_{2v} and that of anthracene is to D_{2h}. The symmetry species, b_{1g}, b_{2g}, b_{3u} and a_u in D_{2h} are related to a_2, b_1, b_1 and a_2, in C_{2v}, respectively.

In the absorption spectra of 9-phenyl-9-silaanthracene, three bands have been attributed to the first ($^1L_a'$), the third ($^1L_b'$) and the seventh ($^1B_b'$) transitions by comparison of the results of MO calculation with those of polarization measurement. These electronic states are represented as follows.

$$\Psi_{\mathrm{I}}(^1L_a') = 0.97\Phi_{33-34} + \ldots$$

$$\Psi_{\mathrm{III}}(^1L_b') = 0.91\Phi_{33-35} + 0.36\Phi_{32-34} + \ldots$$

$$\Psi_{\mathrm{VII}}(^1B_b') = 0.83\Phi_{32-34} - 0.28\Phi_{33-35} + \ldots$$

where Φ_{i-j} is the singly excited electronic configuration corresponding to the transition from the ith to jth MO. The electronic states of anthracene are also given as follows.

$$\Psi_{\mathrm{I}}(^1L_a) = 0.97\Phi_{33-34} + \ldots$$

$$\Psi_{\mathrm{II}}(^1L_b) = 0.74\Phi_{33-35} + 0.62\Phi_{32-34} + \ldots$$

$$\Psi_{\mathrm{VIII}}(^1B_b) = 0.76\Phi_{32-34} - 0.63\Phi_{33-35} + \ldots$$

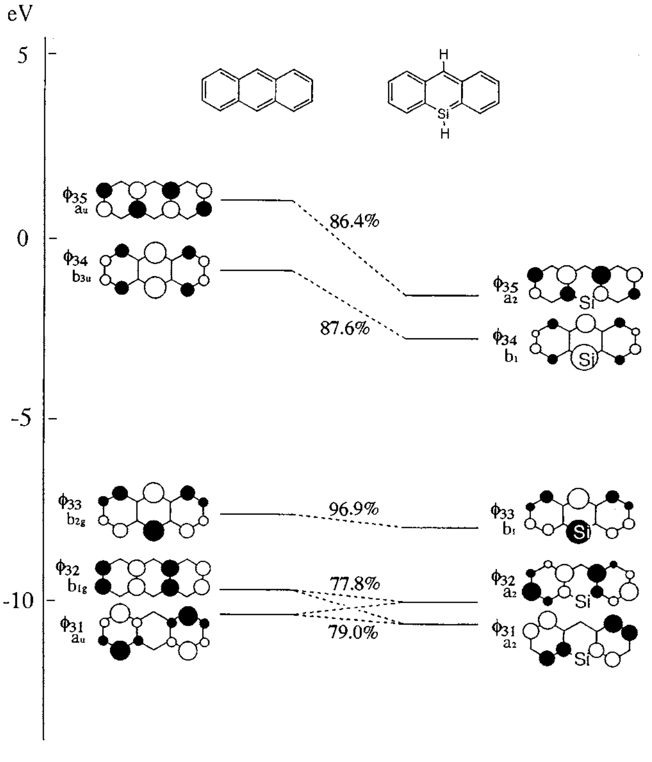


Fig. 8. Correlation diagram of MOs between 9-silaanthracene and anthracene. Figures along connecting lines are contribution weight of the correlating MOs in percent.

Correlation of the molecular orbitals of 9-silaanthracene with those of anthracene was examined by expanding the MO function (ϕ_i) of 9-silaanthracene in terms of those of anthracene (ϕ_m^0): ϕ_i (silaanthracene) = $\Sigma\, C_m^i \phi_m^0$ (anthracene). Here the square of coefficient, $(C_m^i)^2$, shows the contribution weight of ϕ_m^0 to ϕ_i of 9-silaanthracene and the results are shown in Fig. 8 as percentages. As a result ϕ_{33} (b_1 symmetry), ϕ_{34} (b_1) and ϕ_{35} (a_2) of 9-silaanthracene are well correlated with ϕ_{33} (b_{2g}), ϕ_{34} (b_{3u}) and ϕ_{35} (a_u) of anthracene, respectively. ϕ_{31} (a_2) and ϕ_{32} (a_2) of 9-silaanthracene are also correlated with ϕ_{31} (a_u) and ϕ_{32} (b_{1g}) of anthracene. Thus the wavefunctions of three electronic states, $\Psi_{\mathrm{I}}(^1L_a')$, $\Psi_{\mathrm{III}}(^1L_b')$ and $\Psi_{\mathrm{VII}}(^1B_b')$ of 9-silaanthracene can be correlated with those of $\Psi_{\mathrm{I}}(^1L_a)$, $\Psi_{\mathrm{II}}(^1L_b)$ and $\Psi_{\mathrm{VIII}}(^1B_b)$ of anthracene, respectively. The energies of unoccupied MOs, ϕ_{34} (b_1) and ϕ_{35} (a_2) of 9-silaanthracene, are both considerably lower than those of ϕ_{34} (b_{3u}) and ϕ_{35} (a_u) of anthracene, respectively. While the energies of occupied MOs, ϕ_{33} (b_1), ϕ_{32} (a_2) and ϕ_{31} (a_2) of 9-silaanthracene are comparable to those of ϕ_{33} (b_{2g}), ϕ_{32} (b_{1g}) and ϕ_{31} (a_u) of anthracene, respectively. Thus the transition energies of $\Psi_{\mathrm{I}}(^1L_a')$, $\Psi_{\mathrm{III}}(^1L_b')$ and $\Psi_{\mathrm{VII}}(^1B_b')$ of 9-silaanthracene become smaller than those of $\Psi_{\mathrm{I}}(^1L_a)$, $\Psi_{\mathrm{II}}(^1L_b)$ and $\Psi_{\mathrm{VIII}}(^1B_b)$ of anthracene, respectively. Thus the red shifts of these absorption bands are explained.

4. Summary

Photophysical parameters of 9,10-dihydro-9-silaanthracene and 9-phenyl-9,10-di-hydro-9-silaanthracene were determined in 3MP at 77 K. Upon the photolysis of the former, the carbon-centered radicals were generated in both 3MP and EtOH at 77 K via the lowest triplet states, and silylenes were observed in 3MP at 77 K. The latter gives rise to the carbon-centered radical and 9-phenyl-9-silaanthracene in 3MP upon photolysis. Three electronic transition bands of 9-phenyl-9-silaanthracene were correlated with those of anthracene (^1L_a, ^1L_b and ^1B_b transition bands). These assignments were confirmed by the polarization measurement.

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