$$\delta_S = \frac{n_+S_+\delta_+ + n_-S_-\delta_-}{n_+S_+ + n_-S_-} \qquad (18)$$

where n_+ and n_- are the number of positive and negative ions per salt molecule; S_+ and S_- are the effective number of solvent molecules bound to a positive ion and a negative ion, respectively; and δ_+ and δ_- are the respective proton shifts of a solvent molecule bound to a cation or to an anion.

When the values of δ_S for the salts in methanol are compared with those in water,[2a] we notice that the values for a given salt differ by a constant increment of 2.2 ppm, with the methanol shift lying further downfield. This observation in conjunction with eq 18 gives further evidence that, for the salts studied here, the ion-solvent bonding in methanol is essentially the same as those present in aqueous solution.

For NaI we see, from Table I, that δ_S is independent of concentration, on going from 1.11 to 2.80 *m*. For $LiClO_4$, however, at 1.912 *m* δ_S equals −4.47 ppm and at 5.90 *m* δ_S equals −3.84 ppm. At the higher concentration we should expect the proposed model to fail since ion pairing and ion sharing of solvent molecules are likely to occur, thus introducing additional complications which have not been taken into account in the present model.

B. Chemical Shift of the Methyl Protons. When the model is applied to the proton shift of the methyl group, an equation analogous to eq 16 is obtained, namely

$$\delta^* = \frac{Sm}{31.25}[\delta_S^* - \delta_0^*] + \delta_0^* \qquad (19)$$

Here the asterisk is used to indicate that the shift concerns the methyl protons. This equation is consistent with the experimental observations.

As described in the experimental section, we also discovered that the methyl shift of pure methanol δ_0^* is independent of temperature. Now according to equation (19) if the solvation number and δ_S^* are also independent of temperature, then the observed shift δ^* must be independent of temperature. Indeed this is the case. For all of the salt solutions investigated the shift of the methyl protons was found to be independent of temperature. See column seven in Table I. This fact lends credence to the proposed model.

Furthermore, if the solvation number is independent of concentration, then the shift of the methyl protons, according to eq 19, should be a linear function of the salt concentration. For both $LiClO_4$ and NaI a plot of the chemical shift of the methyl protons as a function of molality yields a straight line with an intercept of approximately −3.49 ppm, the shift of the methyl protons in pure methanol.

From a knowledge of the solvation number, *S*, obtained from temperature studies of the hydroxy proton shift, and from a knowledge of δ_0^* we can determine δ_S^*. Values obtained in this manner are presented in Table I. Although the concentration dependence of the methyl proton shift is not as great as that of the hydroxyl proton, it is clearly measureable.

We see here that eq 19 is in agreement with the observation that, for the electrolyte solutions studied, the methyl proton shift is independent of temperature but dependent upon salt concentration.

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Charge-Transfer Spectra of Some Para-Substituted Phenylpentamethyldisilanes. Substituent Effects on the Relative Intensities of Two Charge-Transfer Bands[1]

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Abstract: Relative intensities of two charge-transfer bands of *p*-R-$C_6H_4SiMe_2SiMe_3$ (R = H, Me, Me_3SiCH_2, and MeO)-TCNE complexes in dichloromethane have been determined by computer-aided analyses of the spectra. Experimentally, the relative intensities were correlated to σ^+ constants of the substituents. The results were then interpreted in terms of the Hückel MO models. The longer wavelength band was assigned to the transition from the highest occupied molecular orbital, constructed by the linear combination of the symmetric highest occupied π MO of a benzene with a silicon-silicon bonding σ MO to the lowest unoccupied MO of TCNE. The relative intensities were closely correlated to the fraction of the σ(SiSi) orbital in the highest occupied molecular orbital.

Charge-transfer (CT) spectra of arylpolysilanes are important as a diagnosis demonstrating the σ(SiSi)-π conjugation in these compounds.[2] The CT spectrum of phenylpentamethyldisilane with tetracyanoethylene (TCNE) was first reported by Bock and Alt.[3] They analyzed the CT spectrum as composed of two bands in which one had an absorption maximum at 25,000 cm^{-1}, and the other had an absorption maximum at 20,400 cm^{-1}. Noteworthy is the fact that the latter band had extremely low intensity compared with the former, while benzyltrimethylsilanes, ani-

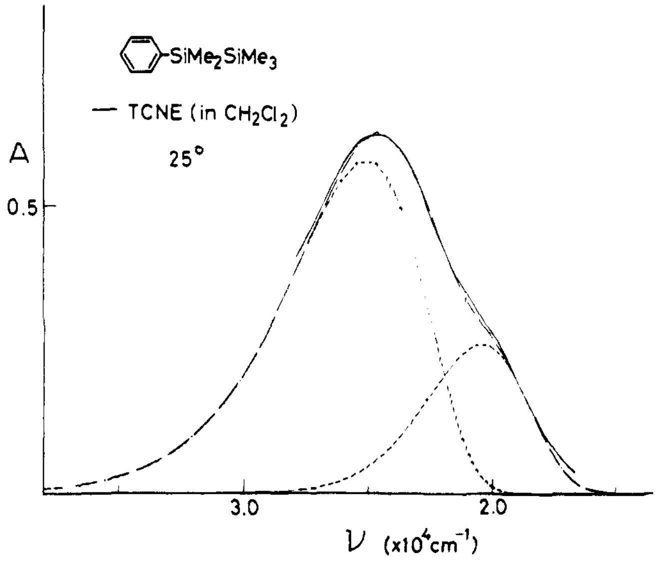

Figure 1. Experimental (—), simulated (— • —), and resolved (- - -) absorption bands for the phenylpentamethyldisilane-TCNE complex in dichloromethane at 25°.

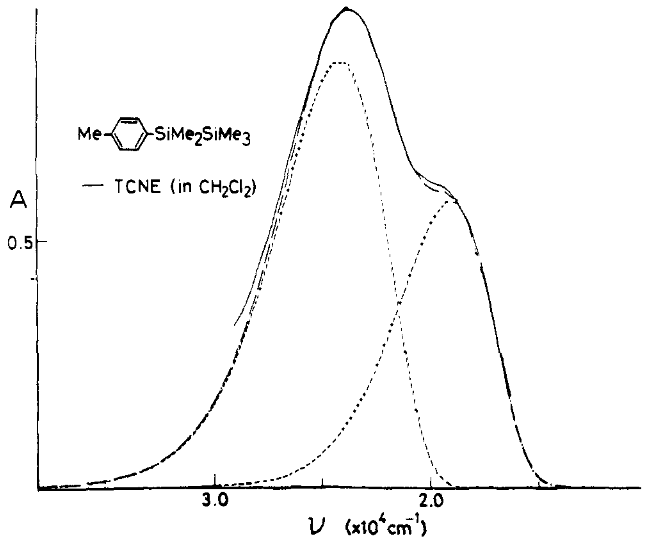

Figure 2. Experimental (—), simulated (— • —), and resolved (- - -) absorption bands for the p-methylphenylpentamethyldisilane-TCNE complex in dichloromethane at 25°.

sole, and even naphthylpentamethyldisilanes[2,4] have been known to show two well-separated CT bands with comparable intensities. The existence of the highest occupied molecular orbital constructed by the σ-π combination of phenylpentamethyldisilane was supported later by its photoelectron spectroscopy.[5] The HOMO should correspond to the low-energy CT band but the reason why the intensity of the band is so low was not explained up to date. In this paper, CT spectra of some para-substituted phenylpentamethyldisilanes with TCNE are analyzed, and the intensity question is clarified.

Results and Discussion

Mono- and para-disubstituted benzenes are well known to complex with TCNE[6] showing two CT absorption bands which on occasion, instead of being resolved into two separate bands, may be observed as a single asymmetric band with an exceptionally large half-bandwidth.

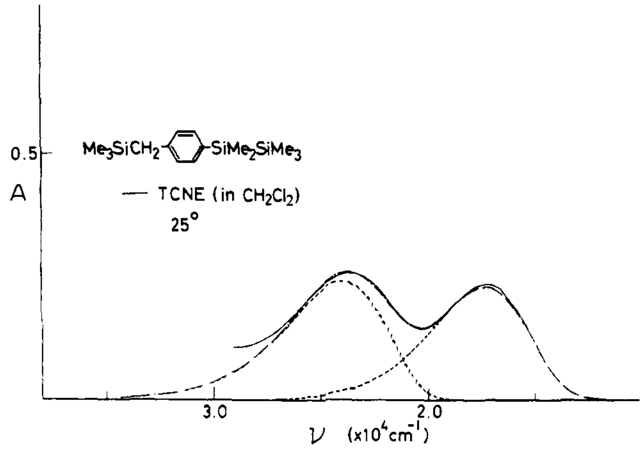

Figure 3. Experimental (—), simulated (— • —), and resolved (- - -) absorption bands for the p-trimethylsilylmethylphenylpentamethyldisilane-TCNE complex in dichloromethane at 25°.

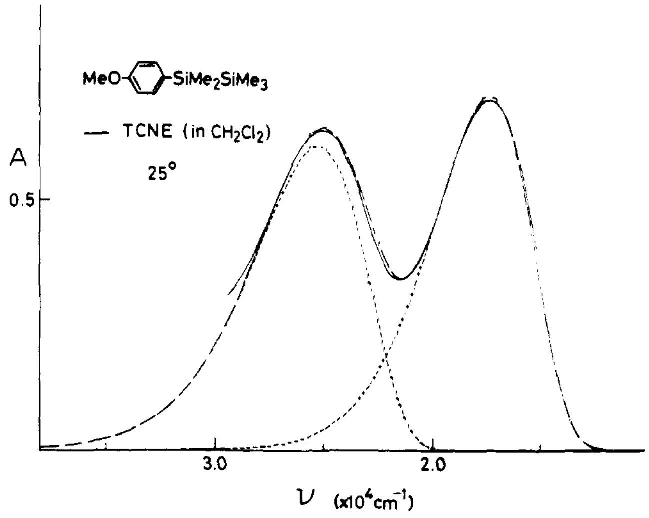

Figure 4. Experimental (—), simulated (— • —), and resolved (- - -) absorption bands for the p-methoxyphenylpentamethyldisilane-TCNE complex in dichloromethane at 25°.

The CT spectra of TCNE complexes with unsubstituted and three para-substituted phenylpentamethyldisilanes (p-R-C$_6$H$_4$SiMe$_2$SiMe$_3$, R = MeO, Me$_3$SiCH$_2$, and Me), as well as their band parameters, were determined by the following procedure. Since the two CT bands of the TCNE complexes overlapped, the overlapping asymmetric bands were resolved by computer simulation in which the individual band shapes were approximated by skewed Gaussian functions (eq 1),[7] where Y_0 is the peak height, X_0 is the

$$Y = Y_0 \exp(-\ln 2\,\{\ln\,[1 + 2b(X - X_0)/\Delta X_{1/2}]/b\}^2) \qquad (1)$$

peak position, $\Delta X_{1/2}$ is the bandwidth at half-height, and b is the asymmetry factor of the Gaussian function. Since the parameter $\Delta X_{1/2}$ for a skewed Gaussian no longer represents the normal half-bandwidth, the values were defined by the following expression

$$\Delta X_{1/2} = (X_U - X_L)b/\sinh b \qquad b \neq 0 \qquad (2)$$

where X_U and X_L are the upper and lower X values at which Y falls to $\frac{1}{2}Y_0$. The area beneath a skewed Gaussian band is given by

$$\text{area} = \tfrac{1}{2}(\pi/\ln 2)^{1/2} Y_0 \Delta X_{1/2} \exp[b^2/(4 \ln 2)] \qquad (3)$$

The results are shown in Figures 1-4 and Table I.

The possibility that two CT bands could originate from

Table I. Band Parameters for Charge-Transfer Spectra of Some Para-Substituted Phenylpentamethyldisilanes ($X-Ph-Si_2Me_5$) with TCNE (25° in CH_2Cl_2)

X	Band	Peak position, cm^{-1}	Peak height	Bandwidth, cm^{-1}	Asymmetry[e]	Area II[f]/area I
H[a]	I	25,100	0.57	6400	0.35	0.33_2
	II	20,500	0.26	4800	0.20	
CH_3[b]	I	24,600	0.84	5800	0.30	0.59_1
	II	19,500	0.57	5100	0.26	
Me_3SiCH_2[c]	I	24,100	0.24	5400	0.35	0.92_0
	II	17,600	0.23	5300	0.25	
MeO[d]	I	25,300	0.60	6000	0.34	1.03_6
	II	17,600	0.70	5400	0.28	

[a] Concentrations of disilane and TCNE were 1.85×10^{-1} mol/l. and 1.32×10^{-2} mol/l., respectively. [b] Disilane, 1.90×10^{-1} mol/l.; TCNE, 1.35×10^{-2} mol/l. [c] Disilane, 4.25×10^{-2} mol/l.; TCNE, 1.69×10^{-2} mol/l. [d] Disilane, 8.40×10^{-2} mol/l.; TCNE, 2.16×10^{-2} mol/l. [e] Asymmetric factor, *b*, in eq 1. [f] Area ratios did not depend on the concentration of each component.

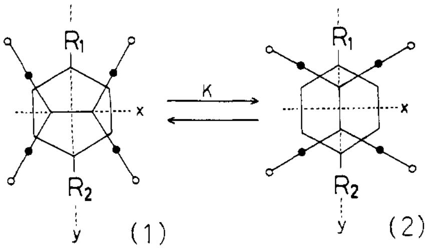

Figure 5. Two orientations of a TCNE-*p*-disubstituted benzene CT complex.

the relative orientation of the donor and acceptor was first pointed out by Orgel with respect to the complexes of chloranil with substituted benzenes.[8] According to Mulliken's maximum overlap principle,[9] interactions of TCNE with substituted benzenes result in the structures **1** and **2** (Figure 5). The occurrence of two CT bands is readily explained in terms of these two isomeric structures (Figure 6). In the X configuration (**1** in Figure 5), and electronic transition from the formerly degenerate e_{1g} orbital having a longitudinal node (y axis) (ϕ_{as}) to the lowest unoccupied TCNE orbital is allowed, while a transition from the orbital with a transverse node (x axis) (ϕ_s) is forbidden. In the Y configuration (**2** in Figure 5), the situation is reversed. Foster[6] has claimed that even if isomers such as those illustrated in Figure 5 exist, they could be taken as representing extreme conformer structures in which the relative rotation of one molecule with respect to its partner readily occurs. In this situation, the intensities of the two CT bands should be almost equal as shown in the charge-transfer complexes of TCNE with naphthalenes,[10] if each isomer has a nearly equal oscillator strength.

However, Holder and Thompson[11] recently have examined the absorption spectra of TCNE complexes with benzene, toluene, *p*-xylene, and *tert*-butylbenzene dissolved in chloroform, and found that all the ratios of band areas [area of the longer wavelength band (CT-II band):area of the shorter one (CT-I band)] are less than unity. These ratios decrease with an increase in the number and size of the alkyl substituent. Thus, with more bulky R_1 and R_2 groups (Figure 5) the Y configuration becomes increasingly less important compared to the X conformer ($K < 1$).

Therefore, the extremely low intensity of the band at the longer wavelength in the TCNE complex with phenylpentamethyldisilane relative to the shorter one could be considered as a result of bulkiness of the pentamethyldisilanyl group. However, the experimental fact demonstrates that the phenomena cannot be interpreted by the steric effect. If the lower intensity of the CT-II band compared with that of the CT-I band is attributable to bulkiness of the pentamethyldisilanyl group, we can expect that the intensity of the CT-II band will be reduced further by an introduction of a para substituent, such as *p*-methyl, *p*-trimethylsilylmethyl, and *p*-methoxy groups. The results, however, are far from this expectation. Introduction of the bulky Me_3SiCH_2 at the para position fails to reflect the predicted change in the relative intensity. Clearly the analysis of the relative intensity in terms of the bulkiness is inadequate, at least in the present case.

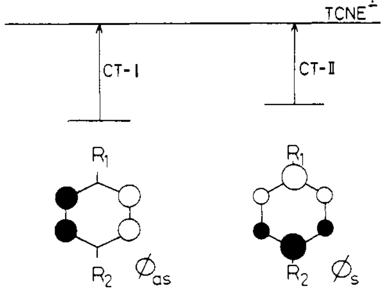

Figure 6. Qualitative MO scheme for a TCNE-*p*-disubstituted benzene CT complex.

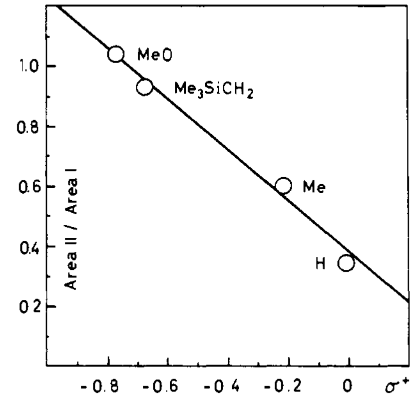

Figure 7. Plot of relative band area (area I/area II) for the absorption spectra of substituted phenylpentamethyldisilane-TCNE complexes vs. σ^+.

Table I shows that the relative area of band II/band I increases with increasing electron donating character of the substituent. We found that the relative areas gave an approximately linear relationship with σ^+ constants[12] of the substituents (Figure 7). It has been shown already that the σ^+ constants can be correlated to frequencies of the CT-II in the TCNE complexes of the substituted benzenes.[13] Therefore, these facts strongly suggest that the low intensity of the CT-II band of phenylpentamethyldisilane can be

Table II. Calculated First Ionization Potentials and Wave Functions of HOMO for Para-Substituted Phenylpentamethyldisilanes (X–Ph–Si_2Me_5)

X	IP,[a] eV	Wave function	σ(SiSi) fraction
H	8.35 (8.39)	$0.851\phi_{Si} - 0.526\phi_S$	0.72
p-Me	8.23 (8.24)	$0.757\phi_{Si} - 0.631\phi_S - 0.171\phi_X$	0.57
p-Me_3SiCH_2	8.02 (7.92)	$0.583\phi_{Si} - 0.710\phi_S - 0.395\phi_X$	0.34
p-MeO	7.93 (7.92)	$0.519\phi_{Si} - 0.713\phi_S - 0.471\phi_X$	0.27

[a] Ionization potentials estimated by the equation of Voigt–Reid (eq 8) are shown in parentheses.

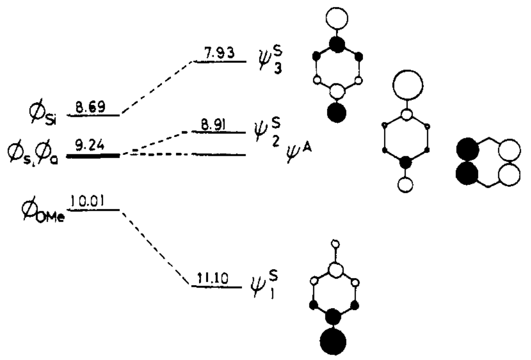

Figure 8. Qualitative π MO scheme for *p*-methoxyphenylpentamethyldisilane.

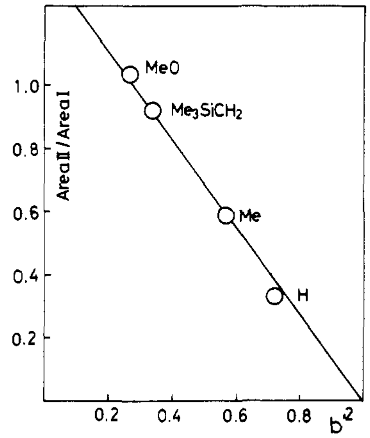

Figure 9. Plot of relative band area (area I/area II) for the absorption spectra of substituted phenylpentamethyldisilane-TCNE complexes vs. σ(SiSi) fraction of HOMO for phenylpentamethyldisilanes.

attributed, not to the bulkiness, but to the electronic effects of the pentamethyldisilanyl group. However, it is not *generally* true that the relative area of CT-II/CT-I of substituted phenylpentamethyldisilane is related to σ^+ constants. For example, the σ^+ constant of the *p*-Me_5Si_2 group determined by CT spectra is 0.62,[5] which is approximately equal to the value of the *p*-Me_3SiCH_2 group. Therefore, the ratio of CT-II/CT-I of *p*-$Me_5Si_2C_6H_4Si_2Me_5$ would be equal to that of *p*-$Me_3SiCH_2C_6H_4Si_2Me_5$. This is not true since the intensity of the CT-II band of *p*-$Me_5Si_2C_6H_4Si_2Me_5$ is quite low.

There are two considerations that we must take into account: low intensities of the σ(SiSi) → π CT compared to the π → π CT transitions and populations of the silicon-silicon σ bonding orbital in the highest occupied molecular orbital (HOMO). Very recently, Traven and West[14] and we[15] found the charge-transfer complexation of permethylpolysilanes with TCNE. The intermolecular σ → π charge transfer was evidenced by both the electronic spectra of the permethylpolysilane-TCNE complexes and the photoinduced ESR signal of the TCNE anion radical. The CT absorption spectra of the TCNE complexes with linear polysilanes had extremely low intensities, possibly due to both low formation constants of the complexes and the low oscillator strengths. In this context, it is reasonable to assign the origin of the CT-II band of phenylpentamethyldisilane to the transition from the σ-like bond. In other words, it has the character of a charge transfer arising from a σ-donor-π-acceptor complex rather than from a π-π complex.

These facts intuitively suggest that populations of the silicon-silicon σ bonding orbital in the HOMO should be important to determine the relative area of the CT-II band to that of the CT-I band, since the CT-II band of phenylpentamethyldisilane should arise from the transition from the HOMO (ψ_{HOMO}) which comprises a linear combination of the symmetric highest occupied orbital of benzene (ϕ_s) and the silicon-silicon σ bonding orbital (ϕ_{Si}) of hexamethyldisilane, as described in eq 4, to the lowest unoccupied molecular orbital of TCNE.

$$\psi_{HOMO} = a\phi_s + b\phi_{Si}$$
$$(a^2 + b^2 = 1 \qquad ab < 0) \tag{4}$$

The interaction diagram and perturbation theory[16] tell us that as the energy level of ϕ_S becomes higher, the less important becomes the contribution of ϕ_{Si} to ψ_{HOMO}. Introduction of an electron-donating group to benzene results in raising the energy level of ϕ_s, and then, the contribution of ϕ_{Si} to ψ_{HOMO} should decrease.

$$\phi_s, E_\pi — \boxed{\psi_{HOMO}} — \phi_{Si}, E_{Si} \tag{5}$$

For para-substituted phenylpentamethyldisilanes the HOMO ($\psi_{HOMO}{}^s$) should be constructed from ϕ_s, ϕ_{Si}, and ϕ_X. The latter stands for a pertinent π-type substituent orbital.

$$\psi_{HOMO}{}^s = a'\phi_s + b'\phi_{Si} + c\phi_X$$
$$(a'^2 + b'^2 + c^2 = 1) \tag{6}$$

The energy level and the wave function of the highest occupied orbital of a substituted phenylpentamethyldisilane may be determined by solving the following secular equation

$$\begin{vmatrix} E_{Si} - E & H_{Si,\pi} & 0 \\ H_{Si,\pi} & E_\pi - E & H_{X,\pi} \\ 0 & H_{X,\pi} & E_X - E \end{vmatrix} = 0 \tag{7}$$

where E_{Si}, E_π, and E_X can be evaluated from the first ionization potentials of hexamethyldisilane,[5] benzene, and pertinent substituent species ($E_{Si} = -8.69$, $E_\pi = -9.24$, $E_{CH_3} = -12.99$, $E_{CH_2SiMe_3} = -10.5$, and $E_{OMe} = -10.01$; the latter three were evaluated from IP values of CH_4,[17] $SiMe_4$,[5] and CH_3OCH_3,[18] respectively). $H_{Si,\pi}$ and $H_{X,\pi}$ stand for $\int \phi_s H' \phi_{Si} d\tau \approx c_1 \int \chi_p H' \phi_{Si} d\tau = (1/3^{1/2})\beta_{Si}$, and $\int \phi_s, H' \phi_X d\tau \approx c_4 \int \chi_p H' \phi_X d\tau = -(1/3^{1/2}))\beta_X$, respectively, where c_1 and c_4 are the coefficients of the atomic orbitals (χ_p) at the point of attachment of the pentamethyldisilanyl and substituent groups in the substituted phenylpentamethyldisilane. Values of β_{Si} and β_X are determined as reproducing the photoelectron first ionization potentials of the corresponding substituted benzenes. Thus, β_{Si}, β_{CH_3}, $\beta_{CH_2SiMe_3}$, and β_{OCH_3} are set equal to −0.95, −2.23, −2.39, and −2.38 eV, respectively. The essential features of qualitative π MO schemes for p-methoxyphenylpentamethyldisilane are shown in Figure 8 as an example. Both the energy levels and the wave functions of the HOMO of para-substituted phenylpentamethyldisilanes[19] can be calculated as shown in Table II. Calculated first ionization potentials are expectedly in good agreement with those estimated by the equation of Voigt-Reid (eq 8)[21] from the observed CT-II frequencies.

$$h\nu_{\mathrm{CT}}(\mathrm{eV}) = 0.83\mathrm{IP}(\mathrm{eV}) - 4.42 \qquad (8)$$

Interestingly and expectedly, the calculated populations of σ(SiSi) orbitals in the HOMO, b'^2, are linearly correlated with the relative area of the CT-II band to that of the CT-I band as shown in Figure 9. These facts indicate that the intensity of the CT-II band depends mainly on the σ fraction in the HOMO. For p-$Me_5Si_2C_6H_4Si_2Me_5$, the calculated σ(SiSi) population is 0.67. This value is rather comparable to that of phenylpentamethyldisilane itself. Therefore, it is not surprising that the relative intensity of the CT-II band of p-$Me_5Si_2C_6H_4Si_2Me_5$ is low in spite of the low absorption energy (~18,500 cm^{-1}).[22]

In conclusion, we must regard that the band with longer wavelength of the TCNE-phenylpentamethyldisilane complex is due to the transition from the highest occupied molecular orbital, constructed from the linear combination of the symmetric highest occupied MO of benzene with the SiSi bonding σ MO to the lowest unoccupied π MO of TCNE, and that the relative band intensities of para-substituted phenylpentamethyldisilane-TCNE complexes reflect the σ(SiSi) population to the HOMO of the donor.

Experimental Section

Materials. Phenyl-,[23] p-methylphenyl-,[24] and p-methoxyphenylpentamethyldisilane[24] were prepared by the standard Grignard reaction similar to the following example.

(p-Trimethylsilylmethylphenyl)pentamethyldisilane was prepared from the Grignard reaction of p-bromobenzyltrimethylsilane[25] (28 g, 0.115 mol) and magnesium (3 g, 0.123 g-atom) with chloropentamethyldisilane[26] (17 g, 0.102 mol) in 77.5% yield: bp 114-115° (2 mm); $n^{20}\mathrm{D}$ 1.5004; $d^{20}{}_4$ 0.8661; MR$_\mathrm{D}$ 100.1 (calcd 98.8); NMR (CCl_4, δ, ppm) −0.04 (s, 9 H), 0.01 (s, 9 H), 0.28 (s, 6 H), 2.04 (s, 2 H), 7.10 (m, 4 H); mass spectrum m/e 294 (M^+). Anal. Calcd for $C_{15}H_{30}Si_3$: C, 61.14; H, 10.26. Found: C, 61.36; H, 10.35.

Charge-Transfer Spectra. Commercially available TCNE was sublimed before use. Dichloromethane was purified according to the literature.[27] Charge-transfer spectra of phenylpentamethyldisilanes with TCNE were measured at 25° in dichloromethane using a Hitachi 139 spectrophotometer.

Computer simulations were carried out as follows by using a Varian Data Machines' ADAPTS in connection with an X-Y recorder driven by a stepping motor. First, 1000 points calculated from the observed 50-70 data by linear approximation between two neighboring points were drawn on the recorder by executing the program "UVSPEC" and then the program "UVPOUT" written with Ebasic language (solid lines in Figures 1-4). Second, 1000 points, calculated from the sum of two skewed Gaussian functions whose parameters are tentatively assumed, were drawn by executing the Ebasic programs "UVPLOT" and the "UVPOUT", and superimposed on the chart obtained above (dot-dash lines in Figures 1-4). Calculations were recorded 4 to 20 times for varied parameters until the observed spectra were reproduced satisfactorily. Each spectrum was separated into two bands by recalculation of the component skewed Gaussian function by using the optimized parameters (dotted lines in Figures 1-4). Areas beneath the band were also calculated by executing "UVAREA".

The HMO perturbation calculation was carried out using the NEAC-TSS Computer System of this Department.

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