

Evidence that the Fluorescence of Phenylsilanes involves the $^1(2p\pi, 3d\pi)$ Intramolecular Charge-transfer State

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Evidence that the fluorescence of phenylsilanes in polar media involves the $^1(2p\pi, 3d\pi)$ intramolecular charge-transfer state is given by the effect of steric twisting on the emission.

The electronic interaction between $2p\pi$ and $3d\pi$ orbitals is currently an interesting aspect of chemistry. The broad and structureless fluorescence spectra of aromatic silanes with large Stokes shifts have been attributed to the intramolecular charge-transfer (C.T.) state.¹ However, no assignment of the C.T. state [$^1(2p\pi, 3d\pi)$ or $^1(2p\pi, \sigma^*)$] has yet been made. We

now demonstrate that the C.T. fluorescence originates from the $^1(2p\pi, 3d\pi)$ state produced by $2p\pi^* \rightarrow 3d\pi$ intramolecular charge transfer.

Samples were chosen in order that molecular conformations arising from steric interactions might affect the intramolecular C.T. emissions which would give information about the

intramolecular C.T. state. All samples were synthesized and purified by the usual method.² The absorption and emission spectra of phenyldisilanes (1), (2), and (3) (*ca.* 10^{-4} mol l⁻¹) in acetonitrile and EPA (ether-isopentane-alcohol, 5:5:2) are shown in Figure 1. The first absorption bands correspond to the ${}^1B_{2u} \rightarrow {}^1A_{1g}$ transition in benzene.³ In acetonitrile at 300 K, dual fluorescences were observed for (1) and (2): one is the normal fluorescence corresponding to the ${}^1B_{2u} \rightarrow {}^1A_{1g}$ radiative transition in benzene³ and the other the intramolecular C.T. fluorescence having a broad and structureless band with a large Stokes shift [11.3×10^3 cm⁻¹ for (1) and 8.7×10^3 cm⁻¹ for (2)]. The fluorescence intensities of the C.T. emissions are in the order (1) > (2) \gg (3), and in contrast the intensities for the normal emissions are (1) < (2) < (3), as can be seen in Figure 1(a). Similarly, dual fluorescences for (1) and (2) were observed even in an EPA rigid matrix at 77 K, but not for (3) [Figure 1(b)]. From the total emission spectra, the quantum yields for the normal ($\Phi_{F.M.}$) and C.T. ($\Phi_{C.T.}$) emissions and the phosphorescence (Φ_P) in an EPA rigid matrix at 77 K were determined to be 0.09, 0.09₇, and 0.35 for (1); 0.17, 0.09₄, and 0.37 for (2); 0.29₈, 0, and 0.62₈ for (3), respectively. The

phosphorescence spectra correspond to the ${}^3B_{1u} \rightarrow {}^1A_{1g}$ radiative transition in benzene considering their vibrational structure. The lifetimes for both normal and C.T. fluorescences at 300 K were very short (<1 ns). The fluorescence response function of the normal fluorescence for (1) or (2) in an EPA rigid matrix at 77 K consisted of fast (<1 ns) and slow [20.₉ ns for (1) or 20.₆ ns for (2)] decay components, while for (3) a single exponential decay (31.₄ ns) was observed. The fluorescence lifetimes of the C.T. state were very short (<1 ns) in an EPA glass at 77 K. These results show the rapid formation of the C.T. state *via* the ${}^1(\pi, \pi^*)$ ${}^1B_{2u}$ state of (1) or (2) which have molecular conformations favourable for intramolecular charge transfer even in an EPA rigid matrix at 77 K. There is also a fast intersystem crossing from ${}^1C.T.$ to ${}^3(\pi, \pi^*)$ owing to the small energy-gap between them. A similar tendency was observed for (4) and (5).

The experimental data can be explained by the following mechanism. If the intramolecular C.T. fluorescence of phenyldisilanes originated from the ${}^1(2p\pi, \sigma^*)$ state, the intensity of the C.T. emissions for (3) or (5) would be large compared with those for (1), (2), and (4), since for (3) and (5) the intramolecular charge transfer from the aromatic π -system to a vacant σ^* orbital of the Si-Si bond would be much more effective than for (1), (2) and (4) owing to the out-of-plane molecular structure (the orbital being able to overlap with the σ^* orbital) arising from steric interactions. However, the experimental results argue against this mechanism. An in-plane or in-plane-like structure is favourable for intramolecular C.T. interactions between π and $3d\pi$ systems. It is possible for (1), (2), and (4) to make an in-plane-like conformation by rotation around the C-Si bond axis but not for (3) and (5). Therefore, it can be said that the intramolecular C.T. fluorescence of phenyldisilanes (or polysilanes) is attributed to the emission from the ${}^1(2p\pi, 3d\pi)$ state produced by the $2p\pi^* \rightarrow 3d\pi$ intramolecular charge transfer. The C.T. emission from the ${}^1(2p\pi, 3d\pi)$ state was not appreciable in nonpolar media. However, the energy level, $E({}^1C.T.)$, for the ${}^1(2p\pi, 3d\pi)$ state in nonpolar media is lower than that, $E({}^1B_2)$, of the locally excited S_1 state, from the intercept of the Lippert-Mataga plot¹ [e.g., $E({}^1B_2) = 36.₂ \times 10^3$ cm⁻¹ and $E({}^1C.T.) = 29.₇ \times 10^3$ cm⁻¹ for (1) in cyclohexane].

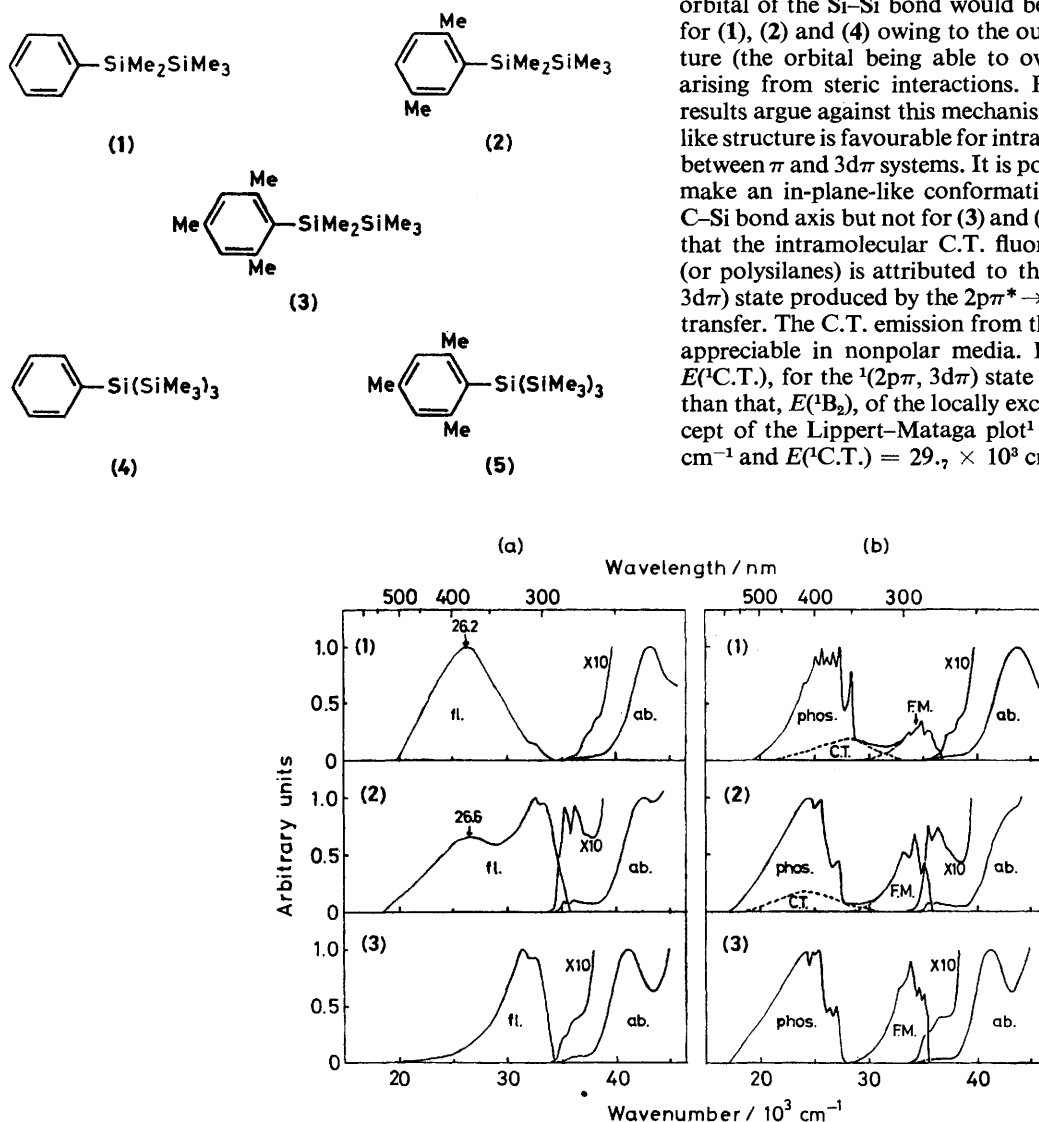


Figure 1. (a) Absorption and fluorescence (excitation at 260 nm) spectra of disilylbenzenes (1), (2), and (3) in acetonitrile at 300 K. (b) Absorption (in EPA at 300 K) and total emission (excitation at 260 nm) spectra (in an EPA rigid matrix at 77 K) of disilylbenzenes (1), (2), and (3). F.M.: normal fluorescence; C.T.: change-transfer fluorescence.

The photochemical reaction of (1) at 254 nm and 300 K took place markedly in cyclohexane, but slightly for (3) indicating that the photochemical reaction may originate from $^1(2p\pi, 3d\pi)$. This result agrees with the reactive state of disilanyl-naphthalenes.⁴

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