The $2p\pi^*-3d\pi$ Interaction in Aromatic Silanes

Fluorescence from the $(2p\pi, 3d\pi)$ Intramolecular Charge-transfer State

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Received 29th March, 1983

The $2p\pi^*-3d\pi$ interaction in the excited state of aromatic silanes has been studied by means of absorption and emission spectroscopy. Broad and structureless fluorescence spectra of phenyldisilanes and naphthyldisilanes with large Stokes shifts have been observed and they have been attributed to the emissions from the intramolecular charge-transfer (c.t.) states with large dipole moments. Evidence that the c.t. emission originates from the ${}^{1}(2p\pi, 3d\pi)$ state produced by the $2p\pi^*$ (aromatic ring) $\rightarrow 3d\pi$ (Si—Si bond) intramolecular charge transfer is given by the effect of steric twisting on the emission. It is shown that the fast formation (≤ 1 ns) of the c.t. state from the locally excited state ${}^{1}(\pi, \pi^*) {}^{1}B_2$ (or ${}^{1}L_b$) of phenyldisilanes takes place, followed by rapid decay (≤ 1 ns) of the intersystem crossing ${}^{1}(2p\pi, 3d\pi) \rightarrow {}^{3}(\pi, \pi^*)$. However, no c.t. emission has been observed for aromatic monosilanes and polycyclic aromatic disilanes (aromatic rings ≥ 3) even in fluid polar solvents. The $2p\pi^* \rightarrow 3d\pi$ intramolecular c.t. mechanism is discussed in comparison with that of the twisted intramolecular charge-transfer (t.i.c.t.) state.

Over the past thirty years silicon chemistry has been extensively studied, and a number of papers and reviews have been published.¹⁻⁸ The photochemical reactions of silicon compounds have been widely investigated.9-11 However, relatively little attention has been paid to mechanistic work until recently.^{12, 13} The electronic interaction between $2p\pi$ and 3d orbitals is currently an interesting aspect of chemistry. It is known that the π -d interaction in aromatic silanes is shown in u.v.,^{7, 14-18} n.m.r.¹⁹ and e.s.r.²⁰ spectra and dipole-moment measurements.^{21, 22} However, the interaction in the ground state is not so large. Athough the u.v. spectra of phenylsilanes have been interpreted in terms of excited-state interactions of the ' π^*-d ' type, no clear evidence of a $2p\pi^*-3d\pi$ interaction of aromatic silanes has yet been found.¹⁵ In previous papers^{12, 13} we found that the intramolecular charge-transfer (c.t.) fluorescence of aromatic disilanes has a broad and structureless band with a large Stokes shift. The c.t. state is closely related to the photochemical reactions of aromatic disilanes.^{13, 23, 24} At that time, no assignment of the c.t. state $[1(2p\pi, 3d\pi) \text{ or } 1(2p\pi, \sigma^*)]$ was made.¹³ We now demonstrate that the c.t. fluorescence originates from the $(2p\pi, 3d\pi)$ state produced by $2p\pi^* \rightarrow 3d\pi$ intramolecular charge transfer. Evidence for the $2p\pi^*-3d\pi$ interaction in aromatic disilanes is shown in the present work. The mechanism of the $(2p\pi, 3d\pi)$ c.t. state formation leading to the longer-wavelength emission is also discussed in comparison with that of the twisted intramolecular charge-transfer (t.i.c.t.) state.

EXPERIMENTAL

MATERIALS

The samples of pentamethylphenyldisilane (1),²⁵ tris(trimethylsilyl)mesitysilane (5),²⁶ tris(trimethylsilyl)phenysilane (4),²⁷ 1-naphthylpentamethyldisilane (7),²⁴ 2-naphthylpentamethyldisilane (8),²⁴ 1-naphthyltrimethylsilane (9)²⁸ and 2-naphthyltrimethylsilane (10)²⁹ were synthesised by the usual methods. Other samples were synthesised as follows (the solvents being purified by the usual methods³⁰).

2,5-Dimethylphenylpentamethyldisilane (2): In a 500 cm³ three-necked flask fitted with a stirrer, a dropping funnel and a reflux condenser was placed 2,5-dimethylphenylmagnesium chloride prepared from 2.1 g (0.086 mol) of magnesium and 12 g (0.086 mol) of 2,5-dimethylchlorobenzene in 150 cm³ of THF. To this was added 10 g (0.06 mol) of chloropentamethyldisilane dissolved in 20 cm³ of THF. The mixture was refluxed for 2 h and then hydrolysed with dilute hydrochloric acid. The organic layer was separated, washed with water and dried over potassium carbonate. Distillation under reduced pressure gave 6.8 g (49% yield) of 2,5-dimethlyphenylpentamethyldisilane, b.p. 75 °C (2 mm); ¹H n.m.r. δ (ppm): 0.06 (9H, s, Me₃Si), 0.36 (6H, s, Me₂Si), 2.30 (3H, s, o-CH₃), 2.35 (3H, s, m-CH₃), 7.03 (2H, m, ring protons), 7.17 (1H, s, ring proton). Calculated analyses for C₁₃H₂₄Si₂: C, 66.02; H, 10.23%. Found: C, 65.86; H, 10.48%.

Mesitylpentamethyldisilane (3): To a mesityl-lithium reagent prepared from 10 g (0.050 mol) of mesitylbromide and 1.5 g of lithium metal in 100 cm³ of ether was added 4 g (0.024 mol) of chloropentamethyldisilane at room temperature. The mixture was refluxed for 5 h and then hydrolysed with water. The organic layer was separated, washed with water and dried over potassium carbonate. Distillation under reduced pressure gave 4.2 g of a light-yellow liquid boiling over a range of 60–75 °C (2 mm). Pure mesitylpentamethyldisilane was isolated by preparative vapour-phase chromatography. ¹H n.m.r. δ (ppm): 0.06 (9H, s, Me₃Si), 0.45 (6H, s, Me₂Si), 2.22 (6H, s, o-CH₃), 2.33 (3H, s, p-CH₃), 6.67 (2H, s, ring protons). Calculated analysis for C₁₄H₂₆Si₂: C, 67.11; H, 10.46%. Found: C, 67.03; H, 10.21%.

9-(Pentamethyldisilanyl)phenanthrene (11): To a solution of 9-lithiophenanthrene prepared from 15 g (0.06 mol) of 9-bromophenanthrene and 36 cm³ (0.06 mol) of butyl-lithium hexane solution in 100 cm³ of a 1:1 mixture of ether and THF at -60 °C was added 9.7 g (0.06 mol) of chloropentamethyldisilane in 15 cm³ of THF. The mixture was stirred for 1 h at room temperature and then hydrolysed with water. The organic layer was separated, washed with water and dried over potassium carbonate. The solvent was evaporated and the residue was distilled under reduced pressure using a short column to give 7.9 g (43% yield) of a colourless liquid, b.p. 165–167 °C (1 mm); ¹H n.m.r. δ (ppm): 0.10 (9H, s, Me₃Si), 0.56 (6H, s, Me₂Si), 7.4–8.1 and 8.5–8.8 (9H, m, ring protons). Calculated analysis for C₁₉H₂₄Si₂; C, 73.95; H, 7.84%. Found: C, 73.77; H, 7.71%.

9-(Pentamethyldisilanyl)anthracene (12): In a 300 cm³ flask was placed 13.0 g (0.05 mol) of 9-bromoanthracene dissolved in a mixed solvent consisting of 80 cm³ of ether and 100 cm³ of THF. To this was added 31 cm³ (0.05 mol) of butyl-lithium hexane solution over a period of 15 min at -60 to -40 °C. The mixture was stirred for 1 h at -20-0 °C. To this was added 8.3 g (0.05 mol) of chloropentamethyldisilane in 10 cm³ of THF at the same temperature. The mixture was then warmed up to room temperature, stirred for 2 h and hydrolysed with water. The organic layer was washed with water and dried over potassium carbonate. The solvent was evaporated and the residue of the flask was distilled under reduced pressure using a short column to give 7.5 g (49% yield) of pale yellow crystals, b.p. 165-168 °C (1 mm); m.p. 87 °C (after recrystallisation from ethanol). ¹H n.m.r. δ (ppm in C₆D₆): 0.16 (9 H, s, Me₃Si), 0.75 (6H, s, Me₂Si), 7.3-7.4, 7.8-7.9 and 8.2-8.6 (9H, m, ring protons). Calculated analysis for C₁₉H₂₄Si₂: C, 73.95; H, 7.84%. Found: C, 73.81; H, 7.59%.

1-(Pentamethyldisilanyl)pyrene (13): In a 500 cm³ three-necked flask was placed 11.3 g (0.040 mol) of 4-bromopyrene dissolved in a 1:1 mixture of ether and THF. To this was added 28 cm³ (0.042 mol) of butyl-lithium hexane solution over a period of 20 min at -60 to -50 °C. The mixture was stirred for 1 h at -50 to -30 °C, and then warmed up to room temperature. Chloropentamethyldisilane (7.0 g, 0.042 mol) was added slowly to the solution of lithiopyrene, using ice to cool to solution. The mixture was stirred for 4 h at room temperature and

hydrolysed with water. The organic layer was washed with water and dried over potassium carbonate. The solvent was evaporated and the resulting crystals (19 g, 90% yield) was chromatographed to give light-yellow crystals of l-(pentamethyldisilanyl)pyrene, m.p. 102–103 °C (recrystallization from ethanol); ¹H n.m.r. δ (ppm): 0.12 (9H, s, Me₃Si), 0.65 (6H, s, Me₂Si), 7.8–8.3 (9H, m, ring protons). Calculated analysis for C₂₁H₂₄Si₂: C, 75.83; H, 7.27%. Found: C, 75.69; H, 7.08%.

The compounds used are as follows:



APPARATUS AND PROCEDURES

All samples were thoroughly degassed by freeze-pump-thaw cycles on a high-vacuum line. The absorption and emission spectra were recorded with Hitachi 200 and 139 spectrophotometers and a Hitachi MPF 2A fluorimeter, respectively. Spectral corrections for emissions were made. The fluorescence quantum yields were measured by comparison with a quinine bisulphate 0.05 mol dm⁻³ H₂SO₄ solution ($\Phi_F = 0.54$).^{31, 32} The fluorescence and phosphorescence quantum yields at 77 K were determined from the fluorescence quantum yield of toluene ($\Phi_F = 0.29$)³³ in MP glass at 77 K. The fluorescence response functions were recorded using a Hitachi nanosecond time-resolved fluorimeter (pulse width 11 ns) and the convolution method was applied.³⁴ The phosphorescence lifetimes were measured using a Hitachi MPF 2A fluorimeter or a transient memory (Kawasaki MR-50E) with a photomultiplier (1P28). Low-temperature experiments were carried out using a cryostat (Oxford DN 704).

RESULTS AND DISCUSSION

ABSORPTION AND EMISSION SPECTRA OF AROMATIC SILANES

Some examples of the solvent shifts of the absorption and fluorescence spectra for phenyldisilane (1: ca. 10⁻⁴ mol dm⁻³) and naphthyldisilanes (7:4 × 10⁻⁵ mol dm⁻³; 8: 8 × 10⁻⁵ mol dm⁻³) at 300 K are shown in fig. 1 and 2, respectively. The first



Fig. 1. Absorption and fluorescence spectra of 1 in various solvents at 300 K. CH: cyclohexane; THF: tetrahydrofuran; EtOH: ethanol; PN: propionitrile; AN: acetonitrile.

absorption band of 1 with vibrational structures at 38.5×10^{-3} cm⁻¹ corresponds to the ${}^{1}B_{2u} \leftarrow {}^{1}A_{1g}$ (${}^{1}L_b \leftarrow {}^{1}A$) transition at 39.3×10^{3} cm⁻¹³⁵ in benzene³⁶ and the second band (43.3×10^{3} cm⁻¹) may correspond to the ${}^{1}B_{1u} \leftarrow {}^{1}A_{1g}$ (${}^{1}L_a \leftarrow {}^{1}A$) transition (49.0×10^{3} cm⁻¹)³⁵ in benzene. The solvent shifts for the former band were scarcely observed and only slightly for the latter band. Dual fluorescences for 1 were observed: one is the normal fluorescence corresponding to the ${}^{1}B_{2u} \rightarrow {}^{1}A_{1g}$ radiative transition in benzene and the other the intramolecular c.t. fluorescence having a broad and structureless band at longer wavelengths. Slight solvent shifts for the former emission were observed, whereas the peak of the longer wavelength emission was shifted to the red depending upon solvent polarity.

Similar results were obtained for 7 and 8, as shown in fig. 2. The absorption spectra of 7 and 8 in non-polar solvents are similar to that of naphthalene. The first $[31.8_5 \times 10^3 \text{ cm}^{-1}$ (7); $31.7 \times 10^3 \text{ cm}^{-1}$ (8)] and second $[34.8 \times 10^3 \text{ cm}^{-1}$ (7); $36.8 \times 10^3 \text{ cm}^{-1}$ (8)] absorption bands correspond to ${}^{1}L_{b} \leftarrow {}^{1}A$ ($33.2 \times 10^3 \text{ cm}^{-1}$)³⁵ and ${}^{1}L_{a} \leftarrow {}^{1}A$ ($36.4 \times 10^3 \text{ cm}^{-1}$)³⁵ transitions in naphthalene,³⁶ respectively. Solvent shifts were also observed. There was very little solvent shift on the normal emission bands (${}^{1}L_{b} \rightarrow {}^{1}A$) at *ca*. $30 \times 10^3 \text{ cm}^{-1}$, but in constrast the broad and structureless emission



Fig. 2. Absorption and fluorescence spectra of 7(a) and 8(b) in various solvents at 300 K. DCE: 1,2-dichloroethane.

band was red shifted in polar solvents. The solvent shifts of the longer-wavelength emission of 1, 7 and 8 indicate that their emitting states are very polar. The broad and structureless emission is not due to an excimer emission judging from the concentration effect on the spectral change. The excitation spectra at both fluorescence band maxima were comparable with those of the absorption bands at wavelengths > 260 nm. The broad and structureless spectra at longer wavelengths are therefore attributed to the emissions from intramolecular charge-transfer (c.t.) states of the compounds. The fact that there is a tendency for the broad and structureless fluorescence of the α -isomer (7) to be more prominent than that of the β -isomer (8) supports this assignment. It is known that in general the intramolecular c.t. character in the excited state of α -substituted naphthalenes is predominant compared with that of β -substituted naphthalenes.³⁷⁻⁴⁰ The anomalous Stokes shifts in fig. 1 and 2 can be ascribed to the change in solute and solvent interaction during the lifetime of the excited state of the aromatic solute molecule.

Similar dual emissions were observed for 2 and 4, as described later, but not for monosilyl derivatives (6, 9 and 10) and polycyclic aromatic compounds (11, 12 and 13: aromatic rings \ge 3) even in polar solvents. The lack of c.t. emission from the monosilyl compounds suggests that the Si—Si bond might be the electron acceptor. For 3 and 5, dual emission were observed in both polar and non-polar solvents at room temperature, but not in MP and EPA rigid matrices at 77 K, as discussed later. The experimental data for the absorption and emission spectra of aromatic silanes in cyclohexane at 300 K are listed in table 1.

sample	$\lambda_{ab}^{m b}$ /nm	ϵ /dm ³ mol ⁻¹ cm ⁻¹	λ ^m /nm	$\Phi_{ m fm}$	$ au_{ m fm}/ m ns$
1	231	$1.1_2 \times 10^4$	285°	$1_{.8} \times 10^{-3}$	< 1
2	234	$1.0_{9} \times 10^{4}$	298 ^c		< 1
3	243	$1.3_{2} \times 10^{4}$	$285{3}^{c}$		< 1
4	241	$1.3_{1} \times 10^{4}$	285.3^{c}		< 1
5	247	$1.4_{1} \times 10^{4}$	285. ³ c	$1_{} \times 10^{-3}$	< 1
6	260^{d}	$3.0^{-} \times 10^{2}$			
7	287	$9.9_{4} \times 10^{3}$	328.	0.05 _e	8.0
8	272	$6.6_{1} \times 10^{3}$	334	0.15	49.6
9	282.5	$7.3^{1} \times 10^{3}$	329	0.25	68. [°]
10	279 [°]	5.1×10^{3}	330.5	0.24	73.
11	301.5	$1.6_{2} \times 10^{4}$	367.	0.095	52.
12	373 [°]	$8.4^{\circ}_{9} \times 10^{3}$	434.	0.72	12.
13	350. ₅	$5.1_{1} \times 10^{4}$	388.3	0.483	343

Table 1. Absorption (λ_{ab}^{a}) and fluorescence band (λ_{fm}^{m}) maxima, fluorescence quantum yields (Φ_{fm}) and lifetimes (τ_{fm}) of aromatic silanes in cyclohexane at 300 K^{*a*}

^{*a*} Data in MP (methylcyclohexane: isopentane = 3:1) were the same as those in cyclohexane. ^{*b*} For details, see text. ^{*c*} The c.t. fluorescences at 340 nm were observed appreciably for 1 and slightly for 2–5. ^{*d*} Corresponding to the ${}^{1}B_{2}$ (${}^{1}L_{b}$) band.

ESTIMATION OF THE DIPOLE MOMENT OF THE INTRAMOLECULAR C.T. STATE

In addition to the solvents shown in fig. 1 and 2, several other solvents were used when recording the fluorescence spectra. These data are listed in table 2. Values of $\Delta \mu$ (= $\mu_{ct} - \mu_g$), where μ_{ct} and μ_g denote the dipole moments of the excited c.t. state and the ground state, respectively, can be estimated from the Lippert-Mataga equation:^{41, 42}

$$\Delta \bar{v}_{et} \approx \text{constant} + \frac{2F(D, n) (\Delta \mu)^2}{hca^3}$$
(1)

where

$$\Delta \bar{v}_{et} = \bar{v}_{ab}^{m} - \bar{v}_{ct}^{m}$$

$$F(D, n) = \left(\frac{D-1}{2D+1} - \frac{n^2 - 1}{2n^2 + 1}\right).$$

 \bar{v}_{ab}^{m} and \bar{v}_{ct}^{m} are the wavenumbers of the peaks of the absorption band and of the corresponding c.t. emission band, respectively, D and n are the dielectric constant and refractive index of the solvent, respectively, and a is the Onsager radius. The observed values of \bar{v}_{ab}^{m} , \bar{v}_{ct}^{m} and the Stokes shift $\Delta \bar{v}_{ct}$ are listed in table 2, together with the values of F(D, n).

A plot of $\Delta \bar{v}_{ct}$ as a function of F(D, n) gives a straight line, as shown in fig. 3. Eqn (1) is approximately satisfied in the present work. The following experimental equations in units of cm⁻¹ are obtained from fig. 3:

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1:
$$\Delta \bar{v}_{ct} = 9087 + 7747 F(D, n)$$
 (2)
(r = 0.768)

:
$$\Delta \bar{v}_{et} = 3419 + 20137 F(D, n)$$
 (3)
(r = 0.935)

8:
$$\Delta \bar{v}_{ct} = 4355 + 12138F(D, n)$$
 (4)
(r = 0.942)

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Table 2. Absorption ($\bar{\nu}_{ab}^m$), normal fluorescence ($\bar{\nu}_{im}^m$) and c.t. fluorescence ($\bar{\nu}_{ct}^m$) maxima and Stokes shifts ($\Delta \bar{\nu}_{ct}$) of 1, 7 and 8 in various solvents at 300 K^a

			1	v			L	20			œ	5	
solvent ^b	$F(D, n)^a$	V ^m bab	V ^m fm	₽ ^m ct	$\Delta \bar{\nu}_{ct}$	V ^m ab	$ ilde{p}^{m}_{\mathrm{fm}}$	V ^m ct	$\Delta \bar{\nu}_{\rm et}$	V ^m ab	₽ ^m fm	V ^m ct	$\Delta ar{ u}_{ m ct}$
CH	0	38.5	~ 34	29.4	9.1	31.7	30.4			31.6 ₅	29.9,		
ether	0.167	38.5	~ 34	28.0	10.5	31.8_{5}	30.4	25.0	6.8_{s}		r Î	ļ	ļ
THF	0.210	38.5	~ 34	28.4	10.1	31.85	29.6,	24.8	$6.9_{\rm k}$	31.6_{5}	29.5	25.0	6.6_5
DCE	0.221	38.5	~ 34	27.0	11.5	31.75	30.4	23.3,	8.4 。	31.65	29.4,	24.5 ₆	7.0°
BN	0.275	38.5	~ 34	27.9	10.6	31.8,	29.6,	22.7_{3}^{2}	9.1,	31.6,	29.5°	24.1	7.5
EtOH	0.289	38.5	~ 34	28.0	10.5	31.75	29.4,	22.4	9.3	31.65	29.5	23.94	7.7,
PN	0.290	38.5	~ 34	27.6	10.9	31.8_{5}	29.6_{7}	22.4 ₈	9.3,	31.6_{5}	29.6_{7}	23.6,	8.0_{4}
AN	0.306	38.5	~ 34	26.2	12.3	31.7_{5}	29.8,	22.4	9.2	31.65	29.6,	23.5	8.15
glycerol	0.263	ł		I	ł	31.7_{5}	29.4	23.0 ₃	8.7,	31.65	29.4	25.0	6.65
DMSO	0.264	-		ţ		31.7_5	28.0 ₉	23.5	8.7_5	,		}	°
^{<i>a</i>} For deta ethanol; PN	ails, see text. : n-propionit	^b CH: C trile; AN:	Cyclohexan	e; ether: c e; DMSO:	liethyl eth dimethyls	er; THF: ulphoxide	tetrahydro ° In unit	furan; DC ts of 10 ³ cn	E: 1,2-dic n ⁻¹ .	chloroethar	le; BN: n-	butylonitr	ile; EtOH:

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Fig. 3. Plots of $\Delta \bar{v}_{et}$ as a function of F(D, n). (a) 1, (b) 7 and (c) 8. For details, see text.

where r is a correlation coefficient. From eqn (2)-(4), the $\Delta\mu$ values for 1, 7 and 8 can be evaluated to be ca. 4.4, 11.3 and 8.8 D, respectively, on the assumption that the Onsager radii for phenyldisilane (1) and naphthyldisilanes (7 and 8) are 3 and 4 Å, respectively. The dipole moments in the ground state of aromatic silanes seem to be small (ca. 0.4₄ D) because of +*I* and -*M* effects.^{21, 22} Thus, the values of μ_{ct} for 1, 7 and 8 are ca. 4.8, 11.7 and 9.2 D, respectively, on the assumption that $\mu_g \approx 0.4$ D. We therefore conclude that the fluorescent state at the longer-wavelength emission has a strongly polar structure with complete charge separation.

ASSIGNMENT OF THE INTERMOLECULAR C.T. STATE

The mechanism for the intramolecular c.t. emission at longer wavelengths is described in this section. There are two possible explanations for the c.t. emission mechanism. One is the $2p\pi^* \rightarrow \sigma^*$ c.t. mechanism: the longer-wavelength emission may be due to intramolecular charge transfer from the aromatic π electron system into a vacant σ^* orbital of the Si—Si bond. On consideration of the likely molecular conformations arising from steric interactions, this $2p\pi^* \rightarrow \sigma^*$ c.t. interpretation may explain adequately the differences between 1- and 2-naphthyldisilanes and the lack of c.t. fluorescence in the monosilane derivatives. If this is so, the intramolecular c.t. state is the ${}^1(2p\pi, \sigma^*)$ state produced by the $2p\pi^* \rightarrow \sigma^*$ c.t. The other is the $2p\pi^* \rightarrow 3d\pi$ c.t. mechanism: the broad and structureless emission may originate from an intramolecular c.t. state resulting from charge transfer from the $2p\pi^*$ orbital of the aromatic ring to the vacant $3d\pi$ orbital of the Si—Si bond.

The assignment of the intramolecular c.t. state has been made experimentally. Samples 1–5 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.





Fig. 4. (a) Absorption and fluorescence spectra of 1, 2 and 3 in acetonitrile at 300 K and (b) absorption (in EPA at 300 K) and emission (in EPA glass at 77 K) spectra of 1, 2 and 3. The emission spectra of 1 and 2 in EPA glass at 77 K consist of the normal (f.m.) and charge-transfer (c.t.) fluorescence spectra and the normal phosphorescence (phos). For details, see text.

The absorption and emission spectra of the phenyldisilanes 1, 2 and 3 (ca. 10^{-4} mol dm⁻³) in acetonitrile (AN) and EPA (ether + isopentane + alcohol, 5:5:2) are shown in fig. 4. In AN at 300 K, dual fluorescence was observed for 1 and 2: one is the normal fluorescence corresponding to the ${}^{1}B_{2u} \rightarrow {}^{1}A_{1g}$ radiative transition in benzene and the other the intramolecular c.t. emission having a broad and structureless band with a large Stokes shift $(12.3 \times 10^3 \text{ cm}^{-1} \text{ for } 1 \text{ and}$ 9.7×10^3 cm⁻¹ for 2). The fluorescence intensities of the c.t. emissions relative to those of the corresponding normal emissions are in the order $1 > 2 \ge 3$, and in contrast the intensities for the normal emissions are 1 < 2 < 3, as can be seen in fig. 4(a). Similarly, dual fluorescence was observed for 1 and 2 even in an EPA rigid matrix at 77 K, but not for 3 [fig. 4(b)]. From the total emission spectra, the quantum yields for the normal (Φ_{fm}) and c.t. (Φ_{ct}) emissions and the phosphorescence (Φ_n) in an EPA rigid matrix at 77 K following 263 nm excitation were determined to be 0.09, 0.09, and 0.35 for 1; 0.17, 0.03 and 0.42 for 2; and 0.29, 0 and 0.62, for 3, respectively. The fluorescence quantum yields for 1 and 2 were very small (ca. 10^{-3}) at room temperature and the lifetimes of dual emissions were very short (< 1 ns). The values of $\Phi_{\rm fm}$ and $\Phi_{\rm ct}$ increased markedly with decreasing temperature. This may be because the photochemical reaction occurs to a considerable extent at room temperature; e.g. the reaction quantum yield for 1 in MP at 300 K is very large (0.86).²³

The experimental data can be explained by the following mechanism. If the intramolecular c.t. fluorescence of phenyldisilanes originated from the $(2p\pi, \sigma^*)$ 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 $2p\pi^*$ orbital to a vacant σ^* orbital of the Si—Si bond would be much more efficient than for 1,

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2 and 4 because of the out-of-plane molecular structure (the π orbital being able to overlap with the σ^* orbital) arising from steric interactions, as shown in fig. 5(b). However, the experimental results argue against this mechanism. An in-plane or in-plane-like structure is more favourable for intramolecular c.t. interactions between π and $3d\pi$ systems, as can be seen in fig. 5(a). There are two vacant $d\pi$ orbitals in



Fig. 5. Schematic molecular conformations: (a) in-plane structure and (b) out-of-plane structure of phenyldisilanes. For details, see text.



Fig. 6. Schematic energy-state diagram for the intramolecular charge-transfer $2p\pi^* \rightarrow 3d\pi (k_{ct})$ of aromatic disilanes. R = phenyl or naphthyl.

a disilane, perpendicular to each other. In a planar phenyldisilane, one $d\pi$ orbital will be perpendicular to the plane of the ring and thus conjugated with the aromatic π orbitals, the other not. The effect of twisting the phenyl group (or the disilarly 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_{Ar} —Si—Si bond were straight. However, the π system cannot overlap with the other $d\pi$ orbital by twisting since the bond angle of C_{Ar} -Si-Si is estimated to be ca. 110°, considering that the Si atom has tetrahedral sp³-hybrid orbitals. That is, the electronic overlap between π and $d\pi$ systems is dominant for a planar structure [fig. 5(a)], but not for an out-of-plane (*i.e.* twisted) conformation [fig. 5(b)]. 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, 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. emissions of naphthyldisilanes (7 and 8) may be ascribed to those from the ${}^{1}(2p\pi, 3d\pi)$ state by considering their features, which are similar to those of phenylsilanes.

The $2p\pi^*-3d\pi$ interaction resulting in formation of the ${}^{1}(2p\pi, 3d\pi)$ c.t. state is caused by (1) the increase in electron-donating power of the aromatic ring upon excitation, because of the promotion of an electron from the $2p\pi$ to $2p\pi^*$; (2) the disilanyl group (or polysilanyl group) provides a vacant $3d\pi$ orbital, which may be produced by the linear combination of 3d atomic orbitals, with a relatively low energy level compared with that of a single 3d atomic orbital [*i.e.* the electron-withdrawing power of the disilanyl (or polysilanyl) group increases]; and (3) the ${}^{1}(2p\pi, 3d\pi)$ energy level is lowered by polarisation energy because of the interaction between the c.t. state species and polar solvent molecules. Thus, the c.t. emission from the ${}^{1}(2p\pi, 3d\pi)$ state can be accounted for by the schematic energy diagram shown in fig. 6.

DYNAMIC BEHAVIOUR OF THE $(2p\pi, 3d\pi)$ C.T. STATE

The lifetimes of the excited phenyldisilanes at room temperature were very short (< 1 ns) and nanosecond time-resolved experiments with phenyldisilanes (1, 2 and 3) in EPA rigid matrices at 77 K were carried out. The fluorescence response function $I_{\rm fm}(t)$ of the normal emission at 290 nm for 1 and 2 [fig. 7(b) and (c), respectively] in an EPA rigid matrix at 77 K consisted of fast and slow decay components $I_{\rm fm}^{\rm f}(t)$ and $I_{fm}^{s}(t)$, respectively. The slow decay function $I_{fm}^{s}(t)$ at the delay time t > 40 ns shows a single-exponential decay $(20_{.9} \text{ ns for } 1; 20_{.6} \text{ ns for } 2)$, and the shape of the $I_{\rm fm}^{\rm s}(t)$ function at $t \leq 40$ ns can be determined by the convolution method.³⁴ The fast decay function $I_{fm}^{f}(t)$ is derived by subtraction of $I_{fm}^{s}(t)$ from $I_{fm}(t)$ under ideal conditions. The $I_{\rm fm}^{\rm f}(t)$ function is very close to the lamp function $I_1(t)$ of the D₂ pulser with a δ function [fig. 7(a)], showing the existence of the short-lived component (≤ 1 ns for 1 and 2) in addition to the long-lived component (ca. 21 ns) in the (π, π^*) state. This fact can be understood by considering the molecular structure in the excited state of disilanes. That is, both in-plane-like and out-of-plane conformations exist in the locally excited state $(\pi, \pi^*) B_2$ of 1 (or 2) in EPA glass at 77 K. There is no conformational change in either the ground or the excited states under such conditions. The intramolecular $2p\pi^* \rightarrow 3d\pi$ c.t. occurs effectively for the former conformation resulting in fast decay, but not for the latter, which has a relatively long lifetime (ca. 21 ns). This finding shows the rapid formation of the c.t. state via the (π, π^*) B_2 state of 1 or 2, which has a molecular conformation favourable for intramolecular c.t. even in EPA glass at 77 K. The fluorescence quantum yields Φ^f_{fm} and Φ^s_{fm} for the shortand long-lived components can be determined to be 0.06, and 0.02, for 1 and 0.10 and 0.07 for 2, respectively, using the following equations:

$$\Phi_{\rm fm}^{\rm f} = \frac{\int_0^\infty I_{\rm fm}^{\rm f}(t) \,\mathrm{d}t}{\int_0^\infty I_{\rm fm}(t) \,\mathrm{d}t} \Phi_{\rm fm} \tag{5}$$

$$\Phi_{\rm fm}^{\rm s} = \frac{\int_0^\infty I_{\rm fm}^{\rm s}(t) \,\mathrm{d}t}{\int_0^\infty I_{\rm fm}(t) \,\mathrm{d}t} \Phi_{\rm fm} \tag{6}$$

and

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where Φ_{fm} denotes the fluorescence quantum yield for the shorter-wavelength emission in EPA glass at 77 K, as listed in table 3. Note that (1) the short-lived component in the ${}^{1}(\pi, \pi^{*})$ state is greater than the long-lived one, showing efficient intramolecular $2p\pi^{*} \rightarrow 3d\pi$ c.t. even in an EPA rigid matrix at 77 K, and (2) the value of the $\Phi_{fm}^{f}/\Phi_{fm}^{s}$ ratio (2.1) for 1 is greater than that (1.4) for 2, as can be expected from their molecular structures. As for 3, which has an out-of-plane molecular



Fig. 7. Fluorescence response functions $I_{\rm fm}(t)$ of 1(b), 2(c) and 3(d) monitored at 290 nm in EPA glass at 77 K and the lamp function $I_1(t)(a)$. $I_{\rm fm}^t(t)$ and $I_{\rm fm}^s(t)$ are the fast- and slow-decay components of the normal fluorescence, respectively. For details, see text.

conformation, a single-exponential decay at 290 nm was observed in EPA glass at 77 K ($\tau_{fm}^s = 31_{.4}$ ns), as shown in fig. 7(*d*), indicating no intramolecular charge transfer. The difference in the decay features for 1, 2 and 3 is ascribed to their molecular conformations. The decay data are fairly consistent with the emission spectra in fig. 5(*b*).

The fluorescence response function $I_{\rm et}(t)$ at the longer wavelengths $(\lambda_{\rm et}^{\rm m} \approx 350 \text{ nm})$ corresponding to the c.t. emission was very close to the $I_{\rm fm}^{\rm f}(t)$ function, indicating the existence of a fast intersystem crossing ¹c.t. $[{}^{1}(2p\pi, 3d\pi)] \rightarrow {}^{3}(\pi, \pi^{*})$. This fast intersystem crossing process $(k_{\rm isc}$ in fig. 8) may be due to the small energy gap $(1.1_7 \times 10^3 \text{ cm}^{-1})$ between them in addition to large l.s. coupling with 3d character in the c.t. state where appreciable s.t. mixing is probably caused by vibronic s.o. coupling between the states. The ${}^{3}(2p\pi, 3d\pi)$ state may exist energetically just below the ${}^{1}(2p\pi, 3d\pi)$ state. However, the intersystem crossing process between ${}^{1}(2p\pi, 3d\pi)$ and ${}^{3}(2p\pi, 3d\pi)$ c.t. states is forbidden according to Lim's rule.⁴³ The relaxation processes for the excited state of 1 (or 2) can be accounted for by the scheme as shown in fig. 8. In benzene and benzene derivatives the S₁ state $[{}^{1}(\pi, \pi^{*}) {}^{1}B_{2u}]$ deactivates *via* fluorescence $(k_{\rm fm})$, internal conversion $(k_{\rm im})$ and indirect $(k_{\rm isc}^{1})$ and direct $(k_{\rm isc}^{1})$ intersystem crossing.³³ When the disilanyl group is introduced into the benzene ring

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	ds for normal (Φ_{im}) and c.t. (Φ_{ci}) fluorescences and for normal phosphorescence (Φ_n), normal fluorescence lifetimes for short (r_{fm}^i) and long (r_{fm}^i)

ample	${ar v_{fm}^m}^{\gamma_{fm}^m}$	${ar v_{ m S_1}^0}/{10^3{ m cm^{-1}}}$	$rac{ar{v}_{ m ct}^{ m m}}{10^3 m cm^{-1}}$	${v_{{ m T}_1}^0}^1/10^3{ m cm}^{-1}$	Φ_{fm}	$\Phi^{\mathrm{f}_{\mathrm{III}}^{\mathrm{f}}}_{\mathrm{fi}}$	$\Phi^{ m s}_{ m fm}{}^{ m b}$	$\Phi^{\mathrm{f}}_{\mathrm{fm}}{}^{b}$	$\tau_{\mathrm{fm}}^{\mathrm{f},b,c}/\mathrm{ns}$	$ au_{\mathrm{fm}}^{\mathrm{s},b,d}$ /ns	Φ_{ct}	Ф	$\tau_p^{q/s}$
-	34.0	36.3	28.5	27.3-	0.09	0.06.	0.02	2.1	-	20	0.09-	0.35	0.20
1	34.2.	35.0	27.6.	27.1	0.17	0.10	0.07	1.4	- - 	20.	0.03	0.42	0.39
ŝ	33.8	34.9	N	26.9	0.29				,	31.,	ļ	0.62	0.21
4	33.0	35.0	28.3-	28.0	0.03	1	ł		- ₩	18	0.03	0.41	0.07
S	33.6,	34.75		27.0	0.17,					27.3		0.15	0.06

^a EPA = ether: isopentane: alcohol = 5:5:2. ^b For details, see text. ^c Experimental errors within $\pm 20\%$. ^d Experimental errors within $\pm 5\%$.

INTRAMOLECULAR CHARGE TRANSFER IN AROMATIC SILANES

such as 1 (or 2), the $2p\pi^* \rightarrow 3d\pi$ c.t. process (k_{ct}) is predominant in comparison with other processes: *i.e.* $k_{et} > k_{fm} + k_{ie} + k_{ise}^{d} + k_{ise}^{d}$. The fast intramolecular c.t. takes place effectively in the S₁ state having an in-plane-like structure in EPA glass at 77 K, followed by rapid intersystem crossing (k_{isc}) to produce the T₁ state [³ (π, π^*)], as described above. A similar tendency was obtained for 4 and 5. These data are summarised in table 3. In contrast, in non-polar MP (methylcyclohexane: isopentane = 3:1) glass at 77 K, relatively long lifetimes with single-exponential decays were obtained as 34 (1), 24 (2) and 30 (3) ns. The relatively long lifetimes are because the efficiency of transfer to the c.t. state is reduced in non-polar MP glass at 77 K.23

The phosphorescence spectra correspond to the ${}^{3}B_{1u} \rightarrow {}^{1}A_{1g}$ radiative transition in benzene. The phosphorescence lifetimes of 1, 2 and 3 in EPA glass at 77 K were short (0.20, 0.39 and 0.21 s, respectively), compared with that (8.8 s) of toluene, because of perturbation by the disilarly group in the ${}^{3}(\pi, \pi^{*})$ state.²³



Fig. 8. Schematic energy-state diagram for the relaxation processes in the excited state of phenyldisilanes (1 and 2). For details, see text and ref. (33).

MECHANISM OF THE $(2p\pi, 3d\pi)$ C.T. STATE COMPARED WITH THAT OF THE T.I.C.T. STATE

The intramolecular c.t. state or exciplexes in the electron donor (D)-acceptor (A) system of D-(CH₂)_n-A ($n \ge 0$) have been extensively studied.⁴⁴⁻⁴⁸ For the case of n = 0(i.e. the D-A system), a strongly dipolar twisted intramolecular charge-transfer (t.i.c.t.) state leading to a longer-wavelength emission is known as an intramolecular c.t. conformation, where the π systems of D and A are twisted with respect to each other.^{44, 49–54} Twisting or internal rotation during the lifetime in the excited state is needed for t.i.c.t. formation.⁵⁴⁻⁵⁷ For instance, c.t. emission is observed for the dimethylaminobenzonitrile (DABN) derivative held rigidly in the perpendicular position, but not for the corresponding derivative with a rigid planar structure.^{49, 51} In contrast, the exciplexes of the sytem with $n \ge 1$ tend to produce c.t. complexes with spatial overlap.44

In the present system of D (phenyl group)-A (disilanyl group), twisting or internal rotation around the C-Si bond axis in an EPA rigid matrix at 77 K is not expected during the lifetime of the excited state, and the Franck-Condon state molecular conformation in the rigid glass at 77 K may be the same as that in the ground state. C.t. emission in EPA glass at 77 K was observed for 1 with a planar or planar-like

structure, but not for 3 with a twisted (perpendicular) structure, as described above. This finding shows that twisting or internal rotation in the excited state is not necessary for $(2p\pi, 3d\pi)$ c.t. formation of phenyldisilanes, although internal rotation around the C—Si bond axis in the compounds enhances formation of the $(2p\pi, 3d\pi)$ state in fluid media. For naphthyldisilanes (7 and 8), the c.t. emission was observed only in fluid polar media, but was not appreciable in a MP or EPA rigid matrix at 77 K and fluid non-polar solvents. These features for 7 and 8 suggest that the c.t. state might be produced by twisting in the excited state according to the t.i.c.t. mechanism.⁴⁹ The discrepancy in the c.t. emission properties between phenyl and naphthyl disilanes can be understood by taking into account the differences in the energy levels of the $1(\pi, \pi)$ π^*) ${}^{1}B_{2}$ (${}^{1}L_{h}$) states (*i.e.* the 0–0 transition energies of the donor groups). The 0–0 transition energy $(36.2 \times 10^3 \text{ cm}^{-1})$ for 1 is much greater than those for naphthyldisilanes $(31.1 \times 10^3 \text{ cm}^{-1} \text{ for } 7 \text{ and } 30.8 \times 10^3 \text{ cm}^{-1} \text{ for } 8)$. For the energy level of the $3d\pi$ vacant orbital of the acceptor (disilarly group), there is no difference between them. As a result, the $2p\pi^* \rightarrow 3d\pi$ c.t. occurs more effectively in 1 than in 7 and 8. The $2p\pi^* \rightarrow 3d\pi$ c.t. for 7 and 8 needs some stabilisation energy due to interaction between the newly produced $(2p\pi, 3d\pi)$ c.t. state and polar solvent molecules, whereas the c.t. process for 1 occurs appreciably in a fluid non-polar solvent. The polar solvents play an important role in lowering the energy level of the $(2p\pi, 3d\pi)$ state by solvation, as stated above.

No intramolecular c.t. emission was observed for polycyclic aromatic disilanes (11, 12 and 13: aromatic rings ≥ 3) whose ${}^{1}(\pi, \pi^{*})$ energy levels[†] are less than 30×10^{3} cm⁻¹. This result indicates that the energy level of ${}^{1}(\pi, \pi^{*})$ should be higher than 30×10^{3} cm⁻¹ in order to produce the ${}^{1}(2p\pi, 3d\pi)$ state from ${}^{1}(\pi, \pi^{*})$. It is known that the energy levels between the donor and acceptor groups are very important for the ground intramolecular c.t. state.⁵⁸ The present system is such a case in the excited state.

The energy of the t.i.c.t. state can be approximately given by^{44, 59}

$$E_{\text{tiet}} = I_{\text{p}}^{*} - E_{\text{a}} - C - \Delta E_{\text{s}}$$
(7)

where I_p^* is the ionisation potential of the donor, E_a is the electron affinity of the acceptor parts of the twisted molecule, C is the Coulomb interaction energy and $\Delta E_{\rm s}$ is the solvent stabilisation energy depending on the temperature and on the polarity of both solvent and solute in the t.i.c.t. state. We examined whether eqn (7) might hold for aromatic disilanes or not. By changing the donor properties the values of E_{tict} might be expected to be dependent upon those of I_p^* ($I_p^* = I_p - E_{00}^*$), where I_p and E_{00}^* represent the ionisation potential in the ground state and the 0-0 transition energy of the donor group. The I_p^* values[‡] were estimated to be 4.49 (benzene), 4.13 (naphthalene), 4.41 (phenanthrene), 4.07 (anthracene) and 4.22 eV (pyrene). There is no distinct relation between the c.t. emission properties and the I_p^* values in the present system. The mechanism for $(2p\pi, 3d\pi)$ intramolecular c.t. formation is different from the t.i.c.t. mechanism. Thus, it is concluded that the interaction between $2p\pi^*$ and a vacant $3d\pi$ orbital is possible when the $2p\pi^*$ energy level is greater than 30×10^3 cm⁻¹ (the number of aromatic rings is 1 or 2) and there is some electronic overlap between the $2p\pi^*$ orbital of the donor (aromatic ring) and the vacant $3d\pi$ orbital of the acceptor (disilaryl). This $(2p\pi, 3d\pi)$ intramolecular c.t. state is related to the photochemical reactions of aromatic disilanes; that is, the photochemical reactions originate from the c.t. state.13, 23, 24

† The 0-0 transition energies for 11, 12 and 13 are 28.6, 24.4 and 26.8×10^3 cm⁻¹, respectively.

 \ddagger The $I_{\rm p}$ and E_{00}^* values were taken from the data in ref. (35).

CONCLUSIONS

(1) Broad and structureless fluorescence spectra of phenyldisilanes and naphthyldisilanes with large Stokes shifts are observed and are attributed to the emissions from the intramolecular c.t. states with large dipole moments. Evidence that the c.t. emission originates from the $1(2p\pi, 3d\pi)$ state produced by $2p\pi^* \rightarrow 3d\pi$ intramolecular charge transfer is demonstrated by the effect of steric twisting on the emission.

(2) For aromatic monosilanes and polycyclic disilanes (aromatic rings \ge 3), no c.t. emission is observed even in polar solvents.

(3) The $2p\pi^*-3d\pi$ charge transfer to produce the ${}^{1}(2p\pi, 3d\pi)$ c.t. state occurs for the following reasons: (a) the energy separation between the $2p\pi^*$ and vacant $3d\pi$ orbitals becomes small upon excitation: the energy level of the ${}^{1}(\pi, \pi^*) {}^{1}B_2$ (or ${}^{1}L_b$) state should be > 30×10^3 cm⁻¹ (aromatic rings = 1 or 2), (b) the disilarly group (or polysilarly group) provides a vacant $3d\pi$ orbital with a relatively low energy level compared with that of a single 3d atomic orbital and (c) the ${}^{1}(2p\pi, 3d\pi)$ energy level is lowered by solvation energy in polar media.

(4) The fast formation (≤ 1 ns) of the ${}^{1}(2p\pi, 3d\pi)$ c.t. state of phenyldisilane (1) from the locally excited state of ${}^{1}(\pi, \pi^{*}) {}^{1}B_{2}$ (or ${}^{1}L_{b}$) occurs effectively, followed by the rapid decay (≤ 1 ns) of intersystem crossing ${}^{1}(2p\pi, 3d\pi) \rightarrow {}^{3}(\pi, \pi^{*})$, even in an EPA rigid matrix at 77 K.

(5) The $2p\pi^* \rightarrow 3d\pi$ intramolecular charge transfer takes place with electronic overlap between the $2p\pi^*$ orbital of the aromatic ring (the electron donor) and the vacant $3d\pi$ orbital of the disilarly group (the electron acceptor), and internal rotation or twisting during the lifetime of the excited state is not necessary for the intramolecular c.t. process, although such twisting enhances the c.t. process. The intramolecular c.t. mechanism for $1(2p\pi, 3d\pi)$ formation is different from the t.i.c.t. mechanism.

This work was supported by a Scientific Research Grant-in-Aid from the Ministry of Education of Japan (no. 56540246 and 57307007). We thank one of the reviewers for his helpful comments.

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