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Magnetic Field Effects on the Photoinduced Electron-Transfer Reactions between Hexamethyldisilane and Aromatic Nitriles in Brij 35 Micellar Solutions

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Transient absorptions due to the anion radicals of several aromatic nitriles were measured in their electron-transfer reactions from hexamethyldisilane by means of a nanosecond laser flash photolysis technique. With direct excitation, the yields of the escaped anion radicals of *p*- and *o*-dicyanobenzenes increased with increasing magnetic field strength from 0 to 1.35 T. At 1.35 T, the yield of the *p*-dicyanobenzene anion radical became 1.23 ± 0.05 times as large as that at 0 T. With triplet sensitization of *p*-dicyanobenzene and 1,2,4,5-tetracyanobenzene, the yields at 1.0 T were 1.61 ± 0.15 and 1.11 ± 0.05 times as large as those at 0 T, respectively. These magnetic field effects can be interpreted by hyperfine coupling and relaxation mechanisms in the case of triplet radical pairs. The effect reveals that electron transfer partially occurs through triplet states of aromatic nitriles even with direct excitation.

1. Introduction

Magnetic field effects on the photoinduced electron-transfer reactions of singlet and triplet excited states have hitherto been studied extensively.^{1,2} In almost all of these reports, however, electron donors have been fairly limited. Especially, no magnetic field effect has been found for any photoinduced electron-transfer reaction of a donor-acceptor system containing a heavy atom such as Si and Ge, because of the spin-orbit interaction of such a heavy atom.

On the other hand, the σ -bonds between group 14 elements (Si-Si, Ge-Ge, and Sn-Sn) have rather low ionization potentials.³ Their values are close to those of carbon-carbon π -bonds, not of their σ -bonds. Therefore, peralkylpolysilanes and germanes have been proved to act as good electron donors.⁴ The spin polarization measurements such as chemically induced dynamic nuclear polarization (CIDNP)⁵ and chemically induced dynamic electron polarization (CIDEP)⁶ are very useful to elucidate the reaction mechanisms of electron transfer. In a previous paper,⁷ we studied photoinduced electron-transfer reactions between hexamethyldisilane and quinones by means of a CIDNP technique. Here, electron transfer easily occurred between the triplet states of quinones and disilane, where the disilane cation and the quinone anion radicals were generated immediately after irradiation. In addition, the generated disilane cation radical has a much larger *g* value than the cation radicals of the usual aromatic compounds. In this circumstance, magnetic field effects due to the Δg mechanism are expected for such reactions.^{1,2}

Photoinduced electron-transfer reactions of aromatic nitriles have been a very active research area because of interest in synthetic chemistry and reaction mechanisms. In the present paper, we also chose hexamethyldisilane as an electron donor and performed a laser flash photolysis study of its photoinduced electron-transfer reactions with several aromatic nitriles in a micellar Brij 35 solution. Here, we found magnetic field effects on the yields of escaped anion radicals in some systems. To clarify the mechanism of the observed magnetic field effects, we have also measured fluorescence spectra, quantum yields, and picosecond fluorescence time profiles of nitriles. As far as we know, this is the first detailed study of the magnetic field effect on a photoinduced electron-transfer reaction containing a heavy atom such as Si.

2. Experimental Section

Material. Hexamethyldisilane ($\text{Me}_3\text{SiSiMe}_3$) supplied by Kanto Chemical Co. was distilled. 1,2,4,5-Tetracyanobenzene (TCNB), 9,10-diicyanoanthracene (DCA), 1,4-dicyanobenzene (*p*-DCNB), 1,2-dicyanobenzene (*o*-DCNB), and xanthone were recrystallized repeatedly from ethanol. Benzonitrile (BN) of guaranteed reagent grade supplied by Aldrich Chemical Co. and 9,10-diphenylanthracene of guaranteed reagent grade supplied by Nakarai Chemicals Ltd. were used without further purification. Poly-

(oxyethylene) (23) dodecyl ether (Brij 35) supplied by Kanto Chemical Co. was used as received. Water was deionized and distilled.

Laser Flash Photolysis. Laser flash photolysis experiments were performed on nitrogen-bubbled solutions at room temperature by using the fourth harmonic (266 nm) of a Quanta-Ray GCR-11 Nd:YAG laser as an exciting light source. The concentrations of hexamethyldisilane, each of the nitriles, and Brij 35 in the employed micellar solution were 1.5×10^{-3} , $(1-1.5) \times 10^{-3}$, and 5.0×10^{-2} mol dm⁻³, respectively. The sample flowed through a quartz photolysis cell with a constant flow rate. The laser flash photolysis apparatus was similar to that published elsewhere.⁸ Magnetic fields (*B*) up to 1.35 T were provided by a Mitsubishi 6MA-EM1275A electromagnet. The lowest magnetic field generated by a countercurrent for canceling the residual field was less than 0.2 mT. Hereafter, the experiments under the lowest magnetic field are denoted as those in the absence of a magnetic field.

Fluorescence. Fluorescence spectra and the fluorescence quantum yield were measured with Jasco FP-777 and Hitachi F-4010 spectrometers, with 9,10-diphenylanthracene being used for the standard.

Fluorescence Time Profiles. Fluorescence time profiles were measured with a single-photon-counting system,⁹ where a Spectra Physics 375B-374 synchronously pumped cavity-dumped dye laser was used as a picosecond excitation light source. This dye laser was excited by the second harmonic of a Spectra Physics 3460 Nd:YAG laser and operated with a pulse width (fwhm) of 6 ps and with a repetition rate of up to 800 kHz. The excitation wavelength was covered by the lasing region of the second harmonic of Rhodamine 6G. The second harmonic was generated with a β -BBO crystal. Fluorescence was detected by a Hamamatsu Photonics R2809U-01 multichannel plate photomultiplier, and its time profile was measured with an EG&G ORTEC single-photon-counting system connected to a NIKON G250 25-cm monochromator. An ORTEC 7800 multichannel analyzer was coupled with an NEC PC9801VX microcomputer system for saving the data. The rise and decay shapes of fluorescence were analyzed by a convolution-simulation method using the observed time profile of the scattered laser light as a reference. Details concerning the apparatus for fluorescence time profile measurements have been published elsewhere.¹⁰

3. Results and Discussion

Transient Absorption Spectra. The Brij 35 micellar solution containing hexamethyldisilane ($\text{Me}_3\text{SiSiMe}_3$) and *p*-dicyanobenzene (*p*-DCNB) was excited with the fourth harmonic of the Nd:YAG laser. The time profiles of the transient absorption ($A(t)$) were measured in the wavelength region of 300–600 nm. The transient absorption spectrum obtained at a delay time of 200 ns after laser excitation is shown in Figure 1. The spectral

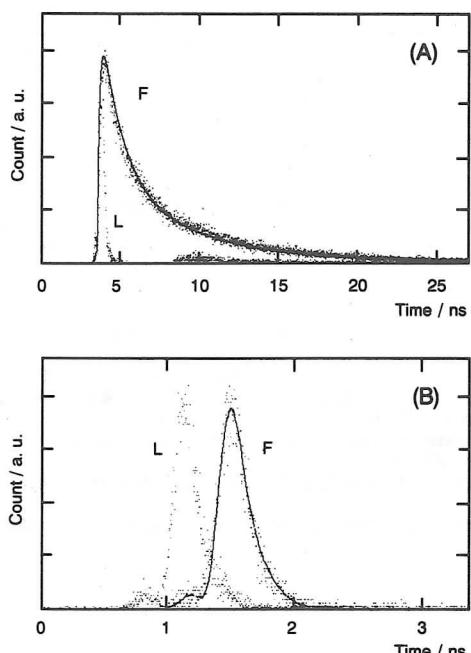


Figure 8. Time profiles of the excitation laser (L) and fluorescence (F) measured with the single-photon-counting system for (A) *p*-DCNB and (B) TCNB in Brij 35 at room temperature. Wavelengths of excitation and observation were (A) 295 and 315 nm and (B) 305 and 330 nm, respectively. The L profile of B was shifted to 329 ps (100 channels), left of the original position. The decay profiles were simulated with the laser shape (L) and lifetimes of (A) 1.3 ns and (B) 66 ps, respectively.

TABLE VI: Fluorescence Quenching Rate Constants of Aromatic Nitriles with $\text{Me}_3\text{SiSiMe}_3$

nitrile	k_{qD} , $\text{s}^{-1} \text{M}^{-1}$	
	in Brij 35	in acetonitrile (ref)
<i>p</i> -DCNB	4.9×10^{10}	2.2×10^{10} (24)
TCNB	<i>a</i>	
BN		4.5×10^9 (24)

^aThe lifetime of TCNB in Brij 35 micellar solution is too short to determine the quenching rate constant.

measurements of magnetic field effects can be estimated to be about 60 ps. On the other hand, the fluorescence lifetime of TCNB in acetonitrile was observed to be 8.6 ns. Therefore, the quantum yield of the triplet state (Φ_T) of TCNB in the former solution should be as small as about 0.7% of the Φ_T value in acetonitrile. This is due to the fast quenching of $^1\text{TCNB}^*$ by Brij 35 and $\text{Me}_3\text{SiSiMe}_3$. Therefore, electron transfer should occur almost through $^1\text{TCNB}^*$ with direct excitation of the Brij 35 micellar solution containing TCNB and $\text{Me}_3\text{SiSiMe}_3$. This is the reason why no magnetic field effect was observed for the TCNB system with direct excitation. On the other hand, the fluorescence lifetime of *p*-DCNB was relatively long in comparison with that of TCNB. Its lifetime in the employed Brij 35 micellar solution for the measurement of the magnetic field effect was about 1.2 ns. Because its lifetime in acetonitrile was 12.5 ns, its Φ_T value in the micellar solution can be estimated to be at least 9.6% of the value in acetonitrile. Thus, we can safely conclude that $^3\text{p-DCNB}^*$ is formed to a certain extent with direct excitation of the Brij 35 micellar solution containing *p*-DCNB and $\text{Me}_3\text{SiSiMe}_3$. This may be the reason why magnetic field effects due to a triplet precursor could be observed for the *p*-DCNB system with direct excitation.

Reaction Scheme. From the present study, the reaction scheme of electron transfer between $\text{Me}_3\text{SiSiMe}_3$ and aromatic nitriles can be summarized as shown in Figure 9. Since the excitation light was selectively absorbed by an aromatic nitrile (A) in the initial stage of the reaction, the singlet excited state of A ($^1\text{A}^*$) should be generated immediately with direct irradiation. Electron transfer occurs from $\text{Me}_3\text{SiSiMe}_3$ to $^1\text{A}^*$ for each of the donor-

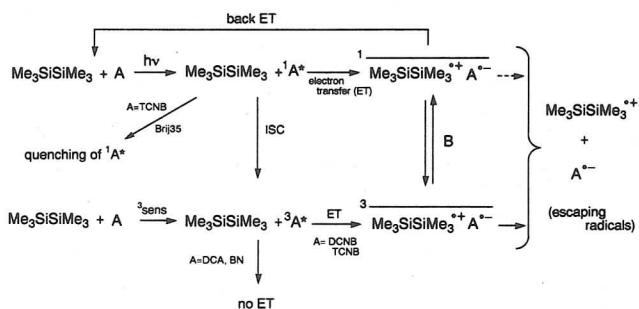


Figure 9. Reaction scheme for the photoinduced electron transfer between hexamethyldisilane and aromatic nitriles in the Brij 35 micellar solution.

acceptor systems used in the present study, giving the singlet radical pair of $\text{Me}_3\text{SiSiMe}_3^+$ and A^- . The generated radical pair disappears by back electron transfer or escape from the cage (which is minor process). Although the lifetime of $^1\text{TCNB}^*$ in the Brij 35 micellar solutions was very short, those of DCNB, DCA, and BN seemed to be relatively long. Therefore, in the singlet excited states of DCNB, DCA, and BN, inter-system crossing (ISC) occurs to generate their triplet ones ($^3\text{A}^*$). Triplet excited states which are formed through ISC from $^1\text{A}^*$ or triplet sensitization with xanthone can also induce electron transfer. However, the triplet energies of DCA and BN are not enough to derive electron from $\text{Me}_3\text{SiSiMe}_3$ to $^3\text{A}^*$. On the other hand, $^3\text{DCNB}^*$ and $^3\text{TCNB}^*$ can produce the triplet radical pairs of $\text{Me}_3\text{SiSiMe}_3^+$ and A^- . It has been widely accepted that electron transfer of aromatic nitriles occurs through their singlet excited states with direct excitation. It is noteworthy, however, that the present study of magnetic field effects has revealed that electron transfer can also occur through their triplet states even with direct excitation.

For each of the generated triplet radical pairs, its triplet (T)-singlet (S) mixing occurs for all triplet levels through the HFCM in the absence of a magnetic field. Because the triplet levels split into three sublevels (T_0 , T_{+1} , and T_{-1}) in the presence of a magnetic field, the $T_{\pm 1}$ -S mixings are almost blocked by the field which is higher than the half-field ($B_{1/2}$) characteristic to the HFCM.²⁸ Thus, only T_0 -S mixing occurs in the presence of a relatively low field ($B_{1/2} < B < 0.1$ T), and T-S conversion of the radical pair is reduced by such a low field (HFCM).^{8,23} The magnetic field effect due to the HFCM, however, should be saturated at a relatively low field. In addition, the relaxations from T_{+1} and T_{-1} to T_0 and S should also be taken into consideration for the interpretation of the effects in high fields ($B > 0.1$ T). The relaxation rate should decrease with increasing B . The magnetic field effects observed for $R(B)$ at high fields ($B > 0.1$ T) can be explained by the RM.^{8,23} Consequently, T-S conversion of the radical pairs is reduced by the field (HFCM and RM), and the yield of the escaping anion radicals is enhanced.

4. Conclusion

In the present study, we found that the yields of the escaped anion radicals of the aromatic nitriles such as *p*-DCNB, *o*-DCNB, and TCNB increased with increasing B from 0 to 1.35 T for electron transfer from $\text{Me}_3\text{SiSiMe}_3$ in the Brij 35 micellar solution. When *p*-DCNB was used, the yield of the escaped $p\text{-DCNB}^-$ at 1.35 T became 1.23 ± 0.05 times as large as that at 0 T with direct excitation. With triplet sensitization of *p*-DCNB and TCNB, the yields at 1.0 T were 1.61 ± 0.15 and 1.11 ± 0.05 times as large as those at 0 T, respectively. These magnetic field effects can be interpreted by the HFCM and RM in the case of triplet radical pairs. The effect also gives new evidence for the electron transfer through triplet states of aromatic nitriles even with direct excitation. This process has been hitherto overlooked.

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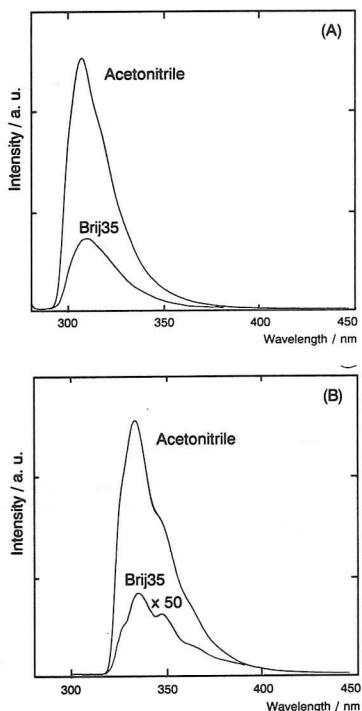


Figure 6. Fluorescence spectra of the acetonitrile and Brij 35 solutions containing (A) *p*-DCNB and (B) TCNB. The spectra were normalized by the molar extinction coefficients of the nitriles and the intensity of exciting light source.

TABLE III: Fluorescence Quantum Yields of *p*-DCNB and TCNB in Acetonitrile and Brij 35 Micellar Solutions at Room Temperature

nitrile	fluorescence quantum yield (Φ_f) ^a	
	in acetonitrile	in Brij 35
<i>p</i> -DCNB	0.94	0.3
TCNB	0.86	0.03

^a Measured with 9,10-diphenylanthracene as the standard.

spectra are shown in Figure 6. The Φ_f values are summarized in Table III. These results show that the Φ_f values of *p*-DCNB and TCNB are reduced by changing the solvent from acetonitrile to Brij 35. Especially, the Φ_f value of TCNB in Brij 35 became as small as 3.5% of the value in acetonitrile. On the other hand, the Φ_f value of *p*-DCNB in Brij 35 was 32% of the value in acetonitrile. These facts indicate that almost all of the $^1\text{TCNB}^*$ is quenched in the Brij 35 micellar solution of TCNB, but that $^1\text{DCNB}^*$ is not so completely quenched.

Second, in order to determine the fluorescence quenching rates by Brij 35 ($k_{qB}[\text{Brij 35}]$), the time profiles of fluorescence in acetonitrile were measured with the picosecond laser as an exciting light source in the absence and presence of Brij 35. Typical results of the time profiles are shown in Figure 7. The obtained fluorescence lifetimes (τ_f) of the *p*-DCNB and TCNB systems are listed in Table IV. The plots of $1/\tau_f$ vs concentration of Brij 35 have good linear relationships:

$$1/\tau_f = 1/\tau_{f0} + k_{qB}[\text{Brij 35}] \quad (5)$$

From the slope of these plots, the k_{qB} values were calculated to be $7.5 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$ for *p*-DCNB and $4.4 \times 10^{10} \text{ s}^{-1} \text{ M}^{-1}$ for TCNB, respectively. These results indicate that the singlet excited state of TCNB can be quenched by Brij 35 with the diffusion-controlled rate. Moreover, we measured the fluorescence lifetime (τ_f') of *p*-DCNB and TCNB in the Brij 35 micellar solution, which is used for the measurements of magnetic field effects in the present study. The τ_f' values were obtained to be as small as 1.3 ns for *p*-DCNB and 66 ps for TCNB as shown in Table V.

Third, in order to determine the fluorescence quenching rate of $\text{Me}_3\text{SiSiMe}_3$ ($k_{qD}[\text{Me}_3\text{SiSiMe}_3]$) in the Brij 35 micellar solution, time profiles of fluorescence were measured in the absence and presence of $\text{Me}_3\text{SiSiMe}_3$. Typical results of the time profiles

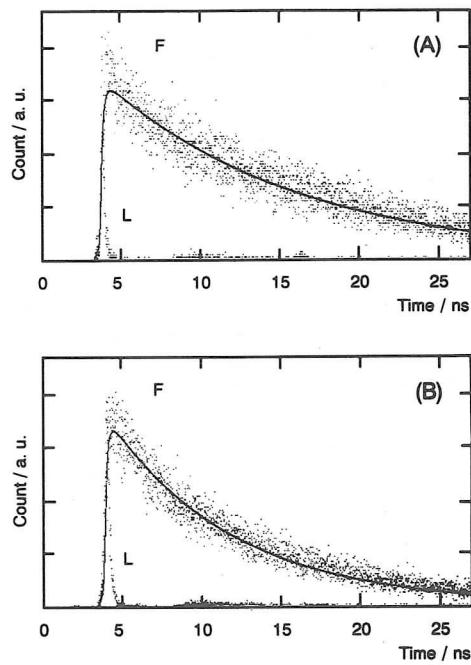


Figure 7. Time profiles of the excitation laser (L) and fluorescence (F) measured with the single-photon-counting system for (A) *p*-DCNB and (B) TCNB in acetonitrile at room temperature. Wavelengths of excitation and observation were (A) 295 and 315 nm and (B) 305 and 330 nm, respectively. The decay profiles were simulated with the laser shape (L) and lifetimes of (A) 12.5 ns and (B) 8.6 ns, respectively.

TABLE IV: Fluorescence Lifetimes (τ_f) of Aromatic Nitriles in Acetonitrile

nitrile	Brij 35, mmol dm ⁻³	τ_f , ns	ref
TCNB	0.0	8.6 ^a	this work
	4.6	3.2 ^a	this work
	19.2	0.90 ^a	this work
	41.5	0.52 ^a	this work
<i>p</i> -DCNB	0.0	12.5 ^a	this work
	18.4	3.3 ^a	this work
	80.0	1.3 ^a	this work
		8.8	27
<i>m</i> -DCNB		13.9	27
<i>o</i> -DCNB		5.7	27
BN		4.2	24

^a The experimental errors of τ_f are within $\pm 5\%$.

TABLE V: Fluorescence Lifetimes (τ_f') of Aromatic Nitriles in the Brij 35 Micellar Solution

nitrile	$\text{Me}_3\text{SiSiMe}_3$, mmol dm ⁻³	τ_f' , ns
TCNB	0.0	0.066
	7.1	0.049
<i>p</i> -DCNB	0.0	1.3
	2.0	1.2
	7.0	0.90
	8.8	0.83

^a The experimental errors of τ_f' are within $\pm 5\%$.

observed for *p*-DCNB and TCNB are shown in Figure 8. The obtained τ_f' values are listed in Table V. The plots of $1/\tau_f'$ for *p*-DCNB vs concentration of $\text{Me}_3\text{SiSiMe}_3$ have a good linear relationship:

$$1/\tau_f' = 1/\tau_{f0}' + k_{qD}[\text{Me}_3\text{SiSiMe}_3] \quad (6)$$

From the slope of the plots, k_{qD} is calculated to be $4.9 \times 10^{10} \text{ s}^{-1} \text{ M}^{-1}$ as listed in Table VI. This value shows that the electron transfer from $\text{Me}_3\text{SiSiMe}_3$ to $^1\text{p-DCNB}^*$ occurs with the diffusion-controlled rate. On the other hand, k_{qD} for TCNB could not be obtained in the Brij 35 micellar solution, because the fluorescence lifetime was too short to determine the rate.

From the τ_f' values listed in Table V, the fluorescence lifetime of TCNB in the employed Brij 35 micellar solution for the

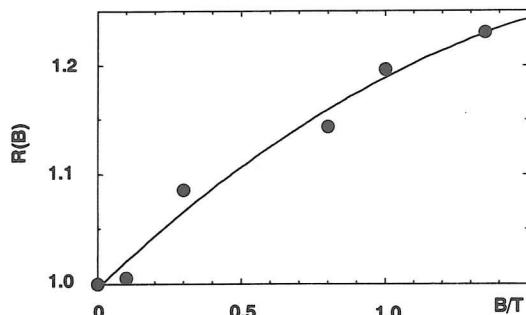


Figure 3. Magnetic field dependence of the ratio $R(B) = Y(B)/Y(0)$ at 350 nm observed by direct excitation of the Brij 35 micellar solution containing $\text{Me}_3\text{SiSiMe}_3$ and *p*-DCNB. The experimental error of $R(B)$ is within ± 0.05 .

TABLE II: Ratio (R) of the Relative Yield of the Escaped Nitrile Anion Radical at 1.0 T to That at 0 T

nitrile	excitation ^a	$R(1.0 \text{ T})$
<i>p</i> -DCNB	D	1.20 ± 0.05^b
	T	1.61 ± 0.15^b
<i>o</i> -DCNB	D	1.16 ± 0.05^b
	T	1.11 ± 0.05^c
TCNB	D	1.00 ± 0.05^b
DCA	D	1.00 ± 0.05^b
	T	1.00 ± 0.05^b
BN	D	1.00 ± 0.05^b

^aD and T mean direct excitation (observed 4 μs after excitation) and triplet sensitization with xanthone (observed 15 μs after excitation), respectively. ^bObserved at 350 nm. ^cObserved at 360 nm.

against B in Figure 3. As clearly seen from this figure, $R(B)$ is increased with increasing B , $R(1.35 \text{ T})$ reaching 1.23 ± 0.05 . When *o*-DCNB was used as an acceptor, a similar magnetic field effect was obtained for $R(B)$ and the $R(1.35 \text{ T})$ value became 1.18 ± 0.05 . The $R(1.0 \text{ T})$ values obtained for *p*-DCNB, *o*-DCNB, TCNB, DCA, and BN are listed in Table II.

Mechanism of Magnetic Field Effects. In the present laser flash photolysis studies, we have found that the yields of the escaped DCNB anion radicals are increased with increasing B . These magnetic field effects can be interpreted by either of the following two mechanisms:^{8,23} (1) The hyperfine coupling and relaxation mechanisms (HFCM and RM) in the case of triplet precursors; (2) the Δg mechanism in the case of singlet precursors.

The photoinduced electron-transfer reactions between hexamethyldisilane and aromatic nitriles have widely been believed to occur through the singlet excited states of nitriles in homogeneous solution such as acetonitrile and dichloromethane.²⁴ Since the g values of $\text{Me}_3\text{SiSiMe}_3^{+}$ and DCNB^{-} are reported to be 2.0075 and 2.0026, respectively,^{25,26} this radical pair has a very large difference in g values ($\Delta g = 0.0049$). Thus, the magnetic field effects by the Δg mechanism may be expected for this system. The obtained lifetime of the radical pair, however, is as long as 1–2 μs . On the other hand, the S-T₀ mixing should be completed in a much shorter time region (<100 ns).¹ Consequently, the observed magnetic field effects are not attributable to the Δg mechanism.

In order to confirm the possibility of the HFCM and RM in the case of triplet precursors, we carried out triplet sensitization of the present electron-transfer reactions, using *p*-DCNB, TCNB, and DCA. Here, xanthone was used as a triplet sensitizer. When *p*-DCNB and TCNB were used, the transient absorption spectra due to the corresponding nitrile anion radicals were observed. These spectra grew with the concomitant decay of the T-T absorption of xanthone. On the other hand, DCA did not give any appreciable spectrum due to its anion radical. These results can be explained by the schematic energy diagram as shown in Figure 4. The triplet energies (E_T) of the aromatic nitriles are also listed in Table I. Figure 4 indicates that the triplet energies of DCNB and TCNB are enough to generate electron transfer from $\text{Me}_3\text{SiSiMe}_3$ to the nitriles but that of DCA is not enough to do so.

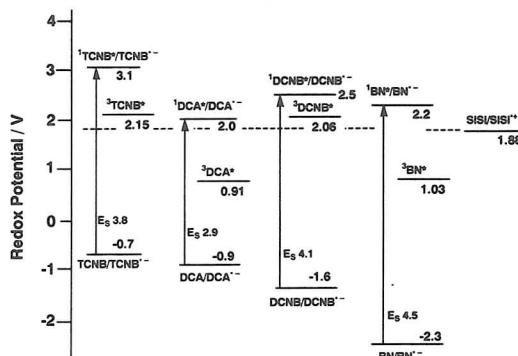


Figure 4. Schematic energy diagram of photoinduced electron transfer between $\text{Me}_3\text{SiSiMe}_3$ and aromatic nitriles.

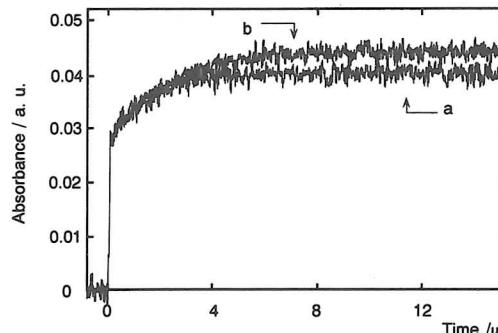


Figure 5. $A(t)$ curves at 360 nm observed by triplet sensitization of the Brij 35 micellar solution containing xanthone, $\text{Me}_3\text{SiSiMe}_3$, and TCNB (a) in the absence and (b) in the presence of a magnetic field of 1.0 T.

Next, the magnetically induced changes of the $A(t)$ curves were investigated for triplet sensitization. Both *p*-DCNB and TCNB showed appreciable magnetic field effects. The typical results for TCNB are shown in Figure 5. We can see from this figure that the yield of the escaped TCNB^{-} increased with increasing B . Since the lifetime of the triplet excited state of xanthone is about 4 μs , $R(B)$ was obtained at 15 μs after laser excitation. The $R(1.0 \text{ T})$ value of the escaped TCNB^{-} became 1.11 ± 0.05 times as large as that at 0 T. Similar results were also observed for *p*-DCNB. The obtained $R(1.0 \text{ T})$ values are listed in Table II.

These magnetic field effects can clearly be interpreted by the HFCM and RM in the case of triplet precursors. As mentioned above, the effects observed with direct excitation of *p*-DCNB and *o*-DCNB are similar to those observed with triplet sensitization of *p*-DCNB and TCNB. Thus, we concluded that the present magnetic field effects were caused by the HFCM and RM in the case of triplet radical pairs. Of course, electron transfer through the singlet excited states of nitriles mainly occurs, but it should give no magnetic field effect. On the other hand, it is noteworthy that electron transfer should also occur through the triplet states of *p*-DCNB and *o*-DCNB with direct excitation and that this process plays a very important part for the appearance of magnetic field effects.

Fluorescence Measurements. As shown in Figure 4, the triplet energy of TCNB is enough to proceed the electron transfer from $\text{Me}_3\text{SiSiMe}_3$ to $^3\text{TCNB}^*$. In this process, magnetic field effects were actually observed. It is not clear, however, why there was no magnetic field effect with direct excitation of TCNB. On the other hand, similar magnetic field effects were observed for the electron transfer between $\text{Me}_3\text{SiSiMe}_3$ and *p*-DCNB with both direct excitation and triplet sensitization. Unfortunately, neither CIDNP nor CIDEPE was observed for the present systems. In order to clarify the difference between direct excitation of DCNB and TCNB, we carried out fluorescence spectra, quantum yields, and picosecond time profile measurements at room temperature.

First, we investigated the fluorescence of *p*-DCNB and TCNB without $\text{Me}_3\text{SiSiMe}_3$. Fluorescence spectra and quantum yields (Φ_f) were measured for the acetonitrile and Brij 35 solutions containing *p*-DCNB and TCNB, respectively. The obtained

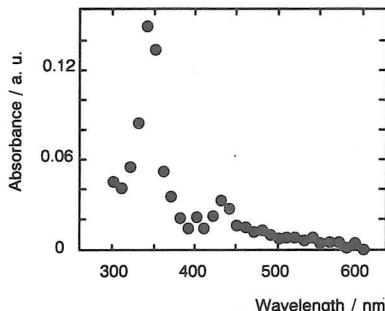
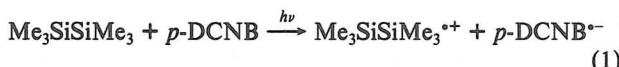


Figure 1. Transient absorption spectrum observed at a delay time of 200 ns after laser excitation of the micellar Brij 35 solution of $\text{Me}_3\text{SiSiMe}_3$ and *p*-DCNB at room temperature.

shape was not changed until 15 μs after excitation. This spectrum has two peaks at 340 and 430 nm, and the $A(t)$ curves at these peaks decayed with the same time profile. These peaks can safely be assigned to the *p*-DCNB anion radical produced through the following electron-transfer reaction:



The assignment of the observed spectrum to $p\text{-DCNB}^{\bullet-}$ was confirmed by the following reasons: (i) The spectral shape and the peak positions of the observed spectrum agree well with those of $p\text{-DCNB}^{\bullet-}$ reported in the literature.¹¹ (ii) The triplet excited state of *p*-DCNB may be generated by irradiation. However, its triplet-triplet (T-T) absorption appears around 500 nm.¹² Thus, the observed spectrum is not due to the T-T absorption. (iii) The hexamethyldisilane cation radical ($\text{Me}_3\text{SiSiMe}_3^{\bullet+}$) should be generated through reaction 1, and the trimethylsilyl radical ($\text{Me}_3\text{Si}^{\bullet}$) and cation (Me_3Si^+) should be formed through the succeeding reaction of $\text{Me}_3\text{SiSiMe}_3^{\bullet+}$:



The transient absorption spectrum of the trialkylsilyl radical ($\text{Et}_3\text{Si}^{\bullet}$) was reported,¹³ and its absorption band lies at a much shorter wavelength region (<320 nm) than the 340-nm peak of $p\text{-DCNB}^{\bullet-}$. Thus, $\text{Me}_3\text{Si}^{\bullet}$ seems to have no absorption in the region of 340–430 nm. On the other hand, there is no report for the absorption spectrum of the trimethylsilyl cation (Me_3Si^+). Since Me_3Si^+ has no conjugated system in its structure, it is not possible for Me_3Si^+ to have absorption bands in such a long-wavelength region (340–430 nm). Concerning the absorption spectrum of $\text{Me}_3\text{SiSiMe}_3^{\bullet+}$, we have recently measured it by means of γ -ray irradiation of $\text{Me}_3\text{SiSiMe}_3$ in a Freon matrix at 77 K.¹⁴ The observed absorption band of $\text{Me}_3\text{SiSiMe}_3^{\bullet+}$ lies at a shorter wavelength region than 340 nm and has no peaks at such wavelengths of 340 and 430 nm. These facts indicate that the observed spectrum in the present study is not due to $\text{Me}_3\text{Si}^{\bullet}$, Me_3Si^+ , and $\text{Me}_3\text{SiSiMe}_3^{\bullet+}$, but to DCNB^{•-}.

The laser flash photolysis measurements were also carried out for the electron donor-acceptor systems containing other nitriles. The systems containing 1,2,4,5-tetracyanobenzene (TCNB), 9,10-dicyanoanthracene (DCA), *o*-dicyanobenzene (*o*-DCNB), and benzonitrile (BN), respectively, gave similar transient absorption spectra, which can safely be assigned to the anion radicals of the corresponding nitriles in comparison with those reported in the literature.¹¹

These results indicate that the photoinduced electron-transfer reactions, such as the reaction shown in eq 1, occur easily for the present systems. Free-energy changes (ΔG_{ET} values) were calculated by the Rehm-Weller equation:¹⁵

$$\Delta G_{\text{ET}} = -E_s - E^{\text{red}} + E^{\text{ox}} - 0.06 \text{ eV} \quad (3)$$

Here, E_s is the lowest singlet-state energy of the corresponding nitrile. E^{red} and E^{ox} are the reduction potentials of the electron acceptor and the oxidation ones of the electron donor, respectively. In Table I, these parameters and the ΔG_{ET} values calculated with eq 3 are listed. For all electron donor-acceptor systems in the

TABLE I: Free-Energy Changes (ΔG_{ET}) for Electron Transfer from $\text{Me}_3\text{SiSiMe}_3$ to Aromatic Nitriles

nitrile	$E_s,^a$ eV	$E^{\text{red}},^b$ V vs SCE	$\Delta G_{\text{ET}},^c$ kJ mol $^{-1}$	E_T, eV
TCNB	3.8	-0.7	-124	2.85 ^d
DCA	2.9	-0.9	-17.4	1.81 ^e
<i>p</i> -DCNB	4.1	-1.6	-65.6	3.66 ^f
BN	4.5	-2.3	-36.7	3.33 ^g

^a Reference 16. ^b In acetonitrile. ^c Calculated using eq 3. $E^{\text{ox}}(\text{Me}_3\text{SiSiMe}_3) = 1.88$ eV (ref 17). ^d Reference 18. ^e Reference 19. ^f Reference 20. ^g Reference 21.

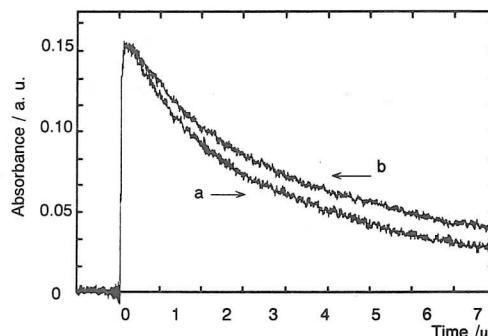


Figure 2. $A(t)$ curves at 350 nm observed by direct excitation of the Brij 35 micellar solution containing $\text{Me}_3\text{SiSiMe}_3$ and *p*-DCNB (a) in the absence and (b) in the presence of a magnetic field of 1.0 T.

present study, the ΔG_{ET} values were shown to be large negative ones. This fact indicates that the exothermic electron-transfer reaction should occur from $\text{Me}_3\text{SiSiMe}_3$ to the singlet excited state of each of the aromatic nitriles.

Magnetic Field Effects on the Time Profile of Transient Absorption ($A(t)$). The $A(t)$ curves were measured at the peak position of each of the Brij 35 micellar solutions of the donor-acceptor systems in the magnetic field range of 0–1.35 T. Although the systems containing BN, TCNB, and DCA did not show any magnetic field effect on the $A(t)$ curves, those containing *p*-DCNB and *o*-DCNB were appreciably affected by the fields. Typical curves obtained at 0 and 1.0 T for the solution containing $\text{Me}_3\text{SiSiMe}_3$ and *p*-DCNB are shown in Figure 2. Here, the $A(t)$ curves have fast and slow decay components. In comparison with the results reported for similar micellar solutions in a previous paper,²² the fast decay component is safely attributable to *p*-DCNB^{•-} in the radical pair of $\text{Me}_3\text{SiSiMe}_3^{\bullet+}$ and *p*-DCNB^{•-} and the slow one to the anion radical that escaped from the pair. The fast component decays by back electron transfer between $\text{Me}_3\text{SiSiMe}_3^{\bullet+}$ and *p*-DCNB^{•-} in the radical pair. The slow component decays by the reaction process of the escaped *p*-DCNB^{•-}.

Then, the time profiles of the $A(t)$ curves were analyzed by a nonlinear least-squares method to satisfy the following equation:

$$A(t) = I_f \exp(-k_f t) + I_s \exp(-k_s t) \quad (4)$$

Here, k_f and k_s are the fast and slow decay rate constants, respectively, and I_f and I_s represent the corresponding preexponential factors.

When the $A(t)$ curves shown in Figure 2 were analyzed by eq 4, no appreciable magnetic field effect was obtained for k_s beyond the experimental error: $k_s = (1.3 \pm 0.2) \times 10^5 \text{ s}^{-1}$. This properly means that the reaction of the escaped *p*-DCNB^{•-} is not influenced by magnetic fields below 1.35 T. On the other hand, k_f seemed to be reduced by the field of 1.0 T. The magnetically induced change, however, was within the experimental error: $k_f(0 \text{ T}) = (9.1 \pm 0.5) \times 10^5 \text{ s}^{-1}$, $k_f(1.0 \text{ T}) = (8.7 \pm 0.5) \times 10^5 \text{ s}^{-1}$. Since the lifetimes of the fast decay were about 1 μs , $A(4 \mu\text{s})/A(0 \mu\text{s}) (=Y)$ can safely represent the relative yield of the escaped anion radical at $t = 4 \mu\text{s}$. Thus, we can see that the $Y(B)/Y(0)$ ratio ($=R(B)$) can give the magnetic field effect on the yield of the escaped *p*-DCNB anion radical. The $R(B)$ values obtained for the reaction between $\text{Me}_3\text{SiSiMe}_3$ and *p*-DCNB are plotted

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