

## Emission from the Excited State of Tetraneopentylidisilene

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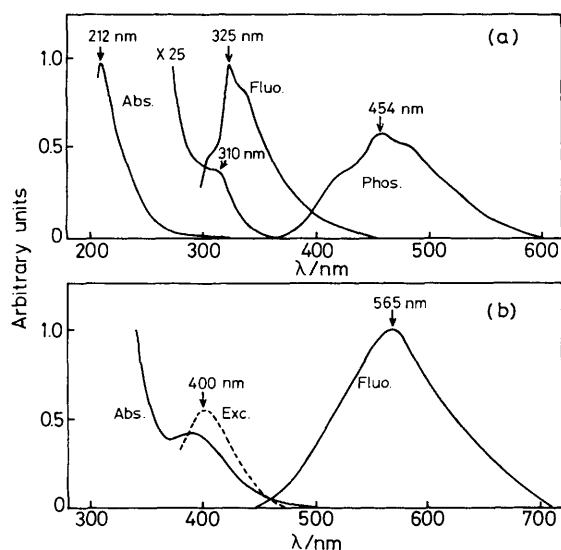
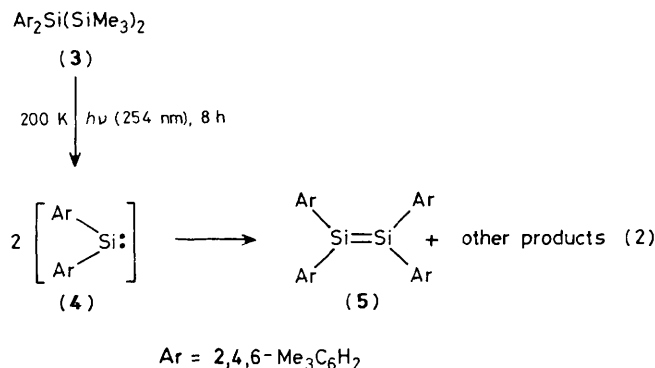
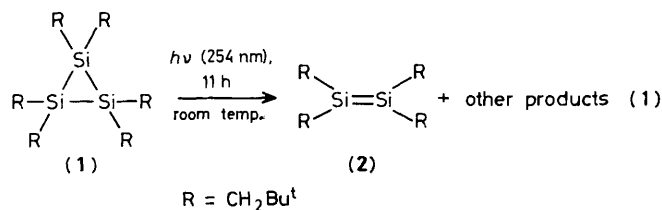
Fluorescence from tetraneopentylidisilene containing only a silicon–silicon double bond as chromophore is observed with a large Stokes shift (7300 cm<sup>-1</sup>) in methylcyclohexane–isopentane glass at 77 K.

Recently, the emission properties of aromatic disilanes have been extensively studied. Dual [local and charge-transfer (C.T.)] emissions of aromatic disilanes have been observed and it has been found that the intramolecular C.T. fluorescence has a broad and structureless band with a large Stokes shift.<sup>1,2</sup> The C.T. emission originates from the <sup>1</sup>(2pπ,3dπ) state produced by the 2pπ\* (aromatic ring) → vacant 3dπ (Si–Si single bond) intramolecular charge transfer.<sup>3–5</sup> The C.T. state has a strongly polar structure with complete charge separation,<sup>3,4</sup> which plays an important role in the photochemical and photophysical properties of aromatic disilanes.<sup>6</sup> It has been shown very recently that the intramolecular C.T. process occurs very rapidly (<10 ps) both in a nonpolar solvent at 293 K and in a polar rigid matrix at 77 K and that at room temperature a long-lived 425 nm transient (which is assigned to a rearranged intermediate) is produced with a rise time of 30 ps, showing that the transient arises from the C.T. state.<sup>7</sup> With regard to the unsaturated disilene systems West *et al.*<sup>8</sup> have reported the fluorescence spectrum of tetramesityl-disilene, but no fluorescence lifetimes and no information on the phosphorescence emission have been reported.

During our studies on the excited-state chemistry of organosilicon compounds, we were interested in the emission of tetraneopentylidisilene, which contains only a silicon–silicon double bond as a chromophore. Disilenes<sup>8–10</sup> having aryl substituents are not always convenient for assessing the electronic properties of silicon–silicon double bonded frameworks, since the aryl substituent will cause perturbations.

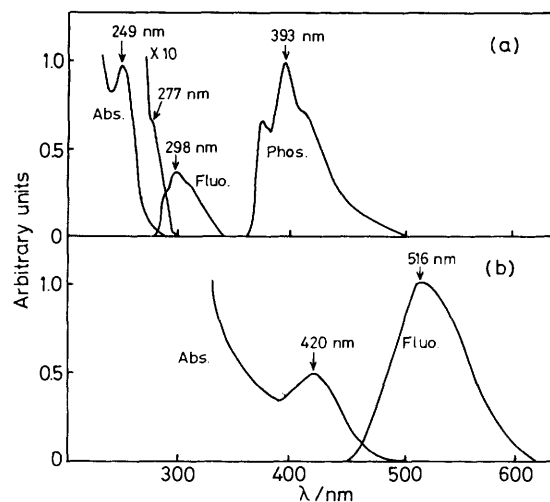
We report here the emission of tetraneopentylidisilene (**2**) with an extremely large Stokes shift (7300 cm<sup>-1</sup>) at 77 K.† It is known that (**2**) with an absorption peak at 400 nm is produced photochemically from hexaneopentylcyclotrisilane (**1**) at room temperature as shown in equation (1).<sup>11</sup> The fluorescence (λ<sub>max</sub> 325 nm) and phosphorescence (λ<sub>max</sub> 454 nm) spectra of (**1**) were recorded in a methylcyclohexane–isopentane (MP; 3 : 1 v/v) glass at 77 K [see Figure 1(a)]. These

† The emission spectra were recorded with a Hitachi M850 spectrofluorimeter and spectral corrections were made. The fluorescence lifetime was measured with a single-photon counting apparatus (Horiba NAES-1100, pulse width 2 nm). All samples were degassed by means of freeze–pump–thaw cycles on a high vacuum line.



**Figure 1.** (a) Absorption (Abs.), fluorescence (Fluo.), and phosphorescence (Phos.) spectra of (1) ( $4.8 \times 10^{-5} \text{ mol dm}^{-3}$ ) in MP glass at 77 K. (b) Absorption spectrum (Abs.) obtained on photolysis of (1) ( $9.8 \times 10^{-3} \text{ mol dm}^{-3}$ ) in MP at 254 nm at room temperature, fluorescence spectrum (Fluo.), excitation at 420 nm, and excitation spectrum (Exc.) monitored at 600 nm, of (2) in MP glass at 77 K.

are ascribed to the  $\sigma^* \rightarrow \sigma$  emissions. The fluorescence decay of (1) comprised two components (4 ns 89%; 47 ns 11%). This may correspond to two components of stereoisomers of (1) at low temperatures.<sup>12</sup> The phosphorescence lifetime of (1) was 1.7 ms. After irradiation of (1) in MP at 254 nm for 11 h at room temperature, the yellow species (2) was produced with other photoproduct(s) as shown in Figure 1(b) and equation (1). The irradiated solution was cooled to 77 K. For (2), the fluorescence spectrum (excited at 420 nm) with a peak at 565 nm was observed in MP glass at 77 K. The excitation spectrum (monitored at 600 nm) with a peak at 400 nm shows that the  $\pi^* \rightarrow \pi$  fluorescence at 565 nm originates from (2). The Stokes



**Figure 2.** (a) Absorption (Abs.), fluorescence (Fluo.), and phosphorescence (Phos.) spectra of (3) ( $3.1 \times 10^{-5} \text{ mol dm}^{-3}$ ) in MP glass at 77 K. (b) Absorption spectrum (Abs.) obtained on photolysis of (3) ( $1 \times 10^{-2} \text{ mol dm}^{-3}$ ) in MP at 200 K and fluorescence spectrum (Fluo.), excitation at 440 nm, of (5) in MP glass at 77 K.

shift for (2) is very large ( $7300 \text{ cm}^{-1}$ ) compared to that ( $4430 \text{ cm}^{-1}$ )<sup>‡</sup> of tetramesityldisilene (see Figure 2). It is unlikely that the emission of (2) with a large Stokes shift arises from an intramolecular C.T. state such as the  $^1(2p\pi, 3d\pi)$  C.T. state of phenyldisilane as described above, since (2) has only a Si=Si chromophore. The large Stokes shift may be ascribed to a large Franck-Condon destabilization energy in the disilenes, especially for (2). The length of the Si=Si bond in the lowest excited singlet ( $S_1$ ) state is, therefore, greater than that in the ground state. The  $\pi-\pi^*$  0-0 transition energy in (2) is determined to be  $21350 \text{ cm}^{-1}$  from the absorption (400 nm) and fluorescence (565 nm) band maxima, which is markedly smaller than that ( $57336 \text{ cm}^{-1}$ )<sup>13</sup> in ethylene. These results show that Si=Si  $3p\pi$  bond is much weaker than the C=C  $2p\pi$  band as has been suggested by West *et al.*<sup>8</sup> The fluorescence lifetime of (2) (excitation at 420 nm) was determined to be 27 ns in MP glass at 77 K. No phosphorescence of (2) at 77 K could be observed in the wavelength range  $<800 \text{ nm}$ . It thus seems that the phosphorescence of the disilenes may appear in the region  $>800 \text{ nm}$ . If this is not the case, the lack of observation of the phosphorescence may be due to either a relatively slow intersystem crossing compared to other deactivation processes in the  $S_1$  state or a relatively small radiative rate constant in the triplet state of (2).

Tetramesityldisilene (5) with an absorption peak at 420 nm was produced by the photolysis of 2,2-dimesitylhexamethyltrisilane (3)<sup>8</sup> at 200 K as shown in equation (2) and Figure 2(b). The fluorescence ( $\lambda_{\text{max}}$ , 298 nm; lifetime 15 ns) and phosphorescence ( $\lambda_{\text{max}}$ , 393 nm; lifetime 1.8 ms) spectra of (3) were recorded and are shown in Figure 2(a). The fluorescence spectrum ( $\lambda_{\text{max}}$ , 516 nm) of (5) in MP glass at 77 K is shown in Figure 2(b). The Stokes shift is determined to be  $4430 \text{ cm}^{-1}$ ,<sup>‡</sup> which is significantly smaller than that ( $7300 \text{ cm}^{-1}$ ) of (2) having only the Si=Si chromophore. It is obvious that the marked difference between them is caused by the perturbation of the mesityl group(s) in (5). The spectral differences between (2) and (5) are not due to the other products in equation (1), since the irradiation time (7–17 h)

<sup>‡</sup> West *et al.*<sup>8</sup> reported that the value of Stokes shift for the fluorescence of (5) was  $4000 \text{ cm}^{-1}$ .

for the photolysis of (1) at 254 nm had no effect on the fluorescence spectrum and lifetime of (2). These results indicate that the strength of Si=Si bond in the  $S_1$  state of (2) is weaker than that of (5). The fluorescence lifetime of (5) was 15 ns in MP glass at 77 K. No phosphorescence of (5) could be observed at 77 K in the wavelength range  $<800$  nm.

At room temperature, emission from (2) or (5) could not be observed. This is due to fast radiationless decay processes in the  $S_1$  state of the disilenes; photochemical isomerization may occur in fluid media.<sup>14</sup>

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