# Dual Fluorescence of Aryldisilanes and Related Compounds. Evidence for the Formation of $(\sigma \pi^*)$ Orthogonal Intramolecular Charge-Transfer States<sup>1</sup>

## Hideki Sakurai,\* Hisashi Sugiyama, and Mitsuo Kira

Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan (Received: June 30, 1989)

Fluorescence and absorption spectra of 14 arylpentamethyldisilanes and related compounds are recorded. Several compounds reveal dual fluorescence corresponding to two singlet excited states. The high polarity of the lowest excited singlet states with charge-transfer nature is evidenced by the solvent shifts. Structural effects clearly demonstrate that Si-Si (and Si-Ge) bonds and aryl groups function as electron donors and acceptors, respectively. The excited-state dipole moment of PhSiMe2SiMe3 is found to be 4.3 D in good agreement with a calculated value of 3.8 D derived by an assumption of planar arrangement of the molecular frame, in which  $\sigma$  and  $\pi$  orbitals are orthogonal to each other, with full charge separation. The orthogonality of  $\sigma$  and  $\pi$  orbitals in the excited states is proved by the stereoelectronic effects on the fluorescence. The circumstance found for the present  $\sigma\pi$  system is similar to twisted intramolecular charge-transfer (TICT) states of  $n\pi$  and sudden polarization in the excited singlet of  $\pi\pi$  systems, and orthogonal intramolecular charge transfer (OICT) is proposed as a general term.

#### Introduction

The concept of the intramolecular charge-transfer (ICT) state has been developed by Nagakura<sup>2</sup> and successfully applied to explain the change in the polarity of molecules on electronic excitation. The real excited states of substituted benzene have been well described in terms of the mixing of the locally excited configuration in benzene and the intramolecular charge-transfer configuration between the benzene ring and the substituent groups. More recently, the ICT structures have been modified to the twisted intramolecular charge-transfer (TICT) state in order to explain dual fluorescence of a number of dialkylaniline derivatives.<sup>3</sup> In TICT states, donor (D) and acceptor (A) groups take a mutually orthogonal conformation and therefore D<sup>+</sup> and A<sup>-</sup> groups have a minimum overlap in the CT states.

Lippert, Luder, and Boos<sup>4</sup> described in 1962 that p-cyano-N,N-dimethylaniline and its N,N-diethyl analogue exhibited two fluorescence bands in fluid solvents of medium and high polarity, and denoted the low- and high-energy fluorescences by a and b bands, respectively. It was evidenced from the solvent shifts of the spectra that the low-energy fluorescence emitting state was highly polar. Lippert et al. ascribed the dual fluorescence to those derived from  ${}^{1}L_{a}$  and  ${}^{1}L_{b}$  states in the Platt classification,<sup>5</sup> where the former emits light of longer wavelength because the more polar  ${}^{1}L_{a}$  state was stabilized more by the reorientation of polar surroundings.

According to their assignment, the transition should be polarized mutually perpendicularly. However, on the basis of the observed parallel transition moments, Rotkiewicz, Grellmann, and Grabowski<sup>6</sup> have concluded that the two emissions are attributable to the existence of two excited species differing in polarity and in the orientation of the NMe<sub>2</sub> group, where the lone-pair orbital is perpendicular in one state but parallel in the other in reference to the plane of the benzene ring.

These assignments were confirmed by Kuhnle and Krowczynski<sup>7a,b</sup> and Chandross and Wight,<sup>7c</sup> who studied a series of model compounds having different orientations of the nitrogen lone-pair orbitals. Their systematic investigations proved that the structure of the strongly polar emitting state of p-cyano-N,Ndimethylaniline corresponds to a twisted rotamer (TICT, twisted intramolecular charge transfer).<sup>3</sup>

More recently, the idea of sudden polarization in the singlet  $\pi\pi^*$  state of olefins and polyenes, in which two adjacent p orbitals have an orthogonal arrangement with full charge separation, has been introduced to explain spectral<sup>8</sup> and photochemical<sup>9</sup> results.

In relation to the photochemistry of aryldisilanes,<sup>10</sup> Shizuka et al.<sup>11</sup> have reported that arylpolysilanes (aryl = phenyl and naphthyl) also exhibit dual fluorescence in polar solvents and assigned the polar emitting state to  $(2p\pi 3d\pi)$  intramolecular charge-transfer states, in which a charge is transferred from the aryl group to the disilaryl group. No orthogonality of the interacting orbitals is required. Their assignments, however, are not compatible with previous analysis of the electronic states<sup>12</sup> or the results of photochemical reactions of arylpolysilanes. The electron transfer in the polar excited states of arylpolysilanes should occur in the direction from  $\sigma(Si-Si)$  (donor) to  $\pi^*$  (acceptor), contrary to their assignment.

We report here that polar fluorescent bands of aryldisilanes and related compounds can be explained satisfactorily by the emission from the intramolecular charge-transfer states where  $\sigma$ (Si-Si) and  $\pi$  systems act as donors and acceptors, respectively. These CT states are stabilized in polar media, and interacting orbitals become favorably orthogonal. The idea of  $(\sigma \pi^*)$  orthogonal charge-transfer (OICT)<sup>13</sup> states will explain successfully

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CHART I



photochemical results of aryldisilanes in both polar and nonpolar media.<sup>10b</sup> It is verified that the polar excited states of arylpolysilanes indeed prefer the orthogonal  $(\sigma \pi^*)$  intramolecular charge-transfer states on the basis of both substituent and geometric effects on the dual fluorescence of arylpentamethyldisilanes and related compounds. The analysis of the excited states is particularly important for elucidating the mechanism of photochemical reactions of arylpolysilanes.<sup>10b</sup>

Recently Rettig has cited the phenyldisilane ICT states as an example of TICT where the Si-Si bond is suggested to be a donor,<sup>3b</sup> in accord with our conclusion. Very recently, Horn and Whitenack<sup>14</sup> have reported electron-transfer fluorescence quenching of electron-deficient benzenes by hexamethyldisilane, giving strong evidence to support the  $\sigma(Si-Si)-\pi^*(benzene)$  OICT mechanism.

#### **Results and Discussion**

Fluorescence of Arylpentamethyldisilanes and Related Compounds (Chart I). Since the previous studies<sup>11</sup> ignored the substituent effects, fluorescence spectra were measured in several solvents such as isooctane (i-Oct), tetrahydrofuran (THF), ethanol (EtOH), and acetonitrile (CH<sub>3</sub>CN) at room temperature for phenyltrimethylsilane (1), tert-butyldimethylphenylsilane (2), phenylpentamethyldisilane (3), (trimethylgermyl)phenyldimethylsilane (4), (trimethylsilyl)phenyldimethylgermane (5), (4-isopropenylphenyl)pentamethyldisilane (6), (4-methylphenyl)pentamethyldisilane (7), (2,4-dimethylphenyl)pentamethyldisilane (8), (4-methoxyphenyl)pentamethyldisilane (9), [4-(N,N-dimethylamino)phenyl]pentamethyldisilane (10), (2methylphenyl)pentamethyldisilane (11), 1,1,2,2-tetramethyl-3,4-benzo-1,2-disilacyclopentene-3 (12), 1,1,2,2-tetramethyl-3,4-

TABLE I: Fluorescence and UV Spectral Data of Arylpentamethyldisilanes and Related Compounds

|       | fluorescence <sup>a,b</sup> |      |      |                    | absorption            |
|-------|-----------------------------|------|------|--------------------|-----------------------|
| compd | i-Oct                       | THF  | EtOH | CH <sub>3</sub> CN | $({}^{l}L_{a})^{b,c}$ |
| 1     |                             |      |      | 34.8               | 47.4                  |
| 2     |                             |      |      | 34.4               | 46.3                  |
| 3     | 33.8                        | 33.8 | 33.8 |                    | 43.4                  |
|       | 29.0                        | 27.6 | 27.5 | 26.5               |                       |
| 4     | 34.1                        | 33.7 | 33.8 | 33.5               | 43.2                  |
|       | 28.5                        | 27.2 | 26.7 | 26.2               |                       |
| 5     |                             | 33.5 | 33.9 | 33.3               | 44.3                  |
|       |                             | 27.3 | 27.9 | 26.6               |                       |
| 6     | 32.9                        | 32.0 | 32.0 | 32.5               | 38.6                  |
|       |                             | 26.3 | 26.4 | 24.7               |                       |
| 7     | 33.7                        | 33.3 | 33.3 |                    | 42.9                  |
|       |                             | 28.3 | 28.0 | 27.0               |                       |
| 8     | 33.6                        | 33.4 | 33.4 | 33.0               | 42.6                  |
|       |                             | 27.5 | 27.0 | 27.0               |                       |
| 9     |                             |      |      | 32.5               | 41.8                  |
| 10    | 29.6                        | 28.7 | 28.4 | 28.6               | 37.0                  |
| 11    | 34.0                        | 33.7 | 33.9 | 33.5               | 43.1                  |
|       | 27.5                        | 27.1 | 27.0 | 26.5               |                       |
| 12    | 33.4                        | 33.2 | 33.5 | 33.4               |                       |
|       | 27.5                        | 26.5 | 27.0 | 26.0               |                       |
| 13    | 34.1                        | 34.0 | 34.0 | 34.0               | 43.1                  |
|       | 29.0                        | 26.8 | 27.0 | 26.0               |                       |
| 14    | 34.5                        | 33.9 | 34.3 | 33.8               | 43.1                  |
|       |                             | 28.3 | 28.0 | 27.4               |                       |

<sup>a</sup>Upper and lower values are for fluorescence b and a, respectively.  $^{b}\nu \times 10^{-4}$  cm<sup>-1</sup>. <sup>c</sup> In hydrocarbon.

benzo-1,2-disilacyclohexene-3 (13), and 1-trimethylsilyl-1methyl-2,3-benzo-1-silacyclopentene-2 (14). The spectral data of 1-14 are listed in Table I.

Compounds except for 1, 2, 9, and 10 exhibit dual fluorescence especially in medium polar solvents as shown in Figure 1. The excitation spectra at both fluorescence bands are almost equal so that two fluorescence bands must be derived from one compound. The emission at longer wavelength is not originated from an excimer because the change in the concentration, for example, of 13 in THF, did not affect the relative intensities of the two fluorescence bands. There is almost no solvent effect on the normal fluorescence b bands observed at ca. 34000 cm<sup>-1</sup>.

In contrast, the red shift was observed for the broad fluorescence a bands at longer wavelength in polar solvents, indicating that the emitting states are polar. Thus by stabilizing the CT states in a polar solvent, the conversion to the OICT state may occur efficiently.

The difference in the frequencies of the  ${}^{1}L_{a}$  absorption and the fluorescence a band maxima,  $v_{ab} - v_{fl}$ , becomes larger with increasing difference of the dipole moments between excited and ground states,  $\mu_e - \mu_g$ , and with increasing polarity of the solvents.

The  $\mu_e - \mu_g$  values can be estimated from the Lippert-Mataga equation<sup>15</sup>

$$v_{ab} - v_{fl} = (2/hc)(\mu_e - \mu_g)^2/a^3\Delta f$$
 (1)

$$\Delta f = (D-1)/(2D+1) - (n^2 - 1)/(2n^2 + 1)$$
 (2)

where h is Planck's constant, c the velocity of light, a the Onsager radii of solutes,<sup>16</sup>  $\Delta f$  the parameter of solvent polarity, D dielectric constant,<sup>17</sup> and n the refractive index of solvents.

Experimentally,  $v_{ab}$ 's are hardly affected by the solvent polarity, so that the  $\nu_{ab}$ 's in hydrocarbons were adopted for calculations and shown in Table I. Figure 2 indicates the Lippert-Mataga plots for 3, 4, 11, and 13 which were measured at four  $\Delta f$ s: 0.0005 for i-Oct, 0.2103 for THF, 0.2895 for EtOH, and 0.3054 for CH<sub>3</sub>CN.

<sup>(13)</sup> In TICT ( $n\pi^*$ ), suddenly polarized ( $\pi\pi^*$ ), and OICT ( $\sigma\pi^*$ ) states, CT states are stabilized by taking a conformation in which donor and acceptor orbitals are mutually perpendicular. To reach such conformations in  $(n\pi^*)$ and  $(\pi\pi^*)$  systems, molecular frames should also be twisted, but in  $(\sigma\pi^*)$  states, molecular frames should be coplanar to get orthogonal orbital arrangement. To avoid possible confusion, we propose OICT as a general term. (14) Horn, K. A.; Whitenack, A. A. J. Phys. Chem. 1988, 92, 3875.

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Figure 1. Fluorescence spectra at room temperature. (a) Phenylpentamethyldisilane (3): —, CH<sub>3</sub>CN, 1.96 × 10<sup>-4</sup> M, excitation at 240 nm; ---, THF, 2.49 × 10<sup>-4</sup> M, excitation at 245 nm; ----, *i*-Oct, 2.72 × 10<sup>-4</sup> M, excitation at 240 nm; (b) (Trimethylgermyl)phenyldimethylsilane (4): —, CH<sub>3</sub>CN, 1.25 × 10<sup>-4</sup> M, excitation at 240 nm; ---, EtOH, 2.68 × 10<sup>-4</sup> M, excitation at 240 nm; ---, THF, 2.59 × 10<sup>-4</sup> M, excitation at 245 nm; ----, *i*-OCT, 2.53 × 10<sup>-4</sup> M, excitation at 240 nm; ---, EtOH, 2.68 × 10<sup>-4</sup> M, excitation at 245 nm; ----, *i*-OCT, 2.53 × 10<sup>-4</sup> M, excitation at 240 nm; ---, EtOH, 2.68 × 10<sup>-4</sup> M, excitation at 245 nm; ----, *i*-OCT, 2.53 × 10<sup>-4</sup> M, excitation at 240 nm; ---, THF, 2.06 × 10<sup>-4</sup> M, excitation at 240 nm; ---, CH<sub>3</sub>CN, 1.82 × 10<sup>-4</sup> M, excitation at 245 nm; ----, *i*-OCT, 2.59 × 10<sup>-4</sup> M, excitation at 240 nm; ---, THF, 2.06 × 10<sup>-4</sup> M, excitation at 240 nm; ---, THF, 1.86 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.59 × 10<sup>-4</sup> M, excitation at 240 nm; ---, THF, 1.86 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.59 × 10<sup>-4</sup> M, excitation at 240 nm; ---, THF, 2.03 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.59 × 10<sup>-4</sup> M, excitation at 240 nm; ---, THF, 2.03 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation at 240 nm; ---, *i*-OCT, 2.02 × 10<sup>-4</sup> M, excitation a



**Figure 2.** Effect of solvent polarity,  $\Delta f$ , on the Stokes shift,  $v_{ab} - v_{fl}$ , of  $3(0), 4(\Box), 11(\Delta), and 13(\diamond)$ 



Figure 3. Charges and coordinates in  $(\sigma \pi^*)$  OICT state of 3.

On the assumption that the Onsager radii for 3 is 3 Å and by the same procedure for the determination adopted by Shizuka et al.,<sup>13c</sup> the  $(\mu_e - \mu_g)$  is calculated to be 4.3 D from the observed slope of 6700 cm<sup>-1</sup> in eq 1. The dipole moments in the ground state of aromatic silanes seem to be small, because the +I and -M effects of the substituent cancel each other. Then, the value of  $\mu_e$  can be taken approximately to be equal to that of  $(\mu_e - \mu_e)$ , namely, equal to 4.3 D. The  $\mu_e$  of the CT emitting state can be calculated to be 3.8 D on the basis of the geometry and the charge distribution under the condition of the orthogonal  $(\sigma \pi^*)$  intramolecular charge-transfer (OICT) state, as shown in Figure 3, in good agreement with the experimental value.<sup>18</sup>

Effects of the Difference of Group IVB Atoms on the Fluorescence of Phenyl-Substituted Group IVB Catenates. Enhanced red shifts of  ${}^{1}L_{a}$  absorption bands of arylpolysilanes have been rationalized at first in terms of  $d-\pi^*$  interaction in the excited state, where an enhanced acceptor function of the disilaryl group due to the  $d\pi$ - $d\pi$  bonding is assumed to cause a significant interaction with the energetically comparable  $\pi^*$  orbital of benzene.<sup>19-25</sup> Later the ground-state interaction between the silicon-silicon  $\sigma$  orbital and  $\pi$  orbitals has been recognized as an important factor in addition to  $d-\pi^*$  interaction, since the lower ionization energy of the metal-metal bond makes the  $\sigma$ - $\pi$  interaction favorable energetically.<sup>12a,26-29</sup>

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Figure 4. Fluorescence spectra of 3, 4, and 5 in acetonitrile at room temperature.

Shizuka's argument on the fluorescence spectra of arylpolysilane<sup>8</sup> is based on the  $(p-d)\pi$  conjugation. Evidence for electron-accepting ability of disilanyl groups in phenylpentamethyldisilane has been obtained by ESR of the anion radicals,<sup>30</sup> electrochemical reduction,<sup>22</sup> and MCD analysis of phenylpentamethyldisilane.<sup>11f</sup> However, the electron-acceptor function has never been known to exceed that of the monosilyl group. Unusual electronic character of disilanyl groups should be attributed to the high-energy level of the  $\sigma(Si-Si)$  orbital<sup>12,22,28,31</sup> which should also play an important role on the CT fluorescence.

Compounds that have only one silicon, 1 and 2, exhibit no CT fluorescence, at least two silicon atoms being required for the CT fluorescence. Shizuka et al.<sup>11</sup> suggested that the stabilization of the CT states due to the  $3d\pi - 3d\pi$  conjugation in polysilanes is important. However, it should be mentioned that catenation should also be necessary for obtaining the capacity as the electron donor with low ionization potentials.<sup>32,33</sup>

To make clear the point, fluorescence spectra of phenylsubstituted group IVB catenates phenylpentametyldisilane (3), (trimethylgermyl)phenyldimethylsilane (4), and (trimethylsilyl)phenyldimethylgermane (5), measured in CH<sub>3</sub>CN, were compared as shown in Figure 4. The CT fluorescence of 4 exhibits red shift in comparison with those of 3 and 5. Since the value of the ionization potential  $(I_p)$  of Me<sub>3</sub>SiGeMe<sub>3</sub> (8.65 eV)<sup>34</sup> is similar to but smaller than that of Me<sub>3</sub>SiSiMe<sub>3</sub> (8.69 eV),<sup>35</sup> the  $\sigma(Si-Ge)-\pi^*$  intramolecular charge-transfer excitation should be even more favorable than the  $\sigma(Si-Si)-\pi^*$ . On the other hand, the 3d-4d conjugation in the Si-Ge bond should be less important than the 3d-3d conjugation in the Si-Si bond since both energy levels and size of 3d and 4d orbitals differ considerably. Therefore, the extent of the stabilization due to 3d-4d interaction must be smaller than that of 3d-3d interaction.<sup>35-37</sup> Hence, the energy level of the CT emitting state of 4 should be higher than that of 3, if the state is assigned to  $(2p\pi 3d\pi)$  ICT, while the inverse should be expected from the  $(\sigma \pi^*)$  ICT concept. The experimental results demonstrate clearly that the CT fluorescence of 4 exhibited red shift as compared with that of 3.

It should also be mentioned that the small difference between

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<sup>(18)</sup> Standard bond lengths and bond angles were used for the calculation of the dipole moment of the OICT state. The negative charge distribution was estimated from the atomic coefficients of the symmetric  $\pi$  LUMO of benzene, and the positive charges were assumed to be localized on two silicon atoms equally (0.5 each).

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Figure 5. Effect of para substituents on fluorescence of 3 in acetonitrile at room temperature.

the excited-state energies of 4 and 5 was observed even though that the same M-M' bond was included. The results may be explained by the decreasing electrostatic energy term,  $\Delta$ , in the  $l(\sigma\pi^*)$  ICT state of 5 in comparison with that of 3. The energy of the  $l(\sigma\pi^*)$  OICT state can be represented by the equation<sup>38</sup>

$$E_{\rm CT} = I_{\rm P} - E_{\rm A} + \Delta + E_{\rm solv} \tag{3}$$

where  $I_{\rm P}$ ,  $E_{\rm A}$ , and  $E_{\rm solv}$  are ionization potentials, electron affinities, and solvation energies, respectively. In all three compounds, the  $E_{\rm A}$ 's are taken to be equal to the  $E_{\rm A}$  of benzene itself, and  $I_{\rm P}$ 's of  $\sigma({\rm Si-Si})$  and  $\sigma({\rm Si-Ge})$  are 8.69 and 8.65 eV, respectively, as described previously. Thus, the energy levels of CT states of 4 and 5 must be equal and must be lower than that of 3, if the same  $\Delta$  and  $E_{\rm solv}$  can be applied to these three compounds. As described later, the favorable geometry of the CT emitting state is in a form in which the  $\sigma(M-M')$  orbital lies orthogonal relative to the  $\pi$ orbitals. In this situation, both positive and negative charges should localize largely on the neighboring atoms between the donor and the acceptor groups.

Therefore,  $\Delta$  may be determined mostly by the electrostatic interaction between charges on the carbon at the 1-position of benzene and on the substituted metal atom. In this consequence, both 3 and 4, which have the same combination of C(aryl)-Si, result in almost the same  $\Delta$  so that the observed lowering of the energy level of 4 may be largely due to the difference of  $I_P$ 's of  $\sigma$ (Si-Si) and  $\sigma$ (Si-Ge) orbitals. On the other hand, the C-(aryl)–Ge combination of 5 may bring on decrease of  $|\Delta|$  possibly due to lowering of the two center repulsion integrals of the type (CC|GeGe) as compared with (CC|SiSi) and/or increase of diatomic distance. Consequently, the stabilization by the decrease of  $I_P$  and the destabilization by lowering  $\Delta$  in 5 may counterbalance each other, and hence, the energy levels of the CT excited states of 3 and 5 become almost equal. Difference of the  ${}^{1}L_{a}$ transition energies between 4 and  $5^{34}$  may be explained in the same line. A similar discussion has been presented for the explanation of the red shift of the  $n-\pi$  transition of silvl ketones from the corresponding germyl ketones, in spite of the lower ionization potential of n electrons of the latter.<sup>39</sup> In conclusion, the requirement of two silicon atoms necessary for CT fluorescence is not owing to lowering the level of the Si-Si acceptor orbitals due to  $3d\pi - 3d\pi$  conjugation but owing to raising the highest occupied orbital levels of the Si-Si donor group.

Effects of Para Substituents on the Fluorescence of Phenylpentamethyldisilane (3). In the above discussion, the effects of  $\sigma$ (metal-metal) donor orbitals on CT fluorescence were demonstrated. Next, the roles of acceptor orbitals will be discussed on the basis of the para-substituent effects on the fluorescence spectra

#### of phenylpentamethyldisilane (3).

Figure 5 shows the effects of various para substituents on the fluorescence of 3: isopropenyl (6), methyl (7), methoxy (9), and N,N-dimethylamino derivatives (10). As can be seen in Figure 5, 6 has a CT fluorescence band at the longest wavelength. The blue shift in CT emission bands was observed from 6 to 3 to 7. However, 9 does not exhibit CT fluorescence. The observed fluorescence of 9 can be assigned to the  ${}^{1}L_{b} \rightarrow A$  emission judging from the position which is almost the same as those of the other  $^1L_b \rightarrow A$  emission. Only one emission band appeared for 10 in between the  ${}^{1}L_{b} \rightarrow A$  emission band of 9 and CT emission bands of 6, 3, and 7. This band can be assigned to the  ${}^{1}L_{a} \rightarrow A$  emission band by considering the following facts. First, the shape of this band is rather sharp as compared with those of CT emission bands, and the intensities do not decrease by decreasing the solvent polarity. Second, the band is located nearly at the region where the CT fluorescence should be observed in nonpolar solvents, even though very polar acetonitrile was used as solvent. Moreover, the band exhibits blue shift by decreasing the solvent polarity, the extent of which is smaller than that of the CT fluorescence but larger than that of the  ${}^{1}L_{b} \rightarrow A$  fluorescence. Third, the band nearly mirrors the absorption band. The  ${}^{1}L_{a}$  state of 6 may be stabilized in a considerable extent due to the  $n(Me_2N) \rightarrow \pi$  charge transfer,<sup>30</sup> so that the energy level of  ${}^{1}L_{a}$  state should go down below that of <sup>1</sup>L<sub>b</sub> state at the Franck-Condon state.

Substituent effects on the transition energy of the CT fluorescence band ( $\bar{\nu}_{\rm f}({\rm CT})$ ) of phenylpentamethyldisilane now give a good evidence for the assignment of the CT state as  ${}^{1}(\sigma\pi^{*})$  ICT instead of the  ${}^{1}(2p\pi 3d\pi)$  ICT state as proposed by Shizuka. As can be expected from eq 3, the energy level of the  ${}^{1}(\sigma\pi^{*})$  ICT state should be lowered with increasing  $E_{\rm A}$  of the substituted benzene moiety in the aryldisilanes. On the other hand, if the CT emitting state is assigned to the  ${}^{1}(2p\pi 3d\pi)$  ICT state by Shizuka's model, the CT fluorescence energy should depend on the  $I_{\rm P}$  rather than the  $E_{\rm A}$  values of the substituted benzene. Thus  $\tilde{\nu}_{\rm f}({\rm CT})$  should decrease with decreasing  $I_{\rm P}$ .

Substituent (and  $I_P$  and  $E_A$  values in eV in parentheses) for the pertinent substituted benzenes are the following:<sup>37,38</sup> CH= CH<sub>2</sub> (8.49, -0.25), H (9.24, -1.15), CH<sub>3</sub> (8.85, -1.11), OMe (8.42, -1.09), and NMe<sub>2</sub> (7.37, -1.24). Increasing the  $E_A$  of benzene by introducing a *p*-isopropenyl caused actually significant red shift of the CT emission band of phenylpentamethyldisilanes. No CT fluorescence was observed in phenylpentamethyldisilanes substituted by *p*-methoxy and *p*-dimethylamino groups, which should be better donors than *p*-methyl. These facts are in good accord with the idea of the  ${}^1(\sigma\pi^*)$  ICT but incompatible with Shizuka's model. Thus the experimental results clearly support the assignment as the  ${}^1(\sigma\pi^*)$  ICT state.

Shizuka et al.<sup>11</sup> indicated that polysilanes with a polycondensed aromatic ring such as anthranyl, phenanthryl, and pyrenylpolysilanes exhibited no CT fluorescence due to low-energy levels of the LUMO's, unfavorable to  $2p\pi-3d\pi$  interaction. However, it should be mentioned that these compounds also have lower ionization potentials in company with higher electron affinities. Consequently, electronic transition in both absorption and fluorescence may occur only within polycondensed aromatic rings.

In conclusion, effects of para-substituents on the fluorescence of phenylpentamethyldisilane (3) should be taken as decisive evidence that the CT emission originates from the  $1(\sigma\pi^*)$  ICT.

Geometry of  ${}^{1}(\sigma\pi^{*})$  Intramolecular Charge-Transfer State. The importance of  $\sigma-\pi$  conjugation between the  $\sigma(Si-Si)$  bond and the benzenoid  $\pi$  system in the ground state of arylpentamethyldisilanes has been confirmed by the UV spectra of 1,1,2,2-tetramethyl-3,4-benzo-1,2-disilacyclopentene-3 (12) and 1-(trimethylsilyl)-1-methyl-2,3-benzo-1-silacyclopentene-2 (14).<sup>29</sup> Figure 6 shows the UV spectrum of newly prepared 1,1,2,2tetramethyl-3,4-benzo-1,2-disilacyclohexene-3 (13) in addition to those of 12, 14, and (2-methylphenyl)pentamethyldisilane (11). No typical transition band of phenyldisilane is observed for 12, in which the Si-Si bond is in the nodal plane of the  $\pi$  system. No  $\sigma-\pi$  conjugation is possible for 12 since the conjugation requires coplanarity between the  $p\pi$  axis and the interacting  $\sigma$  bond, as

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Figure 6. UV spectra of 1,1,2,2-tetramethyl-3,4-benzo-1,2-disilacyclopentene-3 (12) and related compounds.



Figure 7. Fluorescence spectra of 11, 12, 13, and 14 in acetonitrile at room temperature.

for  $n-\pi$  and  $\pi-\pi$  conjugations, although 14, in which the dihedral angle between  $\sigma(Si-Si)$  and  $\pi$  orbitals is 30° and the enhanced  $\sigma - \pi$  conjugation is possible, has intense absorption at around 232 nm. In line with the stereoelectronic effect on the  ${}^{1}L_{a}$  band of phenyldisilane system, the intensity of the corresponding bands of 13, in which the dihedral angle is over 60° at the half-chair form, decreases to a shoulder absorption.

Such stereoelectronic circumstance can be used as conclusive evidence for determining the geometry of ICT state in a similar way to (N,N-dimethylamino)benzonitrile.<sup>3,10,11</sup>

Figure 7 shows fluorescence spectra of 11, 12, 13, and 14 in acetonitrile at room temperature. Remarkable stereoelectronic effects are found; thus, 12 exhibits CT fluorescence but with relatively weak intensity as compared to the normal fluorescence, while 13 emits preferentially from the CT state. The positions of CT fluorescence bands of 12 and 13 are nearly the same as each other and lie in the longest wavelength region among the four. 14 also exhibits CT fluorescence; however, the band shifts to the blue region. The CT fluorescence band of 11 lies in an intermediate region between those of 14 and 12 (and 13). These structural evidences indicate that the most favorable geometry of  $(\sigma \pi^*)$  ICT states is the form in which the  $\sigma(Si-Si)$  orbital is orthogonal to the  $\pi$  orbital (and therefore in the benzene nodal plane) as shown in Figure 8.

This sort of the orthogonality of two interacting orbitals in the CT excited state can be considered in a way analogous to the case of p-(dimethylamino)benzonitrile.<sup>3</sup> However, there is a marked





(c.=\*) 2103  $1(\pi\pi^*)$  sudden polarization **Figure 8.** Preferred geometry of the  $(\sigma \pi^*)$  OICT state of phenylpentamethyldisilane,  $(n\pi^*)$  TICT, and  $(\pi\pi^*)$  sudden polarization.

--\*1 A10

difference in the fluorescence between aryldisilanes and aminobenzonitriles. The dual fluorescence is observed even in the structurally rigid aryldisilanes such as 12, 13, and 14. Although the transition moments of the two emissions have not been determined, the results may suggest that the higher energy emitting state may be attributable to the normal  ${}^{1}L_{h} \rightarrow A$  transition in the aryldisilane case.

The degree of stabilization by solvation must be larger in the orthogonal conformation with completely separated charges than the form with the  $\sigma(Si-Si)$  orbital coplanar to the  $p_{\pi}$  orbital since the former is more polarized than the latter. This is the reason why the energy levels of the excited CT states of 12 and 13 are lower than that of 14. In accord with this, the CT fluorescence band of 11, which can rotate freely to some degree from the perpendicular to the planar form, lies in the intermediate region. As shown in the previous section, the experimental dipole moment of 3 in the CT fluorescence emitting state is in good agreement with the value calculated by assuming the planar geometry.

Effective  $\sigma - \pi$  conjugation, that is, the effective overlap between benzene  $\pi$  and Si-Si  $\sigma$  orbitals, is required for <sup>1</sup>L<sub>a</sub> absorption. Thus one can expect that the OICT state of phenylpentamethyldisilane is formed by rotation after  ${}^{1}L_{a}$  absorption at the perpendicular geometry between the Si–Si bond and the benzene ring plane. However, even 12, which is fixed to the in-plane geometry, exhibits CT emissions of low intensity but of low energy. The OICT state of 12 may be formed via the internal conversion of <sup>1</sup>L<sub>b</sub> state. Although the Franck-Condon factor for the interconversion may be small because of the minimum overlap of the orbitals involved in the transition, any vibration modes with relatively small energy may be enough to give rise to significant interconversion from  $L_b$  to the OICT state.

Compound 14, which cannot take the OICT state, also exhibits CT emissions. However, the emissions are observed only in very polar solvent. The polar emitting states can be stabilized not only by OICT but also by very polar solvent. The essential factors in the fluorescence spectra should be electron-donating and electron-accepting properties of  $\sigma$ (metal-metal) and  $\pi$  orbitals in the interacting system, respectively.

Shizuka et al.<sup>11</sup> also have suggested that the CT emitting state should take the in-phase conformation in which the  $\sigma(Si-Si)$  bond is coplanar with the benzenoid ring judging from the disappearance of CT emission of mesitylpentamethyldisilane. The phenomenon may also be well understood in terms of  $\sigma - \pi$  ICT emission in this compound. Both steric and electronic effects of the methyl group should be considered as factors that affect the CT fluorescence.

Figure 9 shows fluorescence spectra of 3, (2-methylphenyl)pentamethyldisilane (11), (4-methylphenyl)pentamethyldisilane (7), and (2,4-dimethylphenyl)pentamethyldisilane (8) in acetonitrile. The positions of CT fluorescence of 3 and 11 are the same and lie in a longer wavelength region as compared to those of 7 and 8, whose band positions are also the same. These phenomena can be explained as follows. The band of 7 shifts to the blue region in comparison with that of 3 due to the electron-donating property of the 4-methyl group, while the band of 11 practically does not move from that of 3 because the stabilization of the CT state of 11 by higher population of the in-plane form due to the steric effect of 2-methyl group that compensates the destabilization effect by an electron-donating property of the 2-methyl group. The same interpretation can be applied to explain the similarity of the band positions of 7 and 8. For mesitylpentamethyldisilane, three electron-donating methyl groups destabilize the CT emitting state,



Figure 9. Fluorescence spectra of 3, 7, 8, and 11 in acetonitrile at room temperature.

and moreover, the 2,6-dimethyl groups hinder coplanarity of the disilanyl group which should be essential for stabilizing the CT emitting state. This is the likely reason why mesitylpentamethyldisilane exhibits no CT fluorescence.

More recently, Horn and Whitenack have reported that (phenylethynyl)pentamethyldisilanes with a variety of substitutents exhibit intramolecular CT spectra at 77 K which should involve  $\sigma$ (SiSi)- $\pi$ \* CT states.<sup>14</sup> We reached to the same conclusion before for substituted (phenylethynyl)polysilanes.<sup>42</sup> Horn and Whitenack also obtained the same conclusion for phenylpentamethyldisilanes on the basis of quenching experiments.<sup>14</sup>

In conclusion, dual fluorescence of a number of aryldisilanes and related compounds are characterized by the existence of the polar low-energy  $l(\sigma \pi^*)$  ICT states in which donor  $\sigma$  and acceptor  $\pi$  orbitals are favorably orthogonal (OICT). The  $(\sigma\pi^*)$  OICT states resemble, in concept, both  $(n\pi^*)$  TICT states in p-(dimethylamino)benzonitriles and sudden polarization in the  $(\pi\pi^*)$ states of olefins, in which two interacting orbitals are orthogonal in the twisted molecular conformation. These phenomena are in good harmony and we propose OICT as a general term.

### **Experimental Section**

General. <sup>1</sup>H NMR spectra were recorded with a Varian Model EM-390 spectrometer. Infrared spectra were determined with a Hitachi Model EPI-G<sub>2</sub> spectrophotometer. Mass spectra were measured on a JEOL Model JMS-D300 spectrometer. Ultraviolet spectra were determined with a Hitachi 323 spectrophotometer. Fluorescence spectra were measured with a Hitachi MPF-4 phosphorescence spectrophotometer in various solvents in a nonfluorescence cell at room temperature. Tetrahydrofuran and acetonitrile were commercial UV spectral grade. Isooctane and ethanol were purified by the usual method.<sup>4,43</sup> The absence of impurities in these solvents was checked before measurement. The materials were purified by preparative GLC and then by HPLC. The spectra shown in the figures were obtained after subtracting backgrounds from the original spectra.

Materials. tert-Butylphenyldimethylsilane (2),<sup>34</sup> (trimethylgermyl)phenyldimethylsilane (4),44 (trimethylsilyl)phenyldimethylgermane (5),44 [4-(N,N-dimethylamino)phenyl]pentamethyldisilane (10),45 (2-methylphenyl)pentamethyldisilane (11),29 1-(trimethylsilyl)-1-methyl-2,3-benzo-1-silacyclopentene-2 (14),29

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phenyltrimethylsilane (1),<sup>46</sup> phenylpentamethyldisilane (3),<sup>47</sup> (4-methylphenyl)pentamethyldisilane (7),<sup>48</sup> (4-methoxyphenyl)pentamethyldisilane (9),49 and 1,1,2,2-tetramethyl-3,4-benzo-1,2-disilcyclopentene-3 (12)<sup>29</sup> were prepared according to the references.

Preparation of (4-Isopropenylphenyl)pentamethyldisilane (6). p-Chloro- $\alpha$ -methylstyrene (26.36 g, 0.1727 mol) is added to a mixture of magnesium (4.86 g, 0.200 mol), pentamethylchlorodisilane (33.4 g, 0.200 mol), and THF under reflux. The mixture was stirred for 3 h under reflux, hydrolyzed with dilute HCl after cooling, and then extracted with ether. Distillation at a reduced pressure of the ethereal solution after addition of a trace amount of picric acid gave 20.94 g (48% yield) of (4-isopropenylphenyl)pentamethylsilane: bp 90 °C/0.5 mmHg-105 °C/1.5 mmHg; <sup>1</sup>H NMR (90 MHz, CCl<sub>4</sub>, dioxane) δ 0.22 (9 H, s), 0.48 (6 H, s), 2.28 (3 H, m), 5.15 (1 H, m), 5.45 (1 H, m), 7.44 (4 H, s); IR (neat, cm<sup>-1</sup>) 1640, 1610, 1450, 1400, 1245, 1095; MS (70 eV) m/e (%) 248 (M<sup>+</sup>, 3.25), 233 (5.1), 175 (100.0), 160 (36.2), 145 (10.84), 73 (52.71); exact mass found 248.1426, calcd for C14H24Si2 248.1416. Anal. Found: C, 67.70; H, 9.69. Calcd: C, 67.66; H, 9.73.

Preparation of (2,4-Dimethylphenyl)pentamethyldisilane (8). To a lithium reagent, prepared from 27.80 g (0.1500 mol) of 2,4-dimethylbromobenzene and 2.5 g (0.36 mol) of lithium wire in diethyl ether, was added 20.02 g (0.1200 mol) of chloropentamethyldisilane. After being heated at reflux for 24 h followed by the usual workup, the mixture gave 21.51 g (75.8%) of (2,4dimethylphenyl)pentamethyldisilane: bp 98-99 °C/7 mmHg; <sup>1</sup>H NMR (90 MHz,  $CCl_4$ ,  $CH_2Cl_2$ )  $\delta$  0.19 (9 H, s), 0.48 (6 H, s), 2.38 (3 H, s), 2.45 (3 H, s), 6.91 (2 H, m), 7.21 (1 H, m); MS (70 eV) m/e (%) 236 (M<sup>+</sup>, 8.77), 221 (4.28), 163 (100.00), 147 (2.95), 135 (4.84), 73 (9.36); exact mass found 236.1404, calcd for C<sub>13</sub>H<sub>24</sub>Si<sub>2</sub> 236.1414. Anal. Found: C, 66.32; H, 10.40. Calcd: C, 66.02; H, 10.23. UV (*n*-hexane)  $\lambda_{max}$ , nm ( $\epsilon$ ) 235 (14500), 280 (300).

Preparation of 1-[(o-Chlorophenyl)ethyl]-2-chlorotetramethyldisilane. To 19.00 g (0.1015 mol) of 1,2-dichlorotetramethyldisilane in 100 mL of THF was added (o-chlorophenyl)ethylmagnesium chloride prepared from 2.50 g (0.103 mol) of magnesium turnings and 17.51 g (0.1000 mol) of (o-chlorophenyl)ethyl chloride in 500 mL of THF. After heating at reflux for 4 h, the usual workup gave 11.4 g (38.9% yield) of 1-[(ochlorophenyl)ethyl]-2-chlorotetramethyldisilane: bp 92-121 °C/0.08 mmHg; <sup>1</sup>H NMR (90 MHz, CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>) § 0.29 (6 H, s), 0.59 (6 H, s), 1.10 (2 H, m), 2.82 (2 H, m), 6.97-7.33 (4 H, m); MS (70 eV) m/e (%) 277 (0.16), 275 (0.20), 199 (24.06), 197 (100.00), 169 (41.79), 93 (20.66), 73 (20.01), 59 (41.62).

Preparation of 1,1,2,2-Tetramethyl-3,4-benzo-1,2-disilacyclohexene-3 (13). To 1.66 g (0.0722 mol) of sodium dispersion in 100 mL of xylene was added 7.335 g (0.02500 mol) of 1-[(ochlorophenyl)ethyl]-2-chlorotetramethyldisilane in 50 mL of xylene. After refluxing for 6.5 h, the usual workup gave 2.77 g (50.3% yield) of 1,1,2,2-tetramethyl-3,4-benzo-1,2-disilacyclohexene-3: bp 102-115 °C/mmHg; <sup>1</sup>H NMR (90 MHz, CCl<sub>4</sub> CH<sub>2</sub>Cl<sub>2</sub>) δ 0.28 (6 H, s), 0.40 (6 H, s), 1.00 (2 H, m), 2.90 (2 H, m), 6.99-7.45 (4 H, m); IR (neat) no absorption characteristic to  $\nu_{\text{Si-O-Si}}$  from 1000 to 1100 cm<sup>-1</sup>; MS (70 eV) m/e (%) 220 (M<sup>+</sup>; 73.37), 205 (36.70), 161 (32.04), 160 (44.01), 147 (100.00), 145 (95.41); exact mass found 220.1112, calcd for C<sub>12</sub>H<sub>20</sub>Si<sub>2</sub> 220.1104. Anal. Found: C, 65.31; H, 9.29. Calcd: C, 65.38; H, 9.14. UV (*n*-hexane)  $\lambda_{max}$ , nm ( $\epsilon$ ) 232 (sh), 276.5 (500).

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