Singlet-excitation Migration in Pure Liquid Methyl- and Ethylnaphthalenes

Takeshi Ohno* and Shunji Kato

College of General Education, Osaka University, Toyonaka, Osaka 560

(Received September 24, 1980)

The fluorescence quenching of solvent molecules and solute molecules was studied in the alkylnaphthalene solvents. The singlet-excited states of the solvent molecules were quenched by 1,4-bis(trichloromethyl)benzene with the rate parameter of 2.8×10^{10} mol^{-1} dm^3 s^{-1} at 45 °C. This rate parameter is twelve times as great as that of the solute, dibenz[*a,c*]anthracene, in the solvent, 1-methylnaphthalene. The diffusion constant of the excitation migration of the solvent molecule is calculated to be larger (0.35×10^{-4} cm^2 s^{-1} at 45 °C) than that (0.03×10^{-4} cm^2 s^{-1}) of the solute. The temperature coefficient (22 kJ/mol) of the excitation migration is too small to explain the migration mechanism on the hypothesis of the "successive association-dissociation reaction of excimer" proposed by Birks. The presence of a short-range exciton in the liquid is likely.

Since pure liquid aromatic hydrocarbons do not have such long-range periodicity as molecular crystals, it seems difficult to predict, from the point of view of exciton diffusion, the migration rate of the electronic-excitation energy in the molecular liquids,[1] while Lipsky and Burton suggested exciton diffusion in toluene.[2]

The solvent-solvent excitation migration in the liquid scintillator of toluene–2,5-diphenyloxazole has been attributed to multipole-multipole resonance interaction between the solvent molecules, which have been considered to be free from any kind of aggregation.[1]

However, since the singlet-excited states of many aromatic hydrocarbons form excimers which may be shallow traps and/or excitons with the shortest possible length, the role of the excimer in the excitation migration can not be neglected. Birks *et al.*[3] proposed that a sequence of the rapid association and dissociation of an excimer in the singlet-excited state brought about the solvent-solvent excitation migration. Though the excimer dissociation process (detrapping) should be the rate determing step of the excitation migration according to their mechanism, it has not yet been examined.

In this work, the singlet-excitation migration rates of several liquid naphthalenes are examined in the range from 5 to 75 °C. Two mechanisms of the excitation migration, exciton diffusion and the rapid association and dissociation of the excimer will be discussed.

Experimental

Materials. The 1-methylnaphthalene(1-MN, mp: −34 °C) was purified through a 30-cm column of Al_2O_3 followed by distillation using a Widmer column under reduced pressure. The 2-methylnaphthalene(2-MN, mp: 35.2 °C) was purified by two different methods. The purified sample(A) was obtained by three recystallizations from methanol and by subsequent simple distillation under reduced pressure. The other sample(B) was obtained by distillation using a 30-cm Widmer column in place of the simple distillation under reduced pressure. G. R. grade 1-ethylnaphthalene(1-EN, mp: −3.7 °C) and 2-ethylnaphthalene(2-EN, mp: −7.4 °C) were used without further purification.

The dibenz[*a,c*]anthracene(DBA) and pyrene were recrystallized three times from an ethanol solution, followed by sublimation. The 1,4-bis(trichloromethyl)benzene-(TCB), benzophenone, and CBr_4 were purified by two times recrystallizations from an ethanol solution, and *p*-phenylenediamine, from a benzene solution. After the CCl_4 had been refluxed with NaOH, washed with water, and dried by $CaCl_2$, it was distilled. G. R. grade diphenylamine was used without further purification.

Measurements. Quenching constant(K_{SV}): The intensities of the fluorescence were measured by using a Hitachi MPF-2A spectrofluorometer. In the measurement of the emission intensity from a sample of a high optical density such as neat liquids, a triangular cell was used so that we could see a small illuminated part of the sample cell. In order to exclude any error in the measurement, a slit was inserted between the cell and the condenser lens for emission. A N_2-substituted sample in the cell was set in a small thermostat (0—80 °C, ±0.5 °C).

The lifetime of the fluorescence was measured by means of laser excitation. One of the lasers was a compact, high-power N_2-laser with a Blumlein circuit (10 kV, pressure of N_2: 40 mmHg (1 mmHg=133.3 Pa), 2 mJ), which consists of two stainless steel electrodes (3 mmϕ) 20 mm apart, barium titanate capacitors (Taiyo Yuden, 750×14 pF, 25 kV), and a triggered spark gap. The other one was a compact, low-power N_2-laser (10 kV, 10 μJ) containg a coaxial cable as a capacitor.[4] The high-power laser was used for almost allthe samples. The dibenz[*a,c*]anthracene solution was excited by the dye laser (0.02 mol dm^{-3} 2,5-diphenyloxazole benzene solution, 368 nm). The fluorescence decay was recorded by using a Tektronix oscilloscope 475 and Fuji X-ray film or Kodak Recording Film 2475. As for 2-EN with the shortest life the low-power laser was used while a Tektronix sampling scope 661, and Yokogawa 3083 X-Y recorder were used for the detection.

Results and Discussion

Determination of the Molar Enthalpy of Excimer Formation. Each fluorescence spectrum from 280 K to 350 K of liquid naphthalene derivatives consists of a monomer band and an excimer band. At temperatures close to the melting point of the naphthalenes, the strong excimer emission with a peak at 400 nm is the most evident (see Fig. 1). As the temperature is raised, however, the monomer emission without a fine structure becomes stronger than the excimer emission. This situation is very similar to the spectral changes in 1-MN and 2-MN reported by Stevens and Dickinson.[5]

Because both the excimer-formation rate (k_{DM}[M]: 3.5×10^{11} s^{-1}) and the excimer-dissociation rate (k_{MD}: 10^8 s^{-1})[6] are more rapid than the decay rate (k_d: 1.8×10^7 s^{-1}) in the case of 1-MN, an equilibrium between the monomer and the excimer in the excited singlet state exists. The monomer-excimer equilibrium

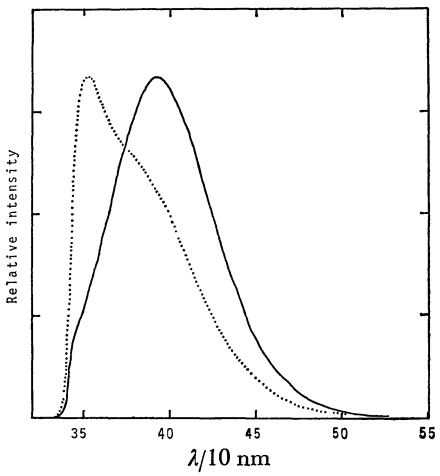

Fig. 1. Fluorescence spectra of liquid 1-MN on excitation at 316 nm.
Solid line: 12 °C, dotted line: 75 °C. The maximum intensity of fluorescence is normalized.

in the excited state is supported by the fact that the Stern-Volmer quenching constant (K_{SV}) obtained by using the excimer band is the same as that obtained by using the monomer band. Further, it is assumed that the intensity of the monomer band (or the excimer band) is proportional to the product of the excited-monomer (or the excimer) concentration and the radiative-rate parameter of the excited monomer (or the excimer), k_{FM} (or k_{FD}). From their dependence on the temperature, one can obtain the molar enthalpy of the excimer formation (ΔH) by using Eq. 1;

$$\ln\frac{I_{352}}{I_{440}} = \ln\frac{\alpha k_{FM}}{k_{FD}[M]} - \frac{\Delta S}{R} + \frac{\Delta H}{RT} \quad (1)$$

where I_{352} and I_{440} are the intensity of the monomer emission measured at 352 nm and that of the excimer measured at 440 nm respectively; α, the apparatus constant; [M], the concentration of the ground-state naphthalene, and ΔS, the molar entropy of the excimer formation. Plotting the left term of Eq. 1 against reciprocal of the temperature (see Fig. 2) gives a linear relation with the slope of $\Delta H/R$ in all cases; the values are shown in Table 1.

The values of ΔH for 1-MN and 2-MN seem similar to the reported values in the ethanol solution,[6] and the ΔH value for 1-EN is close to the value measured by Christophorou and Carter in the neat liquid,[7] though smaller values have been reported in a diluted heptane solution.[8]

Determination of Excitation-migration Coefficient. When the fluorescence of DBA or pyrene is quenched by an adequate quencher in liquid naphthalenes, the quenching-reaction-rate parameter is given by Eq. 2, according to Birks,[3] where N_0 is Avogadro's number; p, the quenching probability; R_{AQ}, the interaction distance, and D_A and D_Q, the diffusion coefficients of DBA (or pyrene) and the quencher respectively;

$$k_q = p4\times10^3 N_0(D_A+D_Q)R_{AQ}. \quad (2)$$

When the solvent fluorescence is quenched by the quencher, a term based on the excitation migration is added to Eq. 2, as Eq. 3 shows;

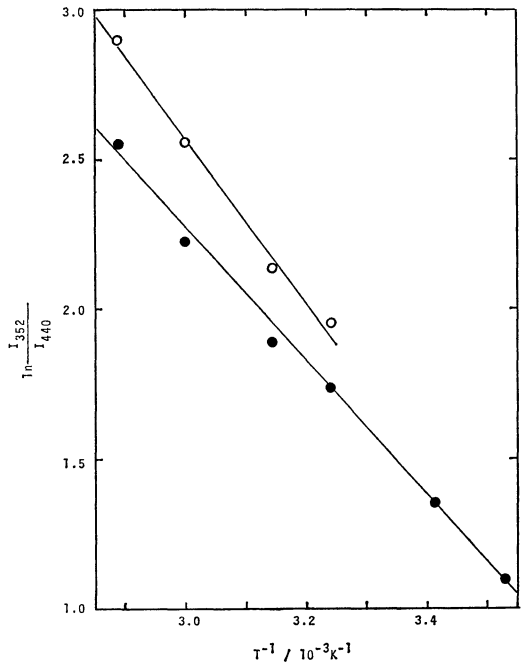

Fig. 2. Temperature dependence of the equilibrium between the excited species of the monomer and the dimer for 1-MN and 2-MN.
●: 1-MN, ○: 2-MN.

Table 1. The molar enthalpy of excimer formation

Fluorescer	Solvent	ΔH/kJ mol^{-1}	Reference
1-MN	Heptane	−29	5
	Ethanol	−20	6
	1-MN	−19	This work
2-MN	Heptane	−29	5
	Ethanol	−21	6
	2-MN	−19	This work
1-EN	1-EN	−26	7
	1-EN	−24	This work
2-EN	2-EN	−20	This work

$$k_q' = p4\times10^3 N_0(D_N+D_Q+\Lambda)R_{NQ} \quad (3)$$

where D_N and Λ are the diffusion coefficients of the solvent naphthalene and the excitation-migration coefficient of the solvent respectively.

Assuming (i) the values of R_{AQ} and R_{NQ} to be the same, and (ii) the values of D_A and D_N to be the same, one can obtain the value of Λ from the difference between the values of k_q and k_q' when an efficient quencher is chosen ($p=1$). The values of k_q and k_q' are calculated in the usual manner from the Stern-Volmer quenching constant and the fluorescence-decay-rate parameter(k_d).

A Stern-Volmer plot is linear in all cases using TCB as a quencher (see Fig. 3). The slopes (the quenching constants in Table 4) become a little steeper as the temperature is increased. While p-phenylenediamine quenches the fluorescence of 2-MN with the same efficiency as TCB, diphenylamine, CCl_4, and benzophenone are inefficient quenchers and the quenching constants are a little smaller (see Table 2).

The values of K_{SV} are sensitive to impurities in the

samples. The carefully purified samples, 2-MN(B), have larger K_{SV} values than 2-MN(A). In the case of 1-MN, the quenching constants obtained by the use of TCB as a quencher are dependent on the temperature in a way similar to those in the case of 2-MN (see Table 3). For 1-EN and 2-EN, TCB is used as a quencher; the measured quenching constants are listed in Tables 5 and 6.

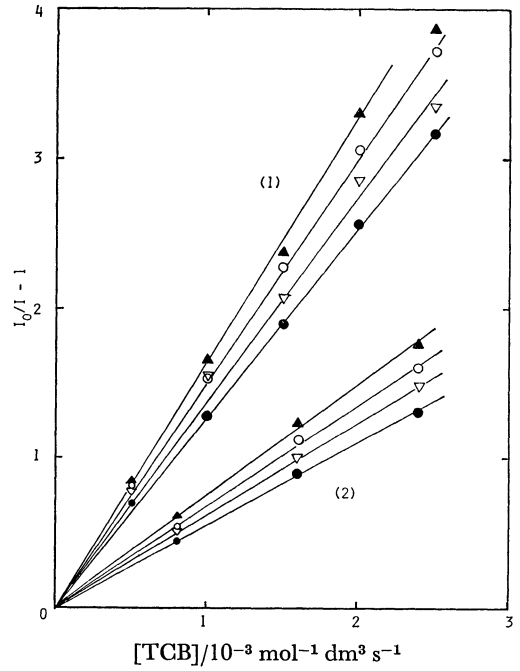

Fig. 3. Stern-Volmer plot for the fluorescence quenching of liquid 2-MN by TCB(1) and diphenylamine(2). ●: 36 °C, ▽: 45 °C, ○: 60 °C, and ▲: 70 °C.

In order to ascertain the product of the molecular diffusion constant (D_A+D_Q) and the interaction distance (R_{AQ}), the quenching constants for one solute in the several liquid naphthalenes are necessary at the same temperatures. DBA was used as a solute for 1-MN and 2-MN, and pyrene, for 1-EN and 2-EN. The values of K_{SV} are shown in Tables 3,4,5, and 6.

Determination of the Fluorescence-decay-rate Parameter. The sampling method and single-pulse method gave the same value of the first-order decay-rate parameter(k_d). As the temperature rises, k_d increases in all cases (see the fourth column of Tables 3,4,5, and 6). The value of k_d is sensitive to impurities in the sample, as is K_{SV}. The fluorescence lifetime of 2-MN(A) is 1/3 as long as that of 2-MN(B). All the k_d values measured are very close to or smaller than those previously reported: 1.7×10^7 s^{-1} for 1-MN at 20 °C, 5×10^7 s^{-1} for 2-MN at 40 °C,[9] and 2.5×10^7 s^{-1} for 1-EN at 20 °C.[8]

k_q, k'_q, D, and A. Both quenching-rate parameters for the solute (k_q) and the naphthalenes (k'_q) in the liquid naphthalenes are calculated from K_{SV} and k_d. The values shown in the fifth column of Tables 3—6 are based on the K_{SV}, using TCB as a quencher; which give the largest values of K_{SV}. The k_q values are in the order of 10^9 mol^{-1} dm^3 s^{-1} in all cases and are assumed to be diffusion-controlled. This is supported by the fact that they are similar to those (2×10^9 mol^{-1} dm^3 s^{-1}) for the triplet-excited state of DBA in liquid 1-MN,[10] which were obtained by using the most efficient quencher of ferrocene.[11]

Assuming $R_{AQ}=1$ nm and $p=1$ for the pair of TCB

Table 2. Quenching constants of fluorescence in neat methylnaphthalene using various quenchers (36 °C)

Fluorescer	Quencher	K_{SV}	$k_d/10^7$ s^{-1}	$k_q'/10^{10}$ mol^{-1} dm^3 s^{-1}
2-MN(A)	TCB	460	4.6	2.1
	CCl_4	370		1.8
2-MN(B)	TCB	1300	1.42	1.8
	Diphenylamine	560		0.77
	p-Phenylenediamine	1300		1.8
	Benzophenone	950		1.4

Table 3. Rate parameters and quenching constants in 1-MN

Fluorescer	T / °C	K_{SV}	k_d / 10^7 s^{-1}	$k_q(k_q')$ / 10^{10} mol^{-1} dm^3 s^{-1}	D_A+D_Q / 10^{-6} cm^2 s^{-1}	A / 10^{-6} cm^2 s^{-1}
1-MN	12	570	1.8	1.0		12
DBA		50	2.0	0.10	1.3	
1-MN	20	730	1.9	1.4		16
DBA		57	2.3	0.13	1.7	
1-MN	32	1000	2.1	2.1		24
DBA		75	2.3	0.17	2.2	
1-MN	45	1200	2.4	2.8		35
DBA		91	2.5	0.23	3.0	
1-MN	60	1400	3.0	4.1		49
DBA		110	2.7	0.29	3.8	
1-MN	75	1600	3.2	5.1		63
DBA		130	2.7	0.34	4.4	

Table 4. Rate parameters and quenching constants in 2-MN

Fluorescer	T / °C	K_{SV}	k_d / 10^7 s^{-1}	$k_q(k_q')$ / 10^{10} mol^{-1} dm^3 s^{-1}	D_A+D_Q / 10^{-6} cm^2 s^{-1}	Λ / 10^{-6} cm^2 s^{-1}
2-MN(A)		460	4.6	2.1		25
2-MN(B)	36	1300	1.4	1.8		21
DBA		73	2.7	0.19	2.6	
2-MN(A)		420	5.6	2.4		28
2-MN(B)	45	1400	1.7	2.3		28
DBA		84	2.9	0.24	3.2	
2-MN(A)		390	7.4	2.9		34
2-MN(B)	60	1500	2.1	3.1		37
DBA		100	3.0	0.31	4.0	
2-MN(A)		390	9.2	3.6		44
2-MN(B)	75	1600	2.4	3.8		47
DBA		100	2.9	0.29	3.9	

Table 5. Rate parameters and quenchching constants in 1-EN

Fluorescer	T / °C	K_{SV}	k_d / 10^7 s^{-1}	$k_q(k_q')$ / 10^{10} mol^{-1} dm^3 s^{-1}	D_A+D_Q / 10^{-6} cm^2 s^{-1}	Λ / 10^{-6} cm^2 s^{-1}
1-EN	15	520	1.8	0.93		10
Pyrene		260	0.52	0.14	1.8	
1-EN	25	580	2.0	1.2		13
Pyrene		320	0.53	0.17	2.2	
1-EN	40	680	2.5	1.7		19
Pyrene		390	0.57	0.22	2.9	
1-EN	55	750	2.9	2.2		25
Pyrene		480	0.62	0.30	3.9	
1-EN	70	820	3.2	2.6		30
Pyrene		590	0.64	0.38	5.0	

Table 6. Rate parameters and quenching constants in 2-EN

Fluorescer	T / °C	K_{SV}	k_d / 10^7 s^{-1}	$k_q(k_q')$ / 10^{10} mol^{-1} dm^3 s^{-1}	D_A+D_Q / 10^{-6} cm^2 s^{-1}	Λ / 10^{-6} cm^2 s^{-1}
2-EN	5	380	1.7	0.67		6.3
Pyrene		260	0.75	0.20	2.6	
2-EN	15	420	2.5	1.0		10
Pyrene		320	0.76	0.24	3.2	
2-EN	25	460	3.0	1.4		14
Pyrene		380	0.77	0.29	3.8	
2-EN	40	500	3.4	1.7		18
Pyrene		460	0.78	0.36	4.8	
2-EN	55	540	4.1	2.2		23
Pyrene		540	0.92	0.49	6.5	
2-EN	70	540	5.0	2.7		27
Pyrene		620	1.1	0.65	8.6	

and DBA at 45 °C, the values of D_A+D_Q are calculated, by using Eq. 1, to be 3×10^{-6} cm^2 s^{-1}. On the same assumption, the values of $D_N+D_Q+\Lambda$ are calculated to be 32×10^{-6} cm^2 s^{-1}. Therefore, it is concluded that Λ is 29×10^{-6} cm^2 s^{-1}, or about 19 times as great as the molecular diffusion constant in liquid 2-MN. This procedure also gives the Λ values in the other cases; they are shown in the last column of Tables 3—6. Though the better-purified sample, 2-MN(B), has a longer fluorescence lifetime than that of 2-MN(A), the Λ values are quite close to those of 2-MN(A). It can be expected that the calculated Λ values for the unpurified samples, 1-EN and 2-EN, will be close to the real values.

These present values of Λ are similar to those obtained in liquid benzene and alkylbenzenes, in which the molecular diffusion constants are of the same order as Λ,[3] so that a difference between the unknown diffusion constant of benzene in the singlet-excited state and that of some solute seems to result in a relatively larger error in the calculation of Λ. It is also noted that Λ is one-fifth as great as that (10^{-4} cm^2 s^{-1}) in the molecular crystal of naphthalene.[13] Eastman, Smutny, and Coppinger reported a little larger value (4.5×10^{10} mol^{-1} dm^3 s^{-1}) of the k_q' of 1-EN by using an aromatic quencher, such as sub-

stituted *p*-quinone, benzophenone, *p*-nitrophenol, and *p*-nitrosophenol.[12] However, it is very difficult to extract the contribution of the excitation migration from them because the Förster-type energy transfer between 1-EN and the quencher must increase the value of k'_q.

The Λ gradually increases with the temperature, as does D. Plotting $\log \Lambda$ against the reciprocal of the temperature, we obtain a curved line, as Figs. 4 and 5 show. Taking the best-fitting straight line through these points, an excitation-migration activation energy of about 17—22 kJ/mol is obtained.

Effect of Dilution on the Value of k'_q. The dilution of 1-MN with hydrogenated naphthalene (*cis*-decaline) makes the quenching reaction parameter smaller. Figure 6 shows the change in the rate parameter with the mole fraction of 1-MN at 20 °C. It should be noted that the rate-parameter increases in the very concentrated region, where some of the nearest neighbours are naphthalene itself. Because a collisional singlet-excitation transfer reaction is very efficient, the dilution effect suggests a collapse of the large molecular assembly responsible for excitation migration with dilution. This will be discussed further in the next section.

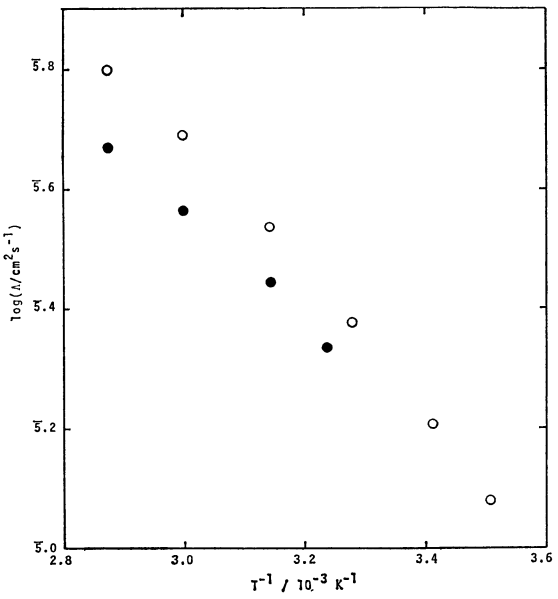

Fig. 4. Temperature dependence of the excitation migration in 1-MN and 2-MN.
○: 1-MN, ●: 2-MN.

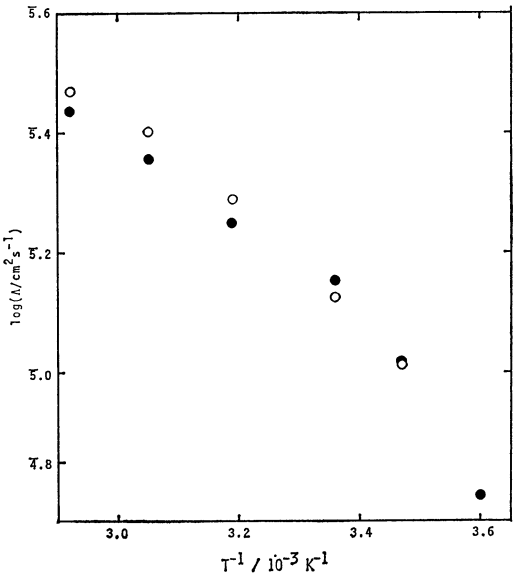

Fig. 5. Temperature dependence of the excitation migration in 1-EN and 2-EN.
○: 1-EN, ●: 2-EN.

Mechanism of Excitation Migration. With respect to the singlet-excitation migration in neat alkylbenzene, two mechanisms of excitation-migration have been proposed; the "association-dissociation reaction of an excimer"[3] and "exciton motion."[2] The "association-dissociation reaction of an excimer"—The formation of an excimer between the excited-singlet state of Molecule A and the neighbouring molecule, B, is followed by its dissociation, resulting in a 50% probability of Molecule B being in the monomer-excited state. The rapidty of the association-dissociation may create a large excitation-migration without any molecular displacement. In this case, Λ is described by Eq. 4[3], where β is the root-mean-square displacement of excitation, and K_e, the equilibrium constant of excimer formation:

$$\Lambda = \beta^2 \frac{k_{DM}[M]}{6(1+K_e[M])} \tag{4}$$

$$\approx \beta^2 \frac{k_{DM}}{6K_e} = (\beta^2/6)\exp(-\Delta E_{MD}/RT). \tag{5}$$

If the product of K_e and [M] is much larger than unity, Eq. 4 can be approximated to Eq. 5. Because K_e is 5.2—20.5 $mol^{-1}\,dm^3$ [6] and [M] is about 7 mol dm^{-3} for 1-MN and 2-MN, the value of Λ can be estimated by Eq. 5 and rewritten using the activation energy of the excimer-dissociation process (ΔE_{MD}).

"Exciton motion"—In neat liquid, there is a kind of singlet-exciton assumed whose length is shorter than that of the molecular crystal because (i) a periodicity in the radial and orientational distributions has been

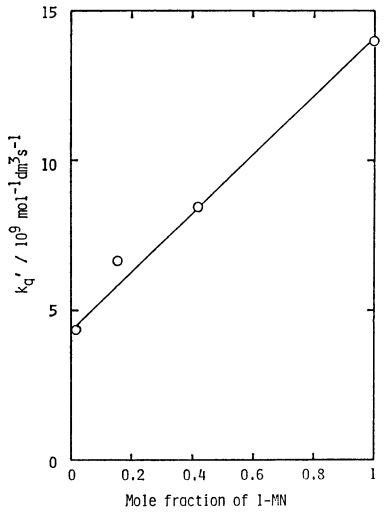

Fig. 6. Change of rate parameter for the fluorescence quenching of 1-MN diluted by *cis*-decaline at 20 °C. The quencher is TCB.

Table 7. Activation energies of excitation migration

Liquid	E_{ex} / kJ mol^{-1}	ΔH / kJ mol^{-1}	$\Delta E'_{MD}$ / kJ mol^{-1}	$\Delta H'$ a) / kJ mol^{-1}
1-MN	22	−19	32	−20
2-MN	18	−19	33	−21
1-EN	17	−24	—	—
2-EN	16	−20	—	—

a) These values were obtained for the ethanol solution by B. K. Selinger (Ref. 6).

recognized for liquid benzene;[14,15] (ii) the absorption spectrum of liquid benzene has a crystal field K-band like that of crystal benzene;[15] and (iii) the band shifts of liquid benzene and 1-EN in the higher-energy region from those of the diluted solution have been explained in terms of excitonic interaction, as have those of the crystal sample.[16,17] Therefore, the excitation energy in neat liquid migrates through the small exciton, while the length of the exciton is shorter than that for the molecular crystal. Though the monomer-excited state is reproduced from a trap of the excimer with a certain temperature, the periodical structure of the liquid is destroyed by thermal motion, so that the excitation migration may not increase monotonically with the temperature. The migration constant of excitation is described by Eq. 6:

$$\Lambda = \Lambda_0(T) \exp\frac{-\Delta E_{MD}}{RT}, \quad (6)$$

where $\Lambda_0(T)$ is intrinsic to the exciton and is as dependent on the temperature as is the length of the exciton.

An experimentally determined value of the activation energy of the migration process is useful for the diagnosis of the migration mechanism. Since a curved line is drawn between log Λ and the reciprocal of the temperature, and since the activation energy gets a little smaller in the higher-temperature region, "exciton motion" is the more reasonable mechanism. It is based on the inference that the migration rate is dependent on both the detrapping and the intrisic exciton length, the latter of which gets smaller with a rise in the temperature. The values of the apparent activation energies are smaller than those of the excimer dissociation process ($\Delta E'_{MD}$) reported in the case of a diluted ethanol solution, as Table 7 shows. Even when taking account of the difference between ΔH in the pure liquid and $\Delta H'$ in the ethanol solution, ΔE_{MD} is considered to be approximately equal to $\Delta E'_{MD} - (\Delta H' - \Delta H)$, whose values are 31 kJ/mol in the cases of both 1-MN and 2-MN, higher than the observed values.

The smaller activation energy may be caused by a decrease in the intrinsic exciton length with a rise in the temperature. However, the collapse of such a liquid exciton at higher temperatures allows excitation transfer through the association-dissociation reaction mechanism at higher temperatures.

It seems that the dilution effect on excitation migration can be understood on the bases of the exciton mechanism. It is reasonable that the gradual increase in k'_q with the mole fraction of 1-MN comes from a concurrent increase in its exciton length. Alternatively, the "association-dissociation reaction of the excimer" mechanism predicts that the value of k'_q will be independent of the concentration of 1-MN for a concentrated solution (0.2 mol dm^{-3}) because of rapid excimer formation.

We wish to thank Dr. T. Okada for permission to use the low-power N_2-laser and the detection system.

References

1) R. Voltz, *Rad. Res. Rev.*, **1**, 301 (1968).
2) S. Lipsky and M. Burton, *J. Chem. Phys.*, **31**, 1221 (1959).
3) J. B. Birks and J. C. Conte, *Proc. Roy. Soc. London, Ser. A*, **303**, 85 (1968).
4) T. Okada, T. Fujita, and N. Mataga, *Z. Phys. Chem. N. F.* **101**, 57 (1976).
5) B. Stevens and T. Dickinson, *J. Chem. Soc.*, **1963**, 5492.
6) B. K. Selinger, *Aust. J. Chem.*, **19**, 825 (1966).
7) L. G. Christophorou and J. G. Carter, *Nature*, **209**, 678 (1966).
8) J. B. Aladekomo and J. B. Birks, *Proc. Roy. Soc. London, Ser. A*, **284** 551 (1965).
9) N. Mataga, M. Tomura, and H. Nishimura, *Mol. Phys.*, **9**, 367 (1965).
10) T. Ohno and S. Kato, unpublished work.
11) M. Kikuchi, K. Kikuchi, and H. Kokubun, *Bull. Chem. Soc. Jpn.*, **47**, 1331 (1974).
12) J. W. Eastman, E. J. Smutny, and G. M. Coppinger, *J. Chem. Phys.*, **53**, 4346 (1970).
13) H. C. Wolf, *Adv. Atom. Mol. Phys.*, **3**, 119 (1967).
14) J. Z. Fischer, "Statistical Theory of Liquids," The Univ. of Chicago Press, Chicago (1964).
15) A. H. Narten, *J. Chem. Phys.*, **48**, 1630 (1968).
16) T. Inagaki, *J. Chem. Phys.*, **57**, 2526 (1972).
17) R. A. MacRae, M. W. Williams, and E. T. Arakawa, *J. Chem. Phys.*, **61**, 861 (1974).