are stable/unstable when the excitation is located primarily on the proton donor/acceptor, respectively.

Conclusion

This study was undertaken in order to model the effects of ground-state hydrogen bonding on the electronic spectra and complex formation in excited states. The excited states of ammonia and water, the subunits of the studied complexes, are of predominant Rydberg character with excited orbitals of large spatial extension.^{4,6-9} Bond dissociation processes were not considered in this paper.

The excited states of the complex can be correlated with those of the individual subsystems. If the excitation is located primarily on the proton acceptor then the complex becomes dissociative in the excited state. Alternatively, when the excitation is located on the donor, the stability of the ground state is retained. In the first case the transition energy is shifted considerably to higher energies whereas in the second case a shift to lower energies results.

The most stable ground-state configuration, in which ammonia is the acceptor, is, therefore, unstable against dissociation into the subunits in the excited state. The structure in which ammonia is the donor is stable and the hydrogen-bonded complex of planar ammonia as donor and water as acceptor conforms to the total minimum on the excited-state surface.

Two higher lying minima were observed which are most important for exciplex formation of tertiary amines. The first is obtained by a rotational relaxation of the water molecule in OH...N (G1) in order to direct a doubly occupied water lone pair to the singly occupied ammonia lone pair orbital. This gives a rather loosely bound complex with not well-defined stoichiometry.

A second relaxation mechanism involves hydrogen atom transfer, along the hydrogen bond. The resulting configuration can be described as a complex between an ammonium and a hydroxyl radical.

Excited-state interactions can be understood in terms of electrostatic interactions of the positively charged core of that moiety, on which the excitation is primarily located, with its polar counterpart.

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Registry No. Ammonia, 7664-41-7; water, 7732-18-5.

Excited-State Behavior of Phenylethynyldisilanes: An Intramolecular Charge-Transfer Emission

Haruo Shizuka,* Katsuhiko Okazaki, Hideaki Tanaka, Masayuki Tanaka,

Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan

Mitsuo Ishikawa,

Department of Synthetic Chemistry, Kyoto University, Kyoto 606, Japan

Minoru Sumitani, and Keitaro Yoshihara

Institute for Molecular Science, Okazaki 444, Japan (Received: September 4, 1986)

Photochemical and photophysical properties of phenylethynyldisilanes in MP (methylcyclohexane/isopentane, 3:1 v/v) have been studied by means of picosecond and nanosecond spectroscopy along with steady-state experiments. Intramolecular charge transfer in the excited singlet state of phenylethynyldisilanes occurs very rapidly (<10 ps) at both 77 and 294 K. This finding shows that internal rotation (or twisting) or solvation is not necessary for the intramolecular CT formation of phenylethynyldisilanes. The mechanism on the intramolecular CT from the (π,π^*) state to the $(2p\pi,3d\pi)$ CT state of the compounds is quite different from that of the usual TICT (twisted intramolecular charge transfer). Two decay components (fast and slow) of the ¹CT state are observed, which are ascribed to the intersystem crossing rates from ¹CT to ${}^{3}(\pi,\pi^{*})$, depending upon the molecular conformations of the ¹CT state of phenylethynyldisilanes. The photochemical reaction to produce silacyclopropenes takes place effectively via the ¹CT state at room temperature, but not in MP glass at 77 K.

Recently, the excited-state chemistry of aromatic disilanes has been extensively studied.¹⁻⁷ Substitution of the disilanyl (or polysilanyl) group into the benzene ring (e.g., phenyldisilane) causes interesting photochemical and photophysical profiles different from those of methyl- and methylene-substituted benzenes.⁸⁻¹¹ Dual (local and CT) emissions have been observed in aromatic disilanes. It has been found that the intramolecular CT fluorescence has a broad and structureless band with a large Stokes shift.^{1,2} The CT emission originates from the $(2p\pi, 3d\pi)$ state produced by the $2p\pi^*$ (aromatic ring) \rightarrow vacant $3d\pi$ (Si-Si bond) intramolecular charge transfer.^{3,4,6} The intramolecular CT state has a strongly polar structure with complete charge separation,^{3,4} which plays an important role in the photochemical and photophysical properties of phenyldisilanes.⁵ It has been shown very

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recently that the intramolecular CT 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 species arises from the CT state.⁷

In a previous paper,² the CT emission of phenylethynylpentamethyldisilane (1) has been preliminarily reported. This paper reports the photochemical and photophysical properties of phenylethynyldisilanes (1-5) studied by means of picosecond and nanosecond spectroscopy together with measurements of the steady-state experiments.



Experimental Section

Materials. The phenylethynyldisilanes (1-5) used were the same as those reported elsewhere.

The solvents used were G.R. grade products from Tokyo Kasei and were purified by the usual method.¹⁴ A mixed solvent of methylcyclohexane and isopentane (3:1 v/v) was used. For the photochemical reactions at 300 K cyclohexane was used as a solvent. The sample concentrations were $10^{-4}-10^{-5}$ M for emission spectroscopy and ca. 10^{-3} M for measurements of reaction quantum yields. All samples were thoroughly degassed by freeze-pump-thaw cycles on a high-vacuum line.

Emission Measurements. Fluorescence spectra were recorded with a Hitachi MPF 2A spectrofluorimeter, and spectral corrections for emission were made. The fluorescence and phosphorescence quantum yields at 77 K were determined relative to toluene $(\Phi_F = 0.29)^{11}$ in MP glass at 77 K. The fluorescence response functions were recorded with a Horiba NAES-1100 nanosecond time-resolved spectrofluorimeter (pulse width 2 ns) equipped with a computer system. The functions were analyzed by the deconvolution method. The phosphorescence lifetimes were recorded with a Hitachi MPF 2A spectrofluorimeter. Picosecond measurements were carried out with a mode-locked Nd3+:YAG laser (fourth harmonic 266 nm, pulse width 10 ps). The buildup and decay functions of charge-transfer fluorescence with a band-pass filter at 380 nm were time-resolved by a streak camera (HTV C1370). Low-temperature experiments were carried out using a cryostat (Oxford DN704).

Photochemical Reactions. A low-pressure mercury resonance lamp was used as the 254-nm radiation source with a Vycor glass filter. Actinometry was carried out with a ferric oxalate solution.^{15,16} The starting materials (1–5) were measured quantitatively by vapor-phase chromatography in order to determine the disappearance quantum yields. A Hitachi 163 vapor-phase chromatograph with a flame ionization detector and an automatic integrator (Takeda Riken TR-2217) was used with a 3-m column filled with silicon DC-200 plus Apieson grease. The photoproduct



Figure 1. Absorption (at 300 K) and emission spectra (at 300 and 77 K) of phenylethynyldisilanes (1-5) in MP. The total emission spectra in MP glass at 77 K consist of the normal (LE) and charge-transfer (CT) fluorescence spectra and the normal phosphorescence (Phos). For details see text.

(4P) was measured spectroscopically at 325 nm ($\epsilon = 940 \text{ M}^{-1}$ cm⁻¹). Measurements of reaction quantum yields by vapor-phase chromatography have been given in detail elsewhere.¹⁶

Results

Absorption and Emission Spectra of Phenylethynyldisilanes. Figure 1 shows the absorption and emission spectra of phenylethynyldisilanes (1-5) in MP (methylcyclohexane/isopentane, 3:1 v/v, ca. 2 \times 10⁻⁵ M) at 300 and 77 K. The fluorescence spectrum at 300 K has a peak around 305 ± 5 nm with vibrational structures and also a long tail at longer wavelengths. The emission around 305 nm originates from the (π,π^*) state, considering the vibrational structures; i.e., this emission corresponds to that from the locally excited state (LE). The tail emission at longer wavelengths is ascribed to that from the intramolecular CT state (¹CT).¹⁻⁶ At 300 K, the fluorescence quantum yields for the LE emissions were about $\sim 10^{-3}$ regardless of the substituents of the Si-Si group. The fluorescence intensity of the tail emission was very small (less than 10% of the LE emission) at 300 K. The longer wavelength emission increased with decreasing temperature. The total emission spectrum of phenylethynyldisilanes in MP glass at 77 K consists of three parts: the normal fluorescence (LE) with vibrational structures from (π,π^*) at 293 nm, the broad and structureless intramolecular CT fluorescence with the peaks 370-395 nm, and the phosphorescence with vibrational structures from ${}^{3}(\pi,\pi^{*})$ at around 410 nm. For instance, the emission quantum yields for 1 were determined to be 0.015 (Φ_{LE}), 0.26 (Φ_{CT}) , and 0.24 (Φ_{P}) . The excitation spectra were very close to the absorbtion spectra. The phosphorescence spectra could be

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Figure 2. (a) Picosecond rise and decay of the intramolecular CT emission of 1 in MP at 294 K monitored at 380 nm and (b) its logarithmic plot.



Figure 3. (a) Picosecond buildup and decay profiles of the CT emission of 1 in MP glass at 77 K monitored at 380 nm and (b) its logarithmic plot.

measured independently by using a rotating chopper. Their lifetimes were close to 1 s. These experimental data obtained are summarized in Table I.

Picosecond Experiments. Figure 2 shows (a) the picosecond rise and decay curves of the intramolecular CT emission of 1 in MP at 294 K monitored at 380 nm and (b) its logarithmic plot.



Figure 4. Temperature effect on the picosecond CT decay profiles of 2 in MP glass.



Figure 5. (a) Plot of log $(\tau_{CT}^t)^{-1}$ of 2 in MP glass at 77 K vs. T^{-1} and (b) plot of log $(\tau_{CT}^s)^{-1}$ of 2 in MP glass at 77 K vs. T^{-1} .

The buildup time is very short (less than 10 ps), showing that the intramolecular CT occurs very rapidly. Two decay components (fast and slow) of 1 are observed ($\tau_{CT}^f = 20$ ps and $\tau_{CT}^s = 120$ ps at 294 K, respectively). The intensity of the fast component is about 85% and the slow one 15% just after laser pulse. Similar results were obtained in the cases of 2, 3, and 5, except for 4 as shown in Table I. The CT emission of 4 decayed single exponentially with a time constant of 90 ps.

The picosecond buildup and decay profiles of the CT emission of 1 in MP glass at 77 K are shown in Figure 3. The rise time of the CT emission is less than 10 ps even in a nonpolar rigid matrix (e.g., MP) at 77 K, and two decay components (one fast, τ_{CT}^{f} = 320 ps, and one slow, τ_{CT}^{s} = 5.8 ns) are observed. The intensity of the fast component is about 45% and the slow one 55% just after pulsing. The picosecond buildup and decay profiles of the CT emission of the other phenylethynyldisilanes (2-4) at 77 K were similar to those of 1. These picosecond data are listed in Table I.

Temperature Effect on Picosecond Decay Profiles of the CT Emission. The temperature effect on the decay features for the CT emission of 2 has been examined by means of picosecond spectrocopy. Figure 4 shows the picosecond decay features for the CT fluorescence of 2 at various temperatures. No change in the time constants of fast (300 ps) and slow (1.9 ns) decay components for the CT emission of 2 was observed in the temperature range 77-115 K. Passing through the melting point at around

Absorptiom M ce Maxima (λ_n^{C} scence Lifetime uyldisilanes in 1 λ_{nm}^{max} a 10 ⁴ h 258 259 259 259 265 263 263	x axima (x, x, x	(at 30(Phosp) Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp Phosp P	 K), Molecula horescence Peruntum Yields f Alsopentame M Alsopentame M	$ \begin{array}{c} {}^{r} {\rm Extinction} \\ {\rm als} \ (\lambda_{\rm Ex}^{\rm ax} \ {\rm at} \ ' \\ {\rm or} \ {\rm LE} \ (\Phi_{\rm LE}), \\ {\rm fixtures} \ (3.1 \\ {\rm fixture} \ (3.1 \ {\rm f$	$\begin{array}{c} \text{Coeffic} \\ \textbf{7}(\textbf{K}), 1\\ \textbf{CT}(\textbf{\varphi}, 1/\textbf{V})\\ \textbf{U}(\textbf{V})\\ \textbf{0.61}\\ 0.51\\ 0.58\\ 0.48\\ 0.65\\ 0.65 \end{array}$	cr), and cr), and Φ _R ^{'c} 0.44	mmx at λ/ ss of the d Phospi h d Phospi d Phospi d Phospi a nm a 293 293 293 293 293 293	Φ _{LE} 0.001 Φ _{LE} 0.015 0.015 0.0019 0.005 0.005	mal Fluo ssion (τ_1 e (Φ_P) a e (Φ_P) a ns $\tau_{1,B,ce}$ ns 21 21 22 21 22 22 24 24	rescence	Peaks ((), the F and Decr $\frac{\Phi_{CT}^{b}}{0.26}$ 0.16 0.05 0.05 0.005	$\begin{array}{c} \lambda^{\rm LE} \ {\rm and} \ \lambda^{\rm LE}_{\rm C1} \ {\rm and} \ \lambda^{\rm LE}_{\rm C1} \ {\rm and} \ \lambda^{\rm LE}_{\rm c1} \ {\rm and} \ \lambda^{\rm LE}_{\rm c2} \ {\rm and} \ \lambda^$	at 300 and 7. I Slow (7 ² T) I d Product (Φ ₁ cT, ⁵ d n 1.9 (38%) 1.9 (38%) 1.9 (38%) 5.8 (57%) 1.9 (38%) 5.8 (57%) 5.8 (57%) 5.8 (57%) 5.8 (57%) 5.8 (57%) 5.8 (57%) 5.8 (57%) 5.4 (47%) 5.4	' K, Resj Jifetimes () Quan () Quan 5.9° 2.0° 5.1°	pectively pectively pectively a of the turn Yie turn Yie num num num 410 411 411 414 414 414 414 414 414 414	 λ, CT CT Emi Hds at 3 Hds at 3 φ_p⁶ 0.24 0.34 0.61 0.13 0.54 	ssion, ⁴ 00 K of 1.1 ₆ 1.105 0.93 0.62 0.93
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Measured with a nanosecond single photon	
2%. ^b Errors 10%. ^c Errors 5%. ^d Parentheses denote percent fast (C_1) and slow (C_3) decay components of the CT emissions. ^e	NAES 1100).
^a Errors withii	counter (Horiba



Figure 6. Temperature effect upon fast (C_i) and slow (C_i) components of the picosecond CT decay of **2** in MP.



Figure 7. Fluorescence response function F(t) of the CT emission (slow decay component) of 1 in MP glass at 77 K monitored at 380 nm obtained by the single photon counting method. L(t) is the Lamp function.

115 K¹⁷ for a mixed solvent of MP, both decay rates $[(\tau_{CT}^{f})^{-1}]$ and $(\tau_{CT}^{s})^{-1}]$ for the CT fluorescence increased significantly with increasing temperature as shown in Figure 5, accompanied by a considerable increase in the ratio of the fast component (C_f) to the slow one (C_s) as can be seen in Figure 6.

Nanosecond Experiments. The LE and CT emissions for the slow components in MP glass at 77 K were measured by means of the single photon counting method (Horiba NAES 1100). Figure 7 shows, for example, the fluorescence decays of 1 monitored at 380 nm in MP glass at 77 K. The CT emission for the slow component of 1 decays with a time constant of 5.9 ns, which agrees well with that (5.8 ns) obtained by picosecond spectroscopy. Similarly, the CT lifetimes for the slow components of phenyl-ethynyldisilanes were the same as those obtained by picosecond measurements within experimental errors (10%). However, the fast component of the CT emission could not be measured by use of the single photon counter.

On the other hand, the lifetimes for the LE emissions of phenylethynyldisilanes in MP galss at 77 K monitored at 293 nm (the peak of LE fluorescences) were obtained to be 21 (1), 22 (2), 21 (3), 26 (4), and 24 ns (5). The lifetime of the LE emission from ${}^{1}(\pi,\pi^{*})$ at 77 K is considerably long compared to that from the slow decay component of the CT state.

Photochemical Reactions. It is known that the photochemical reactions of phenylethynyldisilanes give mainly silacyclopropene (P) as shown in eq $1.^2$ However, the photoproduct P is usually unstable at room temperature, except **4P**.² The photoproduct **4P** can be isolated since it is stable at room temperature in air. This may be due to the fact that the silacyclopropene ring is protected by two mesityl groups. Therefore, the disappearance quantum

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yields (Φ_R) of phenylethynyldisilanes at 254 nm at 300 K have been measured by means of chromatography. The values of Φ_R were obtained to be 0.61 (1), 0.51 (2), 0.58 (3), 0.48 (4), and 0.65 (5). The formation quantum yield Φ_{R}' for the silacyclopropene **4P** was obtained spectroscopically to be 0.44 by use of the ϵ value (940 M^{-1} cm⁻¹ at 325 nm) of 4P. These results indicate that the photochemical reaction of phenylethynyldisilanes at room temperature mainly consists of the photocyclization (eq 1). However, the photochemical reaction of phenylethynyldisilanes occurred scarcely in MP glass at 77 K.

Discussion

The experimental results of phenylethynyldisilanes can be accounted for by Scheme I, where S_1 and S_0 represent the excited and ground states of phenylethynyldisilanes, respectively, ¹CT is the intramolecular charge-transfer state, T₁ is the lowest triplet state of local ${}^{3}(\pi,\pi^{*})$, k_{f} , k_{f}' , and k_{p} are the radiative rate constants from S_1 , ¹CT, and T_1 , respectively, k_d and k_d' are the rate constants for the radiationless transitions from S_1 and 1CT , respectively, without intersystem crossing and photochemical reaction, k_{ISC} , $k_{\rm ISC}'$, and $k_{\rm ISC}''$ are the rate constants for intersystem crossing from S₁ to T₁, from ¹CT to T₁, and from T₁ to S₀, respectively, and $k_{\rm R}$ is the rate constant for the photochemical reaction.

Intramolecular Charge-Transfer Process. At first let us consider the intramolecular CT process in the excited state of phenylethynyldisilanes. Upon excitation, the locally excited singlet state (π,π^*) is produced. Picosecond experiments show that the intramolecular CT occurs very rapidly within 10 ps at both 294 and 77 K. In a previous work on phenyldisilanes,⁷ the buildup time of the CT band is observed to be very short, less than 10 ps. The intramolecular CT state is assigned to the $(2p\pi, 3d\pi)$ state produced by intramolecular CT from $2p\pi^*$ (the aromatic ring) to the vacant $3d\pi$ orbital (the Si-Si bond).^{3,4,6} Considering the present results similar to those of aromatic disilanes, the ¹CT state of phenylethynyldisilanes may be ascribed to the $(2p\pi, 3d\pi)$ state. The intramolecular CT process occurs even in nonpolar (MP) glass at 77 K.¹⁸ This finding shows that internal rotation (or twisting) or solvation is not neccessary for the intramolecular CT formation of phenylethynyldisilanes. Therefore, the intramolecular CT mechanism is quite different from that of the twisted intramolecular charge transfer (TICT).¹⁹⁻²² Dual emissions (LE and CT) of phenylethynyldisilanes (See Figure 1) observed in MP glass at 77 K can be understood keeping in mind the molecular structures of phenylethynyldisilanes. There are two molecular structures as shown in Figure 8. An in-plane or in-plane-like structure is more favorable for intramolecular CT interactions between π and $3d\pi$, as can be seen in Figure 8a. There are two vacant $d\pi$ orbitals in a disilane, perpendicular to each other. In a planar phenylethynyldisilane, one d π orbital will be perpendicular to the plane of the ring and thus conjugated with the aromatic π orbitals and the other will not. (It only conjugates with the $C \equiv C$ group.) The effect of twisting the phenyl group (or the disilanyl group) through 90° will be to break the conjugation with the one $d\pi$ orbital, and it would be expected to allow conjugation with the other if the C=C-Si-Si bond were straight. However, the aromatic π system cannot overlap with the other d π orbital by twisting since the bond angle C-Si-Si is estimated to be ca.

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Figure 8. Schematic molecular conformations (a) in-plane structure and (b) out-of-plane structure of phenylethynyldisilanes. For details see text.



110°, considering that the Si atom has tetrahedral sp³ hybrid orbitals. The electronic overlap between aromatic π and $d\pi$ systems is dominant for a planar structure (Figure 8a) but not for an out-of-plane [i.e., twisted conformation (Figure 8b)]. In the out-of-plane molecular structure, the π orbital is able to interact with the σ orbital of the Si-Si bond. Judging from the result of the fluorescence polarization of phenyldisilane (in-plane long-axis polarization),⁶ there is no possibility of the intramolecular CT from $2p\pi^*$ to σ^* or from σ to $2p\pi$. It has been shown that the CT emission of phenyldisilane is observed in a planar structure but not in a twisted structure and that the CT emission originates from the $(2p\pi, 3d\pi)$ CT state.^{3,4,6} The rapid intramolecular CT rate of $k_{\rm CT}$ (>10¹¹ s⁻¹) obtained is due to the electronic overlap between aromatic $2p\pi^*$ and $3d\pi$ in a planar structure. The LE emission at shorter wavelengths may originate from the locally excited singlet state (π,π^*) having an out-of-plane or twisted structure (Figure 8b). This situation for the intramolecular CT process in phenylethynyldisilanes is the same as that in phenyldisilanes.⁴ Thus, we can understand the reason why the dual (LE and CT) emissions of phenylethynyldisilanes are observed as shown in Figure 1.

Decay Processes in the Excited State of Phenylethynyldisilanes. The locally excited singlet state (π,π^*) is produced upon excitation. In the excited species having a planar molecular structure, the intramolecular CT occurs very rapidly and the (π,π^*) state having a twisted structure decays via the radiative $(k_{\rm f})$ and radiationless $(k_{\rm ISC} \text{ and } k_{\rm d})$ processes. At room temperature, internal rotation or twisting in the (π,π^*) state in fluid media results in formation of a planar molecular structure which is favorable to the intramolecular CT, and the fluorescence quantum yield ϕ_{LE} for the LE emission becomes small ($\sim 10^{-3}$). The fluorescence quantum yield ϕ_{CT} for the CT emission at room temperature is very small ($\leq 10^{-4}$). This is due to the fast decay processes containing the photochemical reaction $(k_{\rm R}, \text{ see eq } 1)$ and intersystem crossing $k_{\rm ISC}'$ as discussed later.

In MP glass at 77 K, the (π,π^*) state having a twisted structure has a relatively long lifetime (21-26 ns), and in the (π,π^*) state having a planar structure the intramolecular CT state is produced very rapidly (<10 ps). There is no internal rotation in the excited state (i.e., no interconversion between planar and twisted molecular structures) in MP glass at 77 K. The CT fluorescence quantum yield ϕ_{CT} is obtained to be 0.05-0.26, though the decay rate for the CT state is large as shown in Table I. This observation suggests that phenylethynyldisilanes having planar or planarlike molecular structure exist in the ground state to a large extent.

Decay Processes in the ¹CT State. The decay processes in the ¹CT state in MP glass at 77 K consist of the intersystem crossing $(k_{\rm ISC})$, the radiative transition $(k_{\rm f})$, and the radiationless decay process (k_d) as shown in Scheme I, where photochemical reaction occurs scarcely. The picosecond buildup and decay profiles of the CT emission of 1, for example, in MP glass at 77 K (as shown

⁽¹⁸⁾ The intramolecular CT of phenyldisilane does not occur in MP glass but in polar solvent (EPA) glass at 77 K.^{3,4,7}
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(21) Rettig, W. J. Phys. Chem. 1982, 86, 1790.
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in Figure 3) show that the rise time for CT emission is less than 10 ps, and there are two decay components [one fast, 320 ps (\approx 45%), and one slow, 5.8 ns (\approx 55%)]. The fast intersystem crossing $k_{\rm ISC}$ ' from the ¹CT state to the local ³(π , π^*) state takes place as a main channel for phenylethynyldisilanes in a rigid matrix at 77 K similar to that for phenylethat the ISC process from ¹CT to the local ³(π , π^*) state occurs effectively.²³ The ¹(2p π ,3d π) CT state plays an important role in the ISC process. The fast ISC process may be due to the small energy gap ((0.85–2.87) × 10³ cm⁻¹) between the ¹CT and local ³(π , π^*) states in addition to large LS coupling with 3d character in the ¹CT state, where appreciable ST mixing is probably caused by vibronic SO coupling between the states. That is, the following equation may hold at 77 K:

$$k_{\rm ISC}' > k_{\rm f}' + k_{\rm d}'$$
 (2)

Two decay components of the fast $(\tau_{CT}^{f})^{-1}$ and slow $(\tau_{CT}^{s})^{-1}$ rates for the CT emission may be concerned with the ISC process in the ¹CT state. The difference between $(\tau_{CT}^{f})^{-1}$ and $(\tau_{CT}^{s})^{-1}$ seems to be related to that between fast $(k_{ISC}')_{f}$ and slow $(k_{ISC}')_{s}$ ISC rates caused by molecular structures of the ¹CT state. That is

$$k_{\rm ISC}' = (k_{\rm ISC}')_{\rm f} + (k_{\rm ISC}')_{\rm s}$$
 (3)

There should be planar and planarlike structures in the ¹CT state because the intramolecular CT occurs very rapidly even in MP glass at 77 K as mentioned above. Considering the fact that the fast component C_f (~50%) in MP glass at 77 K increases very much up to ~90% in a MP fluid medium at 294 K, it is assumed that the ISC rate for a planarlike structure is very much faster than that in a planar structure. Here, a planarlike structure means a little twisted planar structure. This fast ISC problem due to internal rotation or twisting in the ¹CT state becomes clear in the temperature effect on the decay profiles of the ¹CT state of **2**.

There is no change in fast and slow rates of 2 in the temperature range 77-115 K (see Figure 5). Passing through the melting point at around 115 K, both decay rates increase with increasing temperature. This observation suggests that the internal rotation or twisting enhances the decay rate (mainly the ISC rate) in the ¹CT state. The fast (C_f) and slow (C_s) components of 2 are obtained to be 62% and 38%, respectively, in the temperature range 77-115 K. The ratio of C_s/C_f decreases very much with increasing tem-

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perature, passing through the melting point at ~115 K as shown in Figure 6. Similar results were also obtained in the temperature effect on the CT emission of 3. These results strongly support the assumption that the ISC rate for a planarlike structure in the ¹CT state is very much faster than that for a planar structure. It can be said that the ratio of C_s/C_f in MP glass at 77 K reflects that of a planar structure to a planarlike structure in the ground state. The fast decay rate $(\tau_{CT}^f)^{-1}$ of the ¹CT state mainly consists of the fast ISC rate $(k_{ISC})_f$, which markedly depends upon the internal rotation (or twisting).

The phosphorescence quantum yields ϕ_P for the local ${}^3(\pi,\pi^*)$ state are relatively high (0.13–0.61). The lifetimes of the ${}^3(\pi,\pi^*)$ state of phenylethynyldisilanes are close to 1 s. The ISC process $(k_{\rm ISC}'')$ from ${}^3(\pi,\pi^*)$ to S₀ is, therefore, perturbed by the disilanyl group, judging from the values of phosphorescence lifetimes (several seconds) of common aromatic compounds.^{11,24}

At room temperature, the photochemical reaction occurs very effectively in addition to the fast ISC process $(k_{\rm ISC})$ from ¹CT to ³ (π,π^*) . The decay rate $(\tau_{\rm CT})^{-1}$ of the ¹CT state at room temperature can be expressed as

$$(\tau_{\rm CT})^{-1} = k_{\rm ISC}' + k_{\rm f}' + k_{\rm d}' + k_{\rm R} \approx (k_{\rm ISC}')_{\rm f} + k_{\rm R} \qquad (4)$$

In previous work,^{5,7} it has been shown that the photochemical reaction of phenyldisilane originates from the intramolecular CT state. The ¹CT state is the reactive state in aromatic disilanes at higher temperatures. The large reaction quantum yields ϕ_R (0.48–0.65) of phenylethynyldisilanes at room temperature may result from the efficient formation of the ¹CT state. Judging from the values of ϕ_R and the lifetimes of the CT emissions at room temperature in Table I, the value of the rate constant k_R for the photochemical reaction of phenylethynyldisilanes is roughly equal to $(k_{\rm ISC}')_{\rm f}$, the fast intersystem crossing. The value of k_R is, therefore, estimated to be (0.5–3) × 10¹⁰ s⁻¹. On the basis of the data of the disappearance quantum yield ϕ_R (0.48) and the quantum yield ϕ_R' (0.44) for the product formation of 4, the photochemical reaction of 4 mainly consists of the photocyclization as shown in eq 1.

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