Intramolecular charge transfer emission from excited phenyldisilanes without TICT*

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Abstract
Dual (local and CT) emission of phenyldisilanes has been firstly observed. The intramolecular CT process in the excited state occurs very rapidly with a time constant less than 10ps even in rigid glass at 77K. The CT state has a planar structure with an in-plane long axis polarization. These facts show that internal rotation or twisting during the lifetime in the excited state is not necessary for the CT process. It is found that the CT mechanism is quite different from that of TICT.

1. INTRODUCTION

Photophysics and photochemistry of organosilicon compounds have become one of interesting fields in chemistry (ref. 1).

Dual (local and CT) emission of aromatic disilanes has been firstly observed and it has been shown that intramolecular CT fluorescence has a broad and structureless band with a large Stokes shift (refs. 2-6). The CT state has a polar structure with an in-plane long axis polarization (ref. 7). The molecular conformation of phenyldisilanes is a planar structure (not an out-of-plane structure), which is favorable to the CT process (refs. 4, 5). The CT process occurs very rapidly within a time constant of 10ps even in rigid glass at 77K (refs. 6, 8). This finding shows that twisting or internal rotation is not necessary for the CT process. That is, the CT mechanism is quite different from that of twisted intramolecular charge transfer TICT (ref. 9). On the basis of our experimental results, we proposed the mechanism that the CT process originates from the $^1(2p\pi,3d\pi)$ CT state (refs. 3-8). The CT state is produced by intramolecular CT from $2p\pi^*$ (the phenyl ring) to the vacant bonding $3d\pi$ orbital (the Si-Si bond), resulting in the $^1(2p\pi,3d\pi)$ CT state.

However, Sakurai et al. proposed the orthogonal intramolecular charge transfer (OICT) mechanism (refs. 10, 11). That is, the CT state was assumed to be ascribable to the $^1(\sigma,2p\pi^*)$ state. After excitation to $2p\pi^*$, the charge transfer occurs from the σ orbital (the Si-Si bond) to the vacant π orbital of the phenyl ring, resulting in the $^1(\sigma,2p\pi^*)$ state. The resulting $^1(\sigma,2p\pi^*)$ state is stabilized by twisting or internal rotation of the disilanyl group to form an orthogonal electronic structure. This mechanism was proposed based on the facts that the emission peaks of the CT bands shift to red by introduction of an electron-withdrawing group at the para-position of the phenyl ring, and also that the molecule with the (Si-Si) σ bond in out-of-plane conformation to the phenyl ring gives the CT emission at the longest wavelength. Similar mechanism was also proposed by Horn et al. (ref. 12).

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* TICT = Twisted Intramolecular Charge Transfer

Here, we discuss the intramolecular CT mechanism of phenyldisilanes in detail on the basis of the experimental results.

2. RESULTS AND DISCUSSION

2.1 Dual emission of phenyldisilanes

In a course of our study on photophysics and photochemistry of phenyl-disilanes, we firstly observed the intramolecular CT emission in addition to the normal emission localized in the phenyl ring (refs. 2, 4, 5). Figure 1 shows UV absorption and fluorescence spectra of phenylpentamethyldisilane ($\underline{1}$) at 300K in several solvents. There are two absorption bands around 38.5×10^3 and 43.5×10^3 cm^{-1} which are correlated with $^1B_{2u} \leftarrow {}^1A_{1g}$ and $^1B_{1u} \leftarrow {}^1A_{1g}$ transition bands in benzene respectively. These bands scarcely showed any shift with change in solvent polarity. On the other hand, fluorescence spectra give a broad and structureless band in the long wavelength region in addition to the emission band around 33×10^3 cm^{-1} which corresponds to the fluorescence band of benzene: $^1B_{2u} \rightarrow {}^1A_{1g}$ transition. The latter is ascribable to the local emission band (LE) in the phenyl ring and does not show a shift with change in solvent polarity. The former band shifts to red with increasing solvent polarity. This indicates that the emitting state responsible for the broad emission has a polar structure i.e., the intra-molecular CT state.

Similar results are obtained for 1- and 2-naphthyldisilanes. From the Lippert-Mataga equation (ref. 13) the dipole moments in the CT state are estimated as 4.8 ($\underline{1}$), 11.7 (1- naphthyldisilane), and 9.2D (2-naphthyldisilane) (ref. 5).
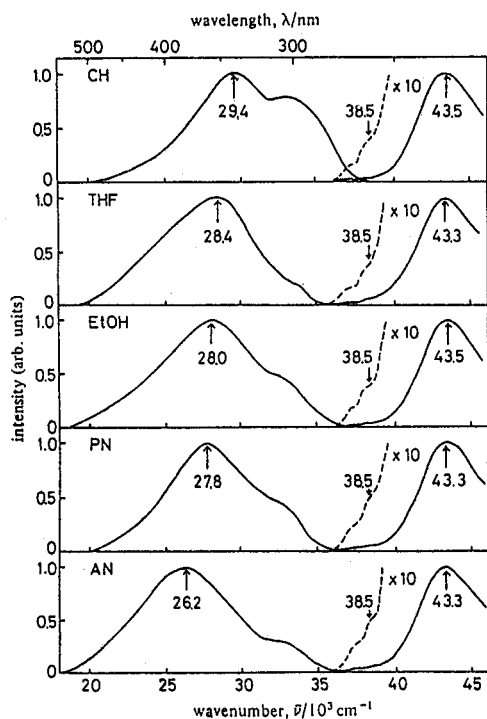

Fig. 1
Absorption and fluorescence spectra
of $\underline{1}$ in various solvents at 300K.
CH: cyclohexane; THF: tetrahydro-furan; EtOH: ethanol; PN: propio-nitrile; AN: acetonitrile (ref. 5).

Dual emission similar to that of $\underline{1}$ is observed for other disilanyl compounds but not for both monosilanyl compounds and polycondensed disilanyl compounds (the number of benzene rings $\geq$ 3). The latter fact suggests that the lowest $2p\pi^*$ energy level should be greater than ca. 3×10^4 cm^{-1} to generate the CT state (ref. 5). The number of silicon atoms greater than two should be needed for the CT emission.

2.2 Assignment of the intramolecular CT state

On the assignment of the CT-state, two explanations were proposed. Sakurai et al. (ref. 10) proposed Orthogonal Intramolecular CT state (OICT) of the $^1(\sigma,2p\pi^*)$ CT state, while we proposed the $^1(2p\pi,3d\pi)$ CT state on the basis of the several experimental results shown below.

2.2.1 Relation between molecular structures and the CT emission

We measured the CT emission of phenyldisilanes having in-plane and out-of-plane structures concerning the phenyl ring and the Si-Si bond.

Figure 2 shows absorption and fluorescence spectra of **1**, **2**, (2,4-dimethylphenyldisilane), and **3** (2,4,6-trimethylphenyldisilane) in acetonitrile at 300K (a) and ether-isopentane-ethanol (EPA) (5:5:2 by volume) rigid glass at 77K (refs. 4, 5). In the fluorescence spectra at 300K the relative intensity of the CT band against LE band becomes small in the order of **1**, **2**, and **3**. At 77K, the CT emission bands are observed for **1** and **2**, but not for **3**. For 2,6-dimethylphenyldisilane (**4**), the CT emission was scarcely observed just like as the case of **3**. Emission quantum yields of the LE, the CT and the phosphorescence bands at 77K are obtained as 0.09, 0.09_7 and 0.35 for **1**, 0.17, 0.03 and 0.42 for **2**, and 0.29_6, 0.0 and 0.62_8 for **3**, respectively.
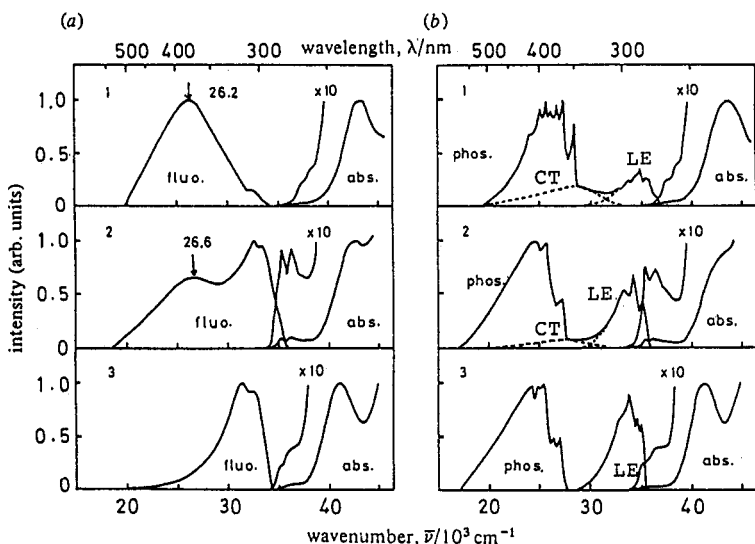

Fig. 2
(a) Absorption and fluorescence spectra of **1**, **2** and **3** in acetonitrile at 300K and (b) absorption (in EPA at 300K) and emission (in EPA glass at 77K) spectra of **1**, **2** and **3**. The emission spectra of **1** and **2** in EPA glass at 77K consist of the normal (LE) and charge-transfer (CT) fluorescence spectra and the normal phosphorescence (phos) (ref. 5).

The compounds **3** (or **4**) has the molecular structutre that two methyl groups at ortho-positions sterically interact with the disilanyl group resulting in an out-of-plane conformation as shown in Figure 3.
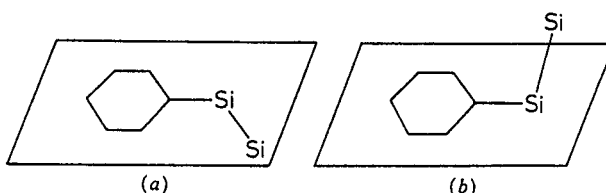

Fig. 3 Molecular structures of (**1**): (a) planar and (b) perpendicular (ref. 5).

Hence, the strong electronic interaction between σ (Si-Si) and π^*-orbital is expected for **3** (or **4**). If the $^1(\sigma,2p\pi^*)$ state were the CT state, an out-of-plane structure would be favorable for the CT emission because of the σ-π interaction. However, the CT emission of **3** (or **4**) having an out-of-plane structure was scarcely observed in contrast to the case of a planar structure. This result shows that

the $^1(\sigma,2p\pi*)$ mechanism is unlikely for the CT emission. According to the OICT mechanism $[^1(\sigma,2p\pi*)]$ the CT emission can be observed when the energy level of HOMO of the aromatic group should be lower than that of the disilanyl group (I_p = 8.7 eV). This consideration, however, is not available for naphthyldisilanes [I_p (naphthalene) = 8.12 eV)] and 2,4-dimethylphenyldisilane **2** [I_p (m-xylene = 8.59 eV)], where the aromatic moieties have smaller I_p values than that of the disilanyl group. In such cases, there is no charge transfer from σ-orbital (Si-Si) to vacant π-orbital (phenyl ring) resulting in $^1(\sigma,2p\pi*)$. However, the CT emission was observed even in these compounds.

2.2.2 Fluorescence polarization spectra

If the OICT mechanism would be available for the CT emission, the electronic transition moment of the CT emission should be polarized perpendicular to the molecular plane of the phenyl ring and to be parallel to that of phosphorescence. On the other hand, if the CT state is the $^1(2p\pi,3d\pi)$ state, the CT emission may have the transition moment polarized approximately parallel to the in-plane molecular long axis, and perpendicular to that of the phosphorescence.

Fluorescence polarization spectra were observed for **1** in EPA rigid glass at 77K (ref. 7). Figure 4 shows the result obtained by excitation at 250nm absorption band, which is assigned to the $^1B_1 \leftarrow ^1A_1$ transition. The emission bands of (a) and (c) are ascribable to the $^1B_2 \rightarrow ^1A_1$ (^1L_b) fluorescence and $^3B_1 \rightarrow ^1A_1$ (^3L_a) phosphorescence, respectively. Emission band (b) expressed by the dotted line is the CT emission. Degree of polarization (P) was calculated by the following equation for each wavelength where f is the instrumental

$$P = (I_{\parallel} - fI_{\perp})/(I_{\parallel} + fI_{\perp})$$

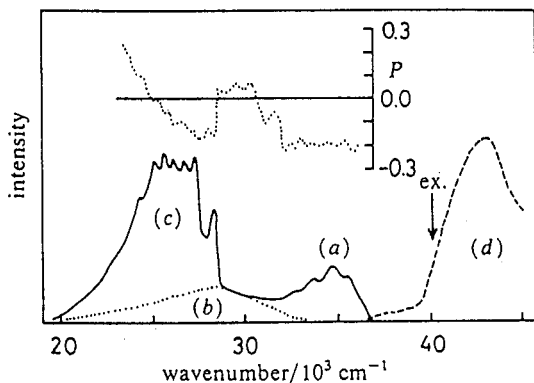correction factor for the polarized light. Value of P is shown by dots in Fig. 4. P is negative in the (a) and (c) region and positive in the region of pure CT emission band. This indicates that the transition moments of the emission of (a) and (c) are polarized perpendicular to that of $^1B_1 \leftarrow ^1A_1$ (^1L_a) absorption polarized parallel to the molecular long axis. These results agree well with the fact that ^1L_b fluorescence (LE) and phosphorescence are polarized parallel to the molecular short axis and normal to the molecular plane, respectively. Positive P value in the pure CT emission region indicates that the CT emission is polarized to parallel to the molecular long axis. That is, the CT state has an in-plane long axis polarization. This is evidence for the mechanism that the CT emission does not originate from the OICT [$^1(\sigma,2p\pi*)$] CT state but the $^1(2p\pi,3d\pi)$ CT state.

Fig. 4
Fluorescence polarization spectra of (**1**) in EPA glass at 77K at the excitation wavelength (ex. = 250nm), where (a) is the emission from the locally excited state $^1(\pi,\pi*)$ ^1L_b, (b) is the emission from the $^1(2p\pi,3d\pi)$ CT state, (c) is the phosphorescence spectrum at 250nm and (d) is the absorption spectrum (ref. 7).

2.2.3 MCD spectra

It is experimentally known that MCD spectra of the monosubstituted benzenes give negative and positive $\Delta\epsilon$ (= $\epsilon_r - \epsilon_\ell$) when the substituent is an electron donating group such as NH_2 and CH_3 and an electron withdrawing group such as NO_2, respectively (ref. 14). Phenyldisilane (**1**) shows positive MCD spectra, supporting the direction of charge transfer given by the CNDO/S-CI calculations including 3d orbitals of silicon atoms (ref. 7). The charge migrated from the phenyl ring to the Si-Si bond was estimated to be 0.55e by use of the calculated results for the in-plane structure.
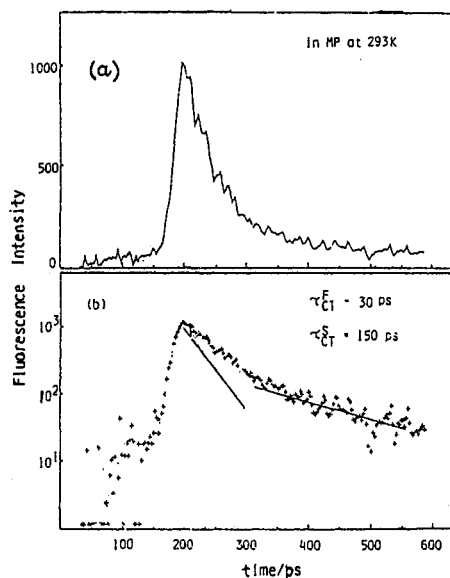

Fig. 5   (a) Picosecond rise and decay of the intramolecular CT emission of phenyldisilane (**1**) in MP at 293K monitored at 350nm, and (b) its logarithmic plot (ref. 8).
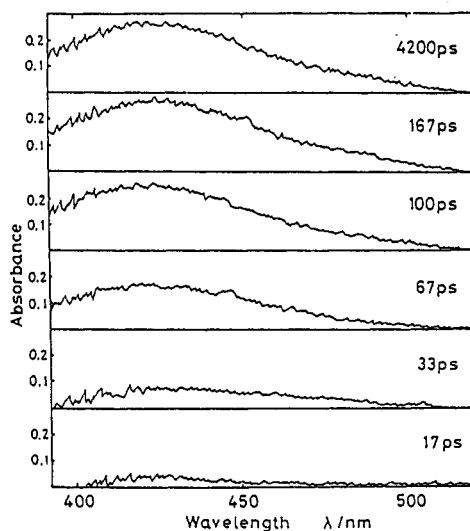
Fig. 6   Build-up profile of the 425nm transient absorption spectra measured by picosecond laser flash photolysis of **1** in MP at 293K, where the times refer to the delay times (ref. 8).

2.2.4 ps- and ns-timeresolved laser experiments

The photophysics and photochemistry of phenyldisilane has been studied by means of ps- and ns-laser spectroscopy (ref. 8). Figure 5 shows the rise and decay features of the CT emission at 350 nm in MP (methylcyclohexane: isopentane 1:1 v/v) at 293K. The build-up for the CT emission (excited at 266nm and monitored at 350nm) is established within 10ps not only in fluid media at 293K. Similarly, the rise was completed within 10ps even in rigid glass at 77K. These results mean that the intra-molecular CT process in the excited state occurs very rapidly within a time constant of 10ps even in rigid glass at 77K. This finding shows that twisting or internal rotation during the lifetime in the excited state is not necessary for the CT formation of phenyldisilane. Therefore, it can be said that the CT mechanism of phenyldisilanes is quite different from that of TICT (ref. 9). That is, the TICT (or OICT) mechanism is excluded for the CT process of phenyldisilanes. Decay curve was analysed by double exponential functions with the fast (τ_{CT}^f = 30ps) and the slow τ_{CT}^s = 150ps) time constants. The fast components is 90% of the initial CT components. The CT fluorescence lifetimes in EPA glass at 77K, were obtained as τ_{CT}^s = 300ps and τ_{CT}^s = 3.16ns, whose initial component ratio was 1:1. These fast and slow components in rigid glass at 77K may be correlated with the molecular structure of phenyldisilane. The molecule with in-plane-like conformation is assigned to the fast component. This conformation allows an effective intersystem crossing resulting in the fast decay. The molecule with in-plane conformation is related to the slow

component, because the lifetime of the CT state is long due to inefficient intersystem crossing. The fast decay of the CT emission is related to the effective ISC ^{1}CT $\rightarrow$ ^{3}L$_a$ (π-π*) at 77K. The reaction quantum yield was very low in rigid glass at 77K. At 293K in MP, a transient absorption band (which was assigned to a rearranged product: silene) at 425nm appeared with a time constant of 30ps as shown in Fig. 6. The reaction quantum yields was obtained as 0.86 (ref. 15). It is concluded that the rearrangement for the silene formation occurs effectively from the CT state with a time constant of 30ps at room temperature. Therefore, the CT state plays an important role for photophysical and photochemical processes of phenyldisilanes (ref.15).

2.2.5 Substituent effects of phenyldisilane on the CT emission

When an electron donating groups such as methoxy or t-butyl group was introduced at the para-position of phenyldisilane, lack of the CT emission was observed (ref. 10). This result was one of reasons for the OICT mechanism. We tried measurements of CT emissions for both p-methoxyphenyldisilane and p-t-buthylphenyldisilane. Strong CT emission having an in-plane long axis polarization was observed in PVA film at 77K (ref. 16). Therefore, the substituent effect on the CT emission does not support the OICT mechanism.

3. CONCLUSION

we have found a new type intramolecular CT emission of phenyldisilanes in both fluid at room temperature and rigid media at 77K. The CT process occurs very rapidly within a time constant 10ps even in rigid glass. This finding shows that twisting or internal rotation during the lifetime in the excited state is not necessary for the CT-state formation: that is, the CT mechanism is quite different from that of TICT (or OICT). The CT state has a planar structure with an in-plane long axis polarization. The experimental results support the ^{1}(2pπ,3dπ) mechanism. At least, it can be said that the CT state has a planar π-like electronic structure.

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