

Chiral Discrimination in Fluorescence Quenching

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Abstract: The requirement of specific geometry for the charge-transfer quenching process has been examined by using chiral compounds as excited molecules and quenchers. Significant differences in the quenching rate were observed for the quenching of (*R*)-(-)-1,1'-binaphthyl fluorescence by (*S*)-(-)- and (*R*)-(+)-*N,N*-dimethyl-1-phenylethylamines, *N,N*-dimethyl-1-phenyl-2-methylpropylamines, and *N,N*-dimethyl-1-phenyl-2,2-dimethylpropylamines in *n*-hexane, while no difference was discerned for the fluorescence quenching of the racemic mixture of 1,1'-binaphthyl. The ratios of the quenching rates, $k_q(R-S)/k_q(R-R)$, increased as the bulkiness of the amine increased and were found to be 1.9, 2.7, and 4.0, respectively, at 22 °C. The difference in the quenching rate indicates that specific orientation is required in the quenching process between 1,1'-binaphthyl and the amines. The ratio $k_q(R-S)/k_q(R-R)$ tended to decrease with increasing solvent polarity. The temperature dependence of $k_q(R-S)/k_q(R-R)$ in *n*-hexane revealed that both the activation enthalpy difference, $\Delta\Delta H^\ddagger$, and the entropy difference, $\Delta\Delta S^\ddagger$, between *R-R* and *R-S* pairs for exciplex formation increased with increasing bulkiness of the amine, and that chiral discrimination in the exciplex formation is controlled by the activation enthalpy difference below 421 K.

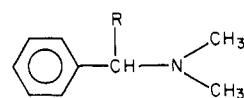
Introduction

It is worthwhile inquiring into the question of whether a specific geometry is required for the charge-transfer or electron-transfer quenching process. Although several works have dealt with the steric influence upon fluorescence quenching rates,¹ no satisfactory answer to this question has to date been given. Taylor et al.^{1d}, for example, have studied the charge-transfer quenching process of singlet excited pyrene using dimethylaniline and 3,5-di(*tert*-butyl)-*N,N*-dimethylaniline as quenchers and inferred from the fluorescence quenching data that the introduction of the bulky *tert*-butyl substituents gives rise to the structural change of the exciplex from a "sandwich-pair geometry" to a "localized-pair geometry".

The study of the fluorescence quenching rate as a function of substitution on excited molecules or quenchers, however, can provide rather limited insight into the geometrical aspect of the exciplex formation. The introduction of substituents implies electronic, as well as steric, changes which can affect the role of the charge-transfer interaction in the excited state. There is no easy way to separate "steric" from "electronic" effects when the influence of bulky substituents on the quenching rate is examined. Furthermore, the distance between the quencher and the excited molecule within the initial state of quenching process, i.e., encounter complex, is also changed. All these factors, introduced by changing substituents, affect the quenching rate value. Such being the case, specific information referring to the geometrical aspect of the exciplex formation may not be readily available.

One possible way to separate "steric" and "electronic" effects is to introduce the concept of chirality into the study. The use of chiral compounds as excited molecules and quenchers enables one to examine pure steric effects upon the quenching rate without being disturbed by the electronic factors, since enantiomers have inherently the same electronic nature, i.e., oxidation-reduction potentials, and the same bulkiness.

In a previous paper,³ we clearly showed that in less polar solvents, the fluorescence quenching rate of (*R*)-(-)-1,1'-binaphthyl is quite different when quenched by (*S*)-(-)- and (*R*)-(+)-*N,N*-dimethyl-1-phenylethylamines (EA, **1a**), suggesting that specific geometry is required for the fluorescence quenching process. In this paper, we have extended the study to other quenchers having



1a, R = CH₃ (EA)
b, R = CH(CH₃)₂ (MPA)
c, R = C(CH₃)₃ (DMPA)

bulky substituents, *N,N*-dimethyl-1-phenyl-2-methylpropylamines (MPA, **1b**) and *N,N*-dimethyl-1-phenyl-2,2-dimethylpropylamines (DMPA, **1c**), and compared the effect of substitution on the quenching rate and the ratio of the quenching rates of the two enantiomers, $k_q(R-S)/k_q(R-R)$. The difference in the geometrical structure of the "encounter complex" and the "transition state" to the relaxed exciplex, deduced from the temperature dependence of $k_q(R-S)/k_q(R-R)$ for these different kinds of quenchers, is also discussed.

Experimental Section

(*R*)-(-)-1,1'-Binaphthyl was purified and resolved by the method as described before.⁴ The optical purity, $[\alpha]_D^{20} -190^\circ$ (*c* 0.2, CH₂Cl₂), is 77.5%. (*R*)-(+)- and (*S*)-(-)-*N,N*-dimethyl-1-phenylethylamine (EA) were obtained from (*R*)-(+)- and (*S*)-(-)-1-phenylethylamine (Norse Laboratories Inc.) by the method of Snyder and Brewster.⁵ (*R*)-(+)- and (*S*)-(-)-1-phenyl-2-methylpropylamine, $[\alpha]_D^{20} \pm 13.5^\circ$ (*c* 2.5, ethanol), were synthesized from optically active isopropylphenylacetic acid by the method of Červinka et al., using (*R*)-(+)- and (*S*)-(-)-1-phenylethylamine as a resolving reagents of the acid.⁶ (*R*)-(+)- and (*S*)-(-)-1-phenyl-2,2-dimethylpropylamine, $[\alpha]_D^{20} \pm 4.3^\circ$ (*c* 4.0, methanol), were synthesized and resolved using *N*-acetyl-L- and -D-leucine as resolving reagents, by the method of Warren et al.⁷ *N,N*-Dimethylations of both 1-phenyl-2-methylpropylamine and 1-phenyl-2,2-dimethylpropylamines were performed by the same method as in the case of EA. All the amines were purified by distillation under reduced pressure and passed through an alumina column using chloroform and *n*-hexane as eluant. The purity of amines was checked by TLC and HPLC before use.

All solvents were of spectrograde, having no background emission. The temperature was controlled using a low-temperature refrigerated circulating bath (NESLAB LT-50). The sample temperature was monitored by thermocouple attached to the sample and was controlled to within $\pm 1.0^\circ$ C. Fluorescence spectra were measured using a Hitachi MPF-4 fluorescence spectrophotometer. Quenching experiments were performed by measuring the relative quantum yield of the 1,1'-binaphthyl fluorescence. The reproducibility of Stern-Volmer constants was $\pm 5\%$ for different samples of equivalent compositions. Corrections in the

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(2) Froelich, P.; Wehry, E. L. "Modern Fluorescence Spectroscopy 2"; Wehry, E. L., Ed.; Plenum Press: New York and London, 1976; Chapter 8.

(3) Irie, M.; Yorozu, T.; Hayashi, K. *J. Am. Chem. Soc.* **1978**, *100*, 2236.

(4) Irie, M.; Yoshida, K.; Hayashi, K. *J. Phys. Chem.* **1977**, *81*, 969.

(5) Snyder, H. R.; Brewster, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 291.

(6) (a) Červinka, O.; Hub, L. *Collect. Czech. Chem. Commun.* **1967**, *32*, 2295. (b) Červinka, O.; Dudek, V.; Hub, L. *Ibid.* **1970**, *35*, 724.

(7) Newman, P. "Optical Resolution Procedures for Chemical Compounds 1"; (Optical Resolution Information Center: Manhattan College, Riverdale, New York, 1978; p 216.

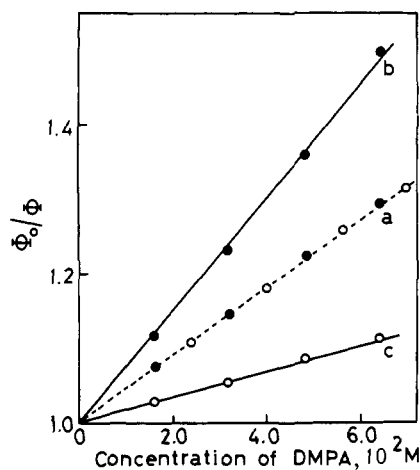


Figure 1. Stern-Volmer plots for the fluorescence quenching of (---) racemic and (—) (R)-(-)-1,1'-binaphthyl by (●) (S)-(-)- and (○) (R)-(+)-*N,N*-dimethyl-1-phenyl-2,2-dimethylpropylamine (DMPA) in *n*-hexane at 22 °C. Concentration of 1,1'-binaphthyl is 1.1×10^{-5} mol/L.

Table I. Fluorescence Quenching Rate Ratios in Various Solvents at 22 °C^a

solvent	ϵ^b	$k_q(R-S)/k_q(R-R)$
<i>n</i> -hexane	1.89	1.9
benzene	2.28	1.8
THF	7.39	1.6
1,2-dichloroethane	10.4	1.5
ethanol	24.3	1.3
acetonitrile	37.5	1.0

^a (R)-(-)-1,1'-Binaphthyl fluorescence was quenched by (S)-(-)- and (R)-(+)-*N,N*-dimethyl-1-phenylethylamines. ^b Dielectric constants at 20 °C.

Stern-Volmer constants to account for the optical purity of the samples were not made.

Results

Photoexcitation of 1,1'-binaphthyl at 310 nm gives a fluorescence around 360 nm. The fluorescence is quenched by adding *N,N*-dimethyl-1-phenyl-2,2-dimethylpropylamine (DMPA), the quenching being similar to a typical exciplex type quenching observed in naphthalene-triethylamine system,⁸ except that the exciplex emission is extremely weak and observed only as a tail of the monomer emission. Figure 1a shows Stern-Volmer plots for the fluorescence quenching of a racemic mixture of 1,1'-binaphthyl by enantiomers, *S*(-) and *R*(+)-DMPA in *n*-hexane. No difference was discerned in the quenching rate. On the other hand, a significant difference in the rates was observed for the quenching of (R)-(-)-1,1'-binaphthyl fluorescence by these enantiomers. Figure 1b and 1c show the Stern-Volmer plots quenched by *S*(-) and *R*(+)-DMPA, respectively. The ratio of the quenching rate $k_q(R-S)/k_q(R-R)$ was found to be 4.0.

The ratios of the quenching rates for the fluorescence quenching of (R)-(-)-1,1'-binaphthyl by *S*(-) and *R*(+)-EA in various solvents are summarized in Table I. The dependence of the ratio on the solvent polarity indicates that the ratio has a tendency to decrease with increasing solvent polarity.

The difference in the quenching rates in less polar solvents increased with increasing bulkiness of the substituent on the asymmetric carbon atom as shown in Table II. The increase of the difference in the quenching rates in 1,2-dichloroethane with increasing bulkiness of the amines was not so large as observed in *n*-hexane. No noticeable difference was observed in acetonitrile solution, even when bulky amines, *R*(+) and *S*(-)-DMPA were used as quenchers.

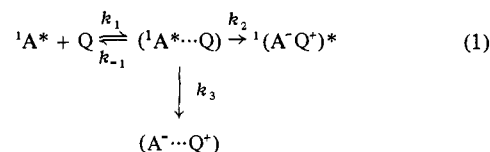
Solvent polarity also alters the Stern-Volmer constant, increasing with increasing solvent polarity, the highest value being

obtained in acetonitrile. The increase of the Stern-Volmer constant is ascribable to the increase of the fluorescence quenching rate, since solvents scarcely alter the fluorescence lifetime of 1,1'-binaphthyl.⁹

The temperature dependence of the quenching rate ratios in *n*-hexane solution is shown in Table III. The ratio $k_q(R-S)/k_q(R-R)$ has a tendency to increase with decreasing temperature although the quenching rates decrease.

Discussion

In order to elucidate the steric and polarity effects on the quenching rate as shown in Figure 1 and Table I, the general scheme of eq 1 of fluorescence quenching was considered. ¹A*



is (R)-1,1'-binaphthyl in the excited singlet state, Q is an optically active amine, ¹A* · · Q is an encounter complex,¹ (A⁻Q⁺) is an exciplex, and (A⁻ · · Q⁺) denotes an ion pair. The rate constant for fluorescence quenching is therefore a function of k_1 , k_{-1} , k_2 , and k_3 .

$$k_q = k_1 \frac{k_2 + k_3}{k_{-1} + k_2 + k_3} = p k_{\text{diff}} \quad (2)$$

$(k_2 + k_3)/(k_{-1} + k_2 + k_3)$ (= *p* factor) is regarded as the reaction probability per encounter of excited 1,1'-binaphthyl with the amine. k_1 is about equal to the diffusion rate constant, k_{diff} ($=8RT/3000\eta$).

(i) **Solvent Polarity Effect.** The dependence of the quenching rate value and the difference of quenching rate between enantiomers on the solvent polarity gives structural information concerning exciplex formation process. In less polar solvents, electron transfer in the loose encounter complex, k_3 process, is negligibly small.¹⁰ The quenching is considered to occur in the contact pair of an excited molecule and a quencher, k_2 process, when specific orientation during the quenching process is required. This results in a significant difference in the fluorescence quenching rate of (R)-1,1'-binaphthyl by *R*- and *S*-DMPA. As the polarity of the solvent becomes higher, the contribution of the electron-transfer reaction to the quenching process becomes significant, causing an increase of the quenching rate with an increase of solvent polarity, as shown in Table II. The quenching rate ratio $k_q(R-S)/k_q(R-R)$, on the other hand, decreases with increasing solvent polarity, as shown in Table I. In acetonitrile, electron transfer in a complex having a loose structure dominates. This makes the quenching rate fast and diminishes chiral discrimination. In a medium polar solvent, e.g., 1,2-dichloroethane, exciplex formation is considered to compete with the electron-transfer reaction. The chiral discrimination observed in this solvent is ascribable to the contribution of the exciplex formation process. These results lead to the conclusion that chiral discrimination in the fluorescence quenching is achieved in the k_2 process and not in the k_3 process. In the encounter complex, the distance between the excited molecule and the quencher is too large to recognize the chirality of its partner molecule. In other words, electron transfer occurs at a distance at which the pair molecules need not specifically orientate with respect to each other.

The quenching rate must be less than the diffusion rate for chiral discrimination to occur. The quenching rates k_q in 1,2-dichloroethane and acetonitrile at room temperature are estimated

(9) Fluorescence lifetimes of 1,1'-binaphthyl are reported to be 3.0 ns^a and 3.5 nsec^b in *n*-hexane and 2-methyl-tetrahydrofuran at room temperature, respectively. (a) Berlman, I. B. "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed.; Academic Press: New York, 1971; p 352. (b) Post, M. F. M.; Langelaar, J.; Van Voorst, J. P. W. *Chem. Phys. Lett.* **1975**, *32*, 59.

(10) Taniguchi, Y.; Nishina, Y.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 764.

(8) Kuzmin, M. G.; Guseva, L. N. *Chem. Phys. Lett.* **1969**, *3*, 71.

Table II. Stern-Volmer Constants and Quenching Rate Ratios at 22 °C in Various Solvents

solvent	ϵ^a	quencher					
		EA		MPA		DMPA	
		K_{sv}^b (L·mol ⁻¹)	$k_q(R-S)/$ $k_q(R-R)$	K_{sv}^b (L·mol ⁻¹)	$k_q(R-S)/$ $k_q(R-R)$	K_{sv}^b (L·mol ⁻¹)	$k_q(R-S)/$ $k_q(R-R)$
<i>n</i> -hexane	1.89	3.6	1.9	11	2.7	4.5	4.0
1,2-dichloroethane	10.4	12	1.5	17	2.2	14	2.5
acetonitrile	37.5	39	1.0	50	1.0	50	1.0

^a Dielectric constants at 20 °C. ^b Stern-Volmer constants of the fluorescence quenching of racemic 1,1'-binaphthyl by *S*-(-) and *R*-(+)-amines

Table III. Temperature Dependence of the Fluorescence Quenching Rate Ratios in *n*-Hexane

temp (°C)	$k_q(R-S)/k_q(R-R)$		
	EA	MPA	DMPA
22.0	1.9	2.7	4.0
10.0	2.2	3.3	5.0
0	2.4	3.7	6.2
-10.0	2.9	4.7	7.9

to be about $\sim 4.0 \times 10^9$ and $\sim 1.3 \times 10^{10}$ L·mol⁻¹·s⁻¹ from the Stern-Volmer constants of Table I,⁹ which are less than the diffusion rate constants in these solvents ($k_{diff} = 8.0 \times 10^9$ and 2.0×10^{10} L·mol⁻¹·s⁻¹ in 1,2-dichloroethane and acetonitrile, respectively). This fact indicates that the condition $k_2 + k_3 \gg k_{-1}$ in eq 2 is not satisfied even in polar acetonitrile, though the contribution of electron transfer in the encounter complex becomes dominant as the solvent polarity increases.

When MPA was used as quencher, the increase of the quenching rate with the increase of the solvent polarity from *n*-hexane to 1,2-dichloroethane was not significant, as shown in Table II. The large k_q value in *n*-hexane for MPA is ascribable to the large contribution of the k_2 value since the contribution of the k_3 term is considered to be negligibly small in the nonpolar solvent. $k_q(R-S)/k_q(R-R)$ increases with increasing bulkiness of the substituent on amines in the medium polar solvent but to a somewhat smaller extent when compared with *n*-hexane. This is due to the nonnegligible contribution of the electron-transfer process, k_3 , in the medium polar solvent.

(ii) **Steric Effect on the Exciplex Formation Process in *n*-Hexane Solution.** k_3 in nonpolar solvents is considered to be small. In *n*-hexane, k_q is approximated to

$$k_q = k_1 \frac{k_2}{k_{-1} + k_2} = p' k_{diff} \quad (3)$$

The k_2 process in eq 3 involves geometric and solvent relaxation of the encounter complex to a relaxed exciplex. As the fluorescence lifetime of 1,1'-binaphthyl is about 3.0 ns in *n*-hexane at room temperature, the quenching rate constants estimated from the Stern-Volmer constants are 1.2×10^9 , 3.7×10^9 , and 1.4×10^9 L·mol⁻¹·s⁻¹ at 22 °C for quenchers EA, MPA, and DMPA, respectively. Since the diffusion rate constant in *n*-hexane at this temperature is about 2.1×10^{10} L·mol⁻¹·s⁻¹, the p' factor in eq 3 is considerably less than one. Under the condition of $k_{-1} \gg k_2$, k_q can be approximated by the following equation:

$$k_q = (k_1/k_{-1})k_2 \quad (4)$$

Since the intermolecular distance in the encounter complex is considered to be fairly large,² both k_1 and k_{-1} processes are thought to be identical for (*R*)-(-)-1,1'-binaphthyl-(*S*)-(-)-amine (*R-S*) and (*R*)-(-)-1,1'-binaphthyl-(*R*)-(+)-amine (*R-R*) pairs. Applying $k_1(R-S) = k_1(R-R)$ and $k_{-1}(R-S) = k_{-1}(R-R)$, the quenching rate ratio $k_q(R-S)/k_q(R-R)$ is ascribable to the exciplex formation rate ratio between *R-S* and *R-R* pairs:

$$\frac{k_q(R-S)}{k_q(R-R)} = \frac{k_2(R-S)}{k_2(R-R)} \quad (5)$$

The ratio increased with increasing bulkiness of the amines as

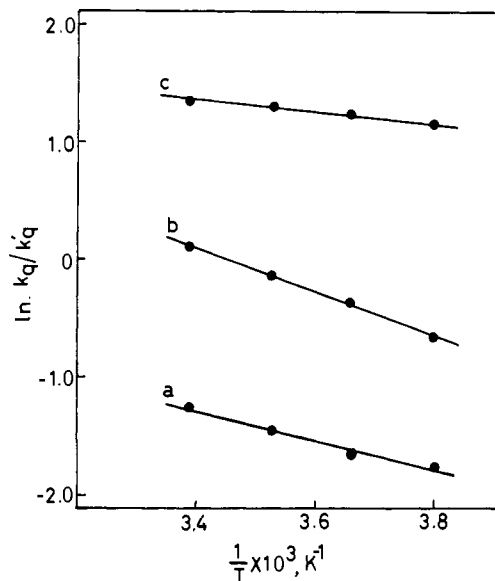


Figure 2. Temperature dependence of the natural logarithms of Stern-Volmer constant ratios between different amines: (a) $k_q(\text{DMPA})/k_q(\text{MPA})$, (b) $k_q(\text{DMPA})/k_q(\text{EA})$, (c) $k_q(\text{MPA})/k_q(\text{EA})$.

shown in Table II. This fact suggests that in *n*-hexane the geometrical structure of Q is definitely an important factor in determining the exciplex formation rate. In other words, a specific geometry is required between A* and Q molecules in the equilibrium exciplex state and the rate of the formation of exciplex, k_2 , depends on the geometrical structure of the A* and Q.

(iii) **Temperature Dependence of k_q Values in *n*-Hexane.** The natural logarithm values of the ratio of Stern-Volmer constants in *n*-hexane between the quenchers of racemic EA, MPA, and DMPA as a function of the reciprocal value of the absolute temperatures are shown in Figure 2. The ratio of Stern-Volmer constants, $K_{sv}(\text{MPA})/K_{sv}(\text{EA})$, at the respective temperatures is equivalent to the ratio of the fluorescence quenching rate, $k_q(\text{MPA})/k_q(\text{EA})$, at those temperatures;

$$\frac{K_{sv}(\text{MPA})}{K_{sv}(\text{EA})} = \frac{k_q(\text{MPA})\tau}{k_q(\text{EA})\tau} = \frac{k_q(\text{MPA})}{k_q(\text{EA})} \quad (6)$$

where τ is a lifetime of singlet excited state of 1,1'-binaphthyl. From transition state theory, the rate constant is generally expressed by the following formula:

$$k = \frac{kT}{h} \exp\left[-\frac{\Delta H^\ddagger - T\Delta S^\ddagger}{RT}\right] = \frac{kT}{h} \exp\left[-\frac{\Delta G^\ddagger}{RT}\right] \quad (7)$$

ΔH^\ddagger and ΔS^\ddagger stand for activation enthalpy and entropy, respectively. Substituting eq 7 in the quenching rate ratio $k_q(\text{MPA})/k_q(\text{EA})$ gives:

$$\frac{k_q(\text{MPA})}{k_q(\text{EA})} = \exp\left[-\frac{\Delta G_q^\ddagger(\text{MPA}) - \Delta G_q^\ddagger(\text{EA})}{RT}\right] = \exp\left[\frac{(\Delta H_q^\ddagger(\text{MPA}) - \Delta H_q^\ddagger(\text{EA})) - T(\Delta S_q^\ddagger(\text{MPA}) - \Delta S_q^\ddagger(\text{EA}))}{RT}\right] \quad (8)$$

The ratios $k_q(\text{DMPA})/k_q(\text{EA})$ and $k_q(\text{DMPA})/k_q(\text{MPA})$ can be derived in a similar manner. As shown in Figure 2, when the natural logarithms of the Stern-Volmer constant ratios are plotted against the reciprocal value of the absolute temperature, the slope and intercept give the values of

$$\begin{aligned} \Delta H_q^*(\text{MPA}) - \Delta H_q^*(\text{EA}) &= 0.90 \pm 0.60 \text{ kcal}\cdot\text{mol}^{-1} \\ \Delta S_q^*(\text{MPA}) - \Delta S_q^*(\text{EA}) &= 5.8 \pm 1.9 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{deg}^{-1} \end{aligned} \quad (9a)$$

$$\begin{aligned} \Delta H_q^*(\text{DMPA}) - \Delta H_q^*(\text{EA}) &= 3.4 \pm 0.7 \text{ kcal}\cdot\text{mol}^{-1} \\ \Delta S_q^*(\text{DMPA}) - \Delta S_q^*(\text{EA}) &= 12 \pm 2 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{deg}^{-1} \end{aligned} \quad (9b)$$

Hence, the following relationship is obtained.

$$\begin{aligned} \Delta H_q^*(\text{DMPA}) > \Delta H_q^*(\text{MPA}) > \Delta H_q^*(\text{EA}) \\ \Delta S_q^*(\text{DMPA}) > \Delta S_q^*(\text{MPA}) > \Delta S_q^*(\text{EA}) \end{aligned} \quad (10)$$

The temperature at which the quenching rate constants $k_q(\text{MPA})$ and $k_q(\text{EA})$ coincide can be determined by substituting eq 9a in eq 8 and solving the following equation.

$$\begin{aligned} (\Delta H_q^*(\text{MPA}) - \Delta H_q^*(\text{EA})) - \\ T \cdot (\Delta S_q^*(\text{MPA}) - \Delta S_q^*(\text{EA})) = 0 \end{aligned} \quad (11)$$

The temperature was 155 K. Similarly temperatures at which $k_q(\text{DMPA}) = k_q(\text{EA})$ and $k_q(\text{DMPA}) = k_q(\text{MPA})$ were determined to be 294 and 433 K, respectively. The relationship between $k_q(\text{EA})$, $k_q(\text{MPA})$, and $k_q(\text{DMPA})$ as a function of the temperature (K) is given in eq 12. This relationship indicates that

$$\begin{aligned} k_q(\text{DMPA}) \geq k_q(\text{MPA}) \geq k_q(\text{EA}) \quad T \geq 433 \\ k_q(\text{MPA}) \geq k_q(\text{DMPA}) \geq k_q(\text{EA}) \quad 294 \leq T \leq 433 \\ k_q(\text{MPA}) \geq k_q(\text{EA}) \geq k_q(\text{DMPA}) \quad 155 \leq T \leq 294 \\ k_q(\text{EA}) \geq k_q(\text{MPA}) \geq k_q(\text{DMPA}) \quad T \leq 155 \end{aligned} \quad (12)$$

the relative rates of the quenching reactions are influenced by the temperature in the range used for the experiments. The reactivity is controlled by the activation enthalpy term at low temperature and by the activation entropy term at high temperature. The quenching rate constants $k_q(\text{EA})$, $k_q(\text{MPA})$, and $k_q(\text{DMPA})$ do not possess an isokinetic temperature. This means the bulkiness of the substituents does not determine the relative reactivity of the quenchers. This is due to the fact that the introduction of substituents implies electronic, as well as steric, changes, which can affect the role of charge-transfer interaction in the excited state.

The estimation of k_1 from the Einstein-Smoluchowski diffusion theory and k_{-1} from random walk theory gives $k_1/k_{-1} = (4\pi rDN/10^3)(r^2/3D) = (4/3)(\pi r^3N/10)$, where r is the interaction radius in the encounter complex, D is the sum of the respective diffusion coefficients of the quencher and the excited molecule, and N is Avogadro's number. k_1/k_{-1} and k_2 are considered to vary with the bulkiness of the substituents of the quenchers. The k_1/k_{-1} value increases as the radius of the amine molecule increases. On the other hand, the value of k_2 depends both on the oxidation potential of the quenchers and the bulkiness of the substituents, since the k_2 process involves a charge-transfer reaction between contact pair molecules. The bulky substituent decreases the oxidation potential,¹¹ while it prevents the access of the quenchers to the excited molecules. Thus, the quenching rate constant is dependent not only on the steric hindrance factor, but also on electronic changes and the distance between the quencher and the excited molecule induced by the substitution.

The largest quenching rate for MPA, in the temperature range examined, suggests that the increase in the quenching rate, caused by the decrease of the oxidation potential, overwhelms the steric hindrance effect on k_2 when changing the substituent from methyl to isopropyl. Introduction of a *tert*-butyl substituent, on the other hand, brings about fairly large steric hindrance in the exciplex

(11) The decrease of oxidation potentials with increasing bulkiness of the substituents was confirmed by a cyclic voltammetric measurement.

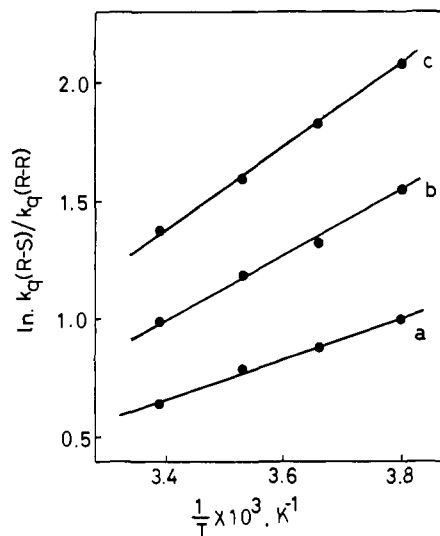


Figure 3. Temperature dependence of the natural logarithms of quenching rate ratios, $k_q(R-S)/k_q(R-R)$. The quenchers are (a) EA, (b) MPA, (c) DMPA.

Table IV. $\Delta\Delta H_2^\ddagger$ and $\Delta\Delta S_2^\ddagger$ Values for Various Quenchers in *n*-Hexane

quencher	$\Delta\Delta S_2^\ddagger$ (cal·mol ⁻¹ deg ⁻¹)	$\Delta\Delta H_2^\ddagger$ (kcal·mol ⁻¹)
EA	5.5 ± 0.8	2.0 ± 0.2
MPA	7.1 ± 1.4	2.7 ± 0.4
DMPA	8.7 ± 1.2	3.4 ± 0.3

formation process, resulting in a decrease of the k_2 value.

(iv) **Temperature Dependent of $k_q(R-S)/k_q(R-R)$ in *n*-Hexane.** The temperature dependence of the quenching rate ratio $k_q(R-S)/k_q(R-R)$ gives specific information referring to the pure steric effect on the fluorescence quenching reactions. The temperature dependence of $k_q(R-S)/k_q(R-R)$ values for various quenchers in *n*-hexane is shown in Table III. Applying the transition state theory to eq 5, $k_q(R-S)/k_q(R-R)$ can be expressed using thermodynamic parameters of the k_2 process as follows:

$$\begin{aligned} \frac{k_q(R-S)}{k_q(R-R)} = \frac{k_2(R-S)}{k_2(R-R)} = \exp\{[(\Delta H_2^*(R-S) - \Delta H_2^*(R-R)) - \\ T(\Delta S_2^*(R-S) - \Delta S_2^*(R-R))]/RT\} = \\ \exp\left[\frac{\Delta\Delta H_2^\ddagger - T\Delta\Delta S_2^\ddagger}{RT}\right] = \exp\left[\frac{\Delta\Delta G_2^\ddagger}{RT}\right] \end{aligned} \quad (13)$$

where $\Delta\Delta H_2^\ddagger = \Delta H_2^*(R-R) - \Delta H_2^*(R-S)$, $\Delta\Delta S_2^\ddagger = \Delta S_2^*(R-R) - \Delta S_2^*(R-S)$, and $\Delta\Delta G_2^\ddagger = \Delta\Delta H_2^\ddagger - T\Delta\Delta S_2^\ddagger$. The natural logarithm value of $k_q(R-S)/k_q(R-R)$ plotted against the reciprocal value of the absolute temperature yields a straight line as shown in Figure 3. The activation enthalpy and entropy differences for the exciplex formation between photoexcited $R-S$ pairs and $R-R$ pairs for all the quenchers examined are listed in Table IV. It should be noted that the relationship $\Delta H_2^*(R-R) > \Delta H_2^*(R-S)$ and $\Delta S_2^*(R-R) > \Delta S_2^*(R-S)$ hold for all enantiomer pairs of the same quenchers. Activation enthalpy and entropy differences are in the order of

$$\begin{aligned} \Delta\Delta H_2^*(\text{DMPA}) > \Delta\Delta H_2^*(\text{MPA}) > \Delta\Delta H_2^*(\text{EA}) > 0 \\ \Delta\Delta S_2^*(\text{DMPA}) > \Delta\Delta S_2^*(\text{MPA}) > \Delta\Delta S_2^*(\text{EA}) > 0 \end{aligned} \quad (14)$$

$\Delta H_2^*(R-R) > \Delta H_2^*(R-S)$ indicates that exciplex formation between $R-R$ pairs has to overcome a larger activation energy compared with $R-S$ pairs. On the other hand, from the viewpoint of the entropy term, the $R-S$ pairs have more strict configurational requirements in the transition state of exciplex formation compared with $R-R$ pairs. The relationship given in (14) indicate that the bulkiness of the substituents determines the relative order of

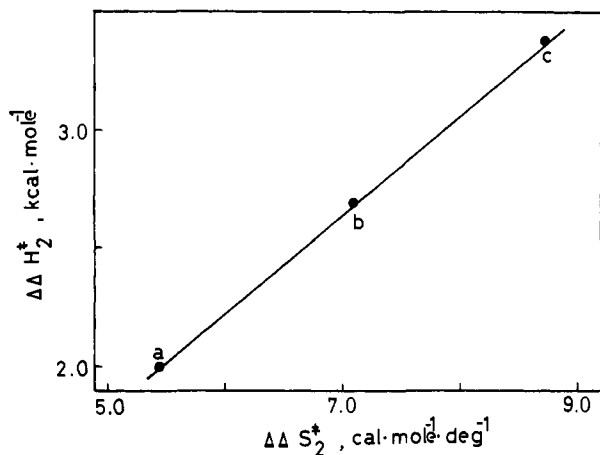


Figure 4. Correlation of $\Delta\Delta S_2^*$ and $\Delta\Delta H_2^*$. The quenchers are (a) EA, (b) MPA, (c) DMPA.

activation energy difference and entropy difference between these three quenchers. The activation energy difference and entropy difference between $R-R$ and $R-S$ pairs increase with increasing bulkiness of the substituents. It also suggests that, although the entropy term compensates for the large activation enthalpy difference, the difference in the activation free energy is still large enough to yield a chiral discrimination in the exciplex formation

process. These results lead to the conclusion that, in the transition state of the "equilibrium exciplex" formation process starting from "encounter complex", specific geometry is required between the excited molecule and the quencher.

The modified isokinetic temperature at which the quenching rate constants $k_q(R-S)$ and $k_q(R-R)$ coincide was found to be 421 K for all the quenchers studied in this reaction series. Below this temperature, which is in the temperature range of the experiment studied, chiral discrimination in the exciplex formation process is controlled by the activation enthalpy difference, $\Delta\Delta H_2^*$; i.e., chiral discrimination is most effective for the most bulky quencher, DMPA. Above this temperature, the activation entropy difference, $\Delta\Delta S_2^*$, controls chiral discrimination in the exciplex formation; i.e., chiral discrimination is most ineffective for the most bulky quencher, DMPA. As a result of this modified isokinetic relationship, linearity between $\Delta\Delta H_2^*$ and $\Delta\Delta S_2^*$ was observed as shown in Figure 4. The slope gave the modified isokinetic temperature of 420 K which is in good agreement with the value obtained from Figure 3. This result supports the suggestion that the reaction proceeds by an identical mechanism throughout the reaction series and that the quenching rate ratio $k_q(R-S)/k_q(R-R)$ represents the pure steric factor in the exciplex formation process, k_2 .

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Determination of Rate Constants for Electron Transfer from Radical Anions of Aromatic Compounds to Diaryl Disulfides

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Abstract: Rate constants for electron transfer from the radical anions of aromatic compounds to diaryl disulfides (ArSSAr) have been determined in tetrahydrofuran. By the change of the reduction potentials of the aromatic compounds from -1.04 to -1.91 V (vs. SCE), the rate constants varied from 0.015 to 2.3×10^6 $M^{-1} s^{-1}$; conventional spectrophotometry has been employed to measure the slow reaction rates, and the xenon-flash photolysis technique has been applied to the fast reaction systems. The reaction including the free ion or the loose ion pair of the thioxanthone sulfone radical anion, $(TO-SO_2)^{\cdot-}$, was faster than that including the tight ion pair. In the case of the $(TO-SO_2)^{\cdot-}, Na^+-PhSSPh$ system, temperature variation yielded the free energy of activation ($\Delta G^\ddagger = 18.7$ kcal/mol) and activation entropy ($\Delta S^\ddagger = -29.1$ eu) at 22.4 °C; the reduction potential of PhSSPh was estimated to be -1.80 V vs. SCE from the ΔG^\ddagger value. Electron-withdrawing substituents of ArSSAr increase the rates and vice versa; the Hammett reaction constants (ρ) were estimated to be ca. $+1.50$ and 1.40 for electron transfer from perylene radical anion and $(TO-SO_2)^{\cdot-}, Na^+$ to ArSSAr, respectively. The factors controlling the rates have been examined.

Disulfides react with an electron, yielding transiently the radical anions which dissociate rapidly into the thiolate anions and the thiyl radicals.¹ These processes are recognized to play an important role in enzymatic and radiobiological reactions.² The dissociative electron attachment processes are so fast that the pulse radiolysis and the flash photolysis techniques have been employed to clarify the elementary reactions. The rate constants close to the diffusion-controlled limit have been reported for the reactions between the disulfides containing amino and peptide groups and a hydrated electron. However, since the amino and peptide groups attached to the disulfides act as the electron-accepting site, the rates do not reflect the nature of the S-S bonds.¹⁻³ In order to

understand the relation between the electron-acceptor ability and the nature of the S-S bond, it may be necessary to measure the rates of electron transfer from electron donors to disulfides without the amino acid groups.

Ionization potentials and electrophilicities of the disulfides have been explained in terms of the electron densities of the highest occupied molecular orbitals (HOMO) of the S-S linkage.^{4,5} On the other hand, electron-acceptor abilities of the disulfides which are related to the nature of the lowest unoccupied molecular orbital (LUMO) of the S-S bond have not been reported.⁶

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(6) Reduction potentials may give information for LUMO, but those values of disulfides have not been estimated because of their irreversible electrochemical processes; thus $E_R(\text{ArSSAr})$ were roughly estimated from peak potentials in cyclic voltammogram of the disulfides.

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