

## Fluorescence from the Intramolecular Charge-transfer State of Aromatic Silanes

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**Summary** Broad and structureless fluorescence spectra of 1-disilanyl- and 2-disilanyl-naphthalenes and also disilanylbenzene with large Stokes shifts were observed in polar media, which were attributed to the emissions from intramolecular CT states of the compounds.

ALTHOUGH the u.v. spectra of phenylsilanes have been interpreted in terms of excited-state interactions of the 'd- $\pi^*$ ' type,<sup>1</sup> no clear evidence of a 2p $\pi^*$ -3d interaction for aromatic silanes has yet been given. We report on the emission spectra of silanyl aromatic compounds in polar solvents,

which are interesting as the first examples of fluorescence spectra observed for the  $2p\pi^* \rightarrow 3d\pi$  (or  $2p\pi^* \rightarrow \sigma^*$ ) intramolecular charge-transfer (CT) states.

All the following samples were synthesized and purified according to the usual method:<sup>2</sup>  $\text{PhSiMe}_3$ ,  $\text{PhSiMe}_2\text{SiMe}_3$ ,  $1\text{-NpSiMe}_3$ ,  $\text{SiMe}_3\text{SiMe}_2\text{Np-1}$ ,  $2\text{-NpSiMe}_3$ ,  $\text{SiMe}_3\text{SiMe}_2\text{Np-2}$ ,  $\text{SiMe}_3\text{SiMe}_2\text{Pn-9}$ ,  $\text{SiMe}_3\text{SiMe}_2\text{An-9}$ , and  $\text{SiMe}_3\text{SiMe}_2\text{Py-1}$ , where Ph, Np, Pn, An, and Py denote phenyl, naphthyl, phenanthryl, anthranyl, and pyrenyl, respectively. For  $\text{PhSiMe}_2\text{SiMe}_3$ ,  $\text{SiMe}_3\text{SiMe}_2\text{Np-1}$ , and  $\text{SiMe}_3\text{SiMe}_2\text{Np-2}$  a broad and structureless emission with a large Stokes shift was observed in polar solvents. As an example, the absorption and fluorescence spectra of  $\text{SiMe}_3\text{SiMe}_2\text{Np-1}$  ( $4 \times 10^{-5}$  mol  $\text{l}^{-1}$ ) and  $\text{SiMe}_3\text{SiMe}_2\text{Np-2}$  ( $8 \times 10^{-5}$  mol  $\text{l}^{-1}$ ) in various solvents at 300 K are shown in the Figure. The

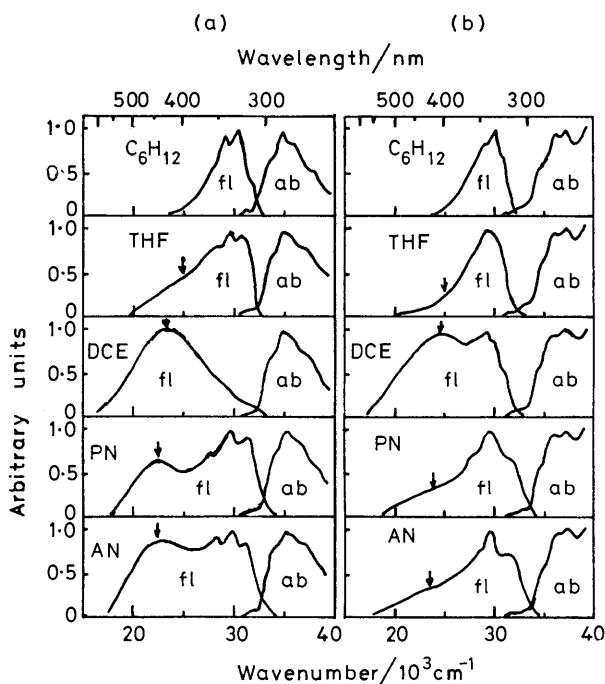


FIGURE. Solvent effects on absorption and fluorescence (excitation at 287 nm) spectra of (a)  $\text{SiMe}_3\text{SiMe}_2\text{Np-1}$  ( $4 \times 10^{-5}$  mol  $\text{l}^{-1}$ ) and (b)  $\text{SiMe}_3\text{SiMe}_2\text{Np-2}$  ( $8 \times 10^{-5}$  mol  $\text{l}^{-1}$ ) at 300 K. Solvents  $\text{C}_6\text{H}_{12}$ : cyclohexane (dielectric constant 2.023); THF: tetrahydrofuran (7.58); DCE: 1,2-dichloroethane (10.36); PN: propionitrile (27.20); AN: acetonitrile (37.50).

longer wavelength emission is not due to an excimer emission judging from the concentration effect on the spectral change. There is a tendency for the broad and structureless fluorescence of the 1-Np-isomer to be more prominent than that of the 2-Np-isomer (Figure). There was hardly any solvent effect on the normal emission bands ( ${}^1L_b \rightarrow {}^1A$ ) at ca.  $30,000 \text{ cm}^{-1}$ , but, in contrast, the broad and structureless emission band shifts to the red in polar solvents, indicating that the emitting state is polar. The excitation spectra

at both fluorescence bands were comparable with those of the absorption bands. Similar results were also obtained for  $\text{PhSiMe}_2\text{SiMe}_3$ . However, for the other samples longer wavelength emission bands were not observed, as discussed later.

In addition to the solvents as shown in the Figure, several other solvents (diethyl ether, ethanol, glycerol, and *n*-butyronitrile) were used to record the fluorescence spectra. Values of  $\Delta\mu$  ( $= \mu_{\text{CT}} - \mu_{\text{g}}$ ), where  $\mu_{\text{CT}}$  and  $\mu_{\text{g}}$  are the dipole moments of the excited state and the ground state, respectively, can be estimated from the Lippert-Mataga equation.<sup>3</sup> The  $\Delta\mu$  values were about 11 ( $\text{SiMe}_3\text{SiMe}_2\text{Np-1}$ ), 9 ( $\text{SiMe}_3\text{SiMe}_2\text{Np-2}$ ), and 4.6 D ( $\text{PhSiMe}_2\text{SiMe}_3$ ), on the assumption that the Onsager radii for disilanyl-naphthalenes and disilanyl-benzene are 4 and 3 Å respectively. The dipole moments in the ground state of aromatic silanes seem to be small because of  $+I$  and  $-M$  effects.<sup>4</sup> Thus, the values of  $\mu_{\text{CT}}$  are approximately equal to those of  $\Delta\mu$ . We therefore conclude that the fluorescent state for the longer wavelength emission has a strongly polar structure with complete charge separation. The broad and structureless emission may originate from an intramolecular CT state resulting from charge transfer from the  $2p\pi^*$  orbital of the aromatic ring to the  $3d\pi$  vacant orbital of the disilanyl substituent. The  $2p\pi^* \rightarrow 3d\pi$  CT state leading to the longer wavelength emission is produced in these compounds for the following reasons. (i) The energy separation between the  $2p\pi$  and  $3d$  orbitals becomes small upon excitation (the electron-donating power of the aromatic ring increases upon excitation); (ii) the disilanyl group (or polysilanyl group<sup>†</sup>) provides a vacant  $3d\pi$  orbital, which may be produced by the linear combination of  $3d$  atomic orbitals, having a relatively low energy level compared with that of a single  $3d$  atomic orbital (the electron-withdrawing power of the disilanyl group increases); (iii) the  $2p\pi^* \rightarrow 3d\pi$  CT energy level is lowered by the polarization energy due to the interaction between the CT state species and polar solvent molecules. An alternative interpretation is that the longer wavelength emission is due to intramolecular charge transfer from the aromatic  $\pi$  electron system into a  $\sigma^*$  orbital of the Si-Si bond. On consideration of the likely molecular conformations arising from steric interactions this  $\pi \rightarrow \sigma^*$  CT interpretation explains adequately the differences between 1- and 2-disilanyl-naphthalenes and the lack of CT fluorescence in the monosilane derivatives.

CT emission was not observed for monosilyl derivatives and disilyl polycyclic aromatic compounds ( $\geq 3$  aromatic rings) even in polar solvents. The energy level of the lowest excited singlet state of such polyaromatic compounds is too low to prevent the  $2p\pi^* \rightarrow 3d\pi$  (or  $2p\pi^* \rightarrow \sigma^*$ ) interaction. The intramolecular CT state is of importance in the photochemical and photophysical processes of silanyl aromatic compounds.<sup>5</sup>

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<sup>†</sup> E.g. For  $\text{PhSi}(\text{SiMe}_3)_3$ , similar longer wavelength emission was also observed.

<sup>1</sup> E.g. H. Sakurai, H. Yamamori, and M. Kumada, *Chem. Commun.*, 1968, 198.

<sup>2</sup> M. Ishikawa, M. Oda, N. Miyoshi, L. Fabry, M. Kumada, T. Yamabe, K. Akagi, and K. Fukui, *J. Am. Chem. Soc.*, 1979, **101**, 4612, and references cited therein.

<sup>3</sup> E.g. J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley-Interscience, London, 1970, p. 115.

<sup>4</sup> H. Soffer and T. De Vries, *J. Am. Chem. Soc.*, 1951, **73**, 5817.

<sup>5</sup> H. Shizuka, H. Obuchi, M. Ishikawa, and M. Kumada, unpublished results.