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Unstable Excimer Formation in *cis*-1,2-Di(2-naphthyl)cyclobutane

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An unstable intramolecular excimer which is formed in an excited state of *cis*-1,2-di(2-naphthyl)cyclobutane is investigated. The excimer formation-rate constants and dissociation-rate constants in fluid solutions at low temperatures were determined by picosecond time-resolving measurements. The formation processes are interpreted in relation to the bending motion of the cyclobutane ring. Photophysical characteristics of unstable excimers are shown in this system.

Intramolecular excimer formation has been investigated in a number of compounds having two or more aromatic chromophores in a molecule. Since Hirayama's noted work for various diphenylalkanes, it has been confirmed that the most favorable geometry for a stable excimer is a symmetrical sandwich-like parallel arrangement of aromatic planes at a distance of 0.3—0.4 nm. This is easily achieved for a compound in which two chromophores along the alkane chain are separated by three carbon atoms.1) This result was also confirmed for naphthalene derivatives.2,3)

But, the existence of an unstable excimer, besides the stable excimer, was found in poly(*N*-vinylcarbazole).4,5) It has been reported that the unstable excimer, which is often called a second excimer, comes from a partially overlapping structure of two aromatic rings. Much attention has been paid to the unstable excimers since their photophysical behavior is closely related to the relaxation processes of excitation energy in polymer systems. Recently, unstable excimer formation was reported in a few bichromophoric model compounds.6,7) Studies on such compounds are useful in clarifying the geometry and conformation of the unstable excimer due to the well defined molecular structure and simple relaxation process.8)

In the present work, we report on a new kind of unstable excimer formed in the compound *cis*-1,2-di(2-naphthyl)cyclobutane. Its detailed photophysical characteristics and excimer formation mechanisms are elucidated by means of photostationary and time-resolving measurements. This information will be important for interpreting the excited-state kinetics in more complex polymer systems.

Experimental

Materials. *cis*-1,2-Di(2-naphthyl)cyclobutane (DNCB) was prepared by the photodimerization of 2-vinylnaphthalene in a benzene solution.9) The products were fractionated by column chromatography on silica gel with hexane–dichloromethane (7:1) as the eluent. The obtained DNCB was recrystallized from methanol solution prior to use: mp 95—97 °C; NMR (CCl_4) δ=2.5—2.7 (2H, m), 4.1—4.3 (1H, m), and 6.8—7.6 (7H, m). 2-Ethylnaphthalene (Aldrich Chemical Co.) was used as a monomeric model compound. Spectrograde hexane (Nakarai Chemicals Ltd.) was used as a solvent without further purification.

Measurements. All spectroscopic measurements were carried out in hexane solutions degassed by repeated freeze-thaw cycles at *ca.* 10^{-3} Pa. The concentrations were adjusted to 10^{-4} mol dm^{-3}, at which intermolecular excimer formation was negligible. Fluorescence spectra were measured with a Shimadzu RF-502 spectrofluorophotometer whose spectral response was calibrated according to a standard tungsten lamp. The quantum yields of fluorescence were determined relative to that of quinine sulfate in 0.5 mol dm^{-3} sulfuric acid.10) The decay curves of fluorescence were measured by a single photon counting technique (Ortec Inc., 9200 nanosecond fluorescence spectrometer). For the measurements of the rise and decay curves in the picosecond time region, the 4th harmonic (266 nm, 20 ps) of a passively mode-locked Nd^{3+}: YAG laser was used as an exciting light source. The emission was detected by a Hamamatsu Photonics streak camera (C979) and digitized by a TV camera/microcomputer system (C1000).11,12) Suitable combinations of optical filters were used in order to isolate the monomer fluorescence and the excimer fluorescence.

Results

The absorption spectra of DNCB and 2-ethylnaphthalene are very similar, although a slight red shift of 1.5—2 nm is observed for DNCB. Such a red shift has been reported for a similar compound, *cis*-1,2-diphenylcyclopentane,13) and observed for compounds in which plural naphthyl groups are closely linked intramolecularly, *e.g.*, poly(2-vinylnaphthalene).

The fluorescence spectra of DNCB in hexane at various temperatures are shown in Fig. 1. The spectra clearly show broad excimer emission at 400 nm in the low-temperature range, but the excimer emission is not observed either at room temperature or at 77 K in a rigid glass solvent. The fluorescence excitation spectra for the excimer emission band and for the monomer emission band at a wavelength of about 330 nm agree well with the absorption spectrum. Quantum yields of the monomer and excimer emission are shown in Fig. 2, together with the monomer emission quantum yields of 2-ethylnaphthalene. The quantum yields of excimer emission (Φ_D) have the largest value at an extremely low temperature, −95 °C, which is the freezing point of the solvent. As the temperature increases, Φ_D decreases monotonously, and the quantum yields of monomer emission (Φ_M) increase slightly because of the dissociation of excimer. A further increase of temperature rapidly quenches both of the monomer and excimer fluorescence. The total emission quantum yields of DNCB show much smaller values than those of 2-ethylnaphthalene in the high-temperature region, shown in Fig. 2. These results show that DNCB is able

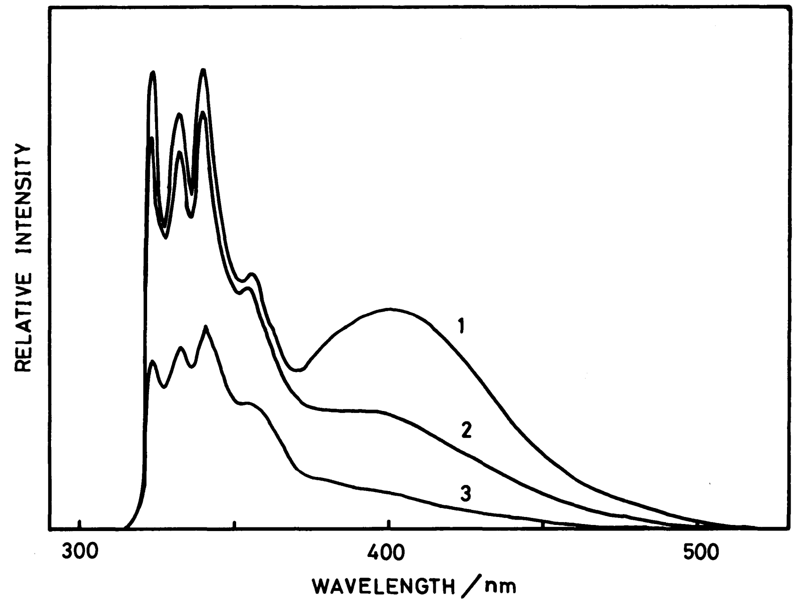

Fig. 1. Fluorescence spectra of DNCB in hexane. 1: −80 °C, 2: −50 °C, and 3: −20 °C.

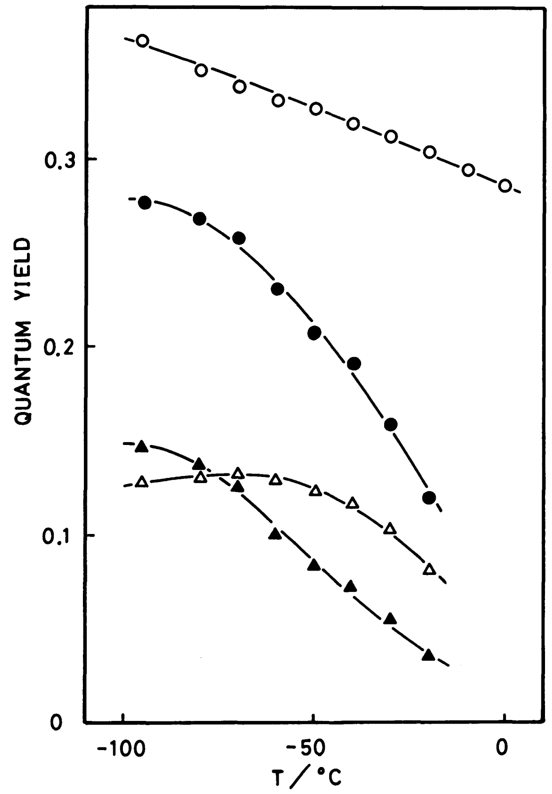

Fig. 2. Fluorescence quantum yields of monomer emission (△), excimer emission (▲) and total emission (●) of DNCB, and quantum yields of monomer emission of 2-ethylnaphthalene (○).

to form an intramolecular excimer by a dynamic process after photoexcitation. The formation process can be achieved by a little conformational change whose rate is very fast even at low temperatures. Since the formed excimer state is not stable, it dissociates to the monomer state or deactivates to the ground state radiationlessly, with increasing temperature.

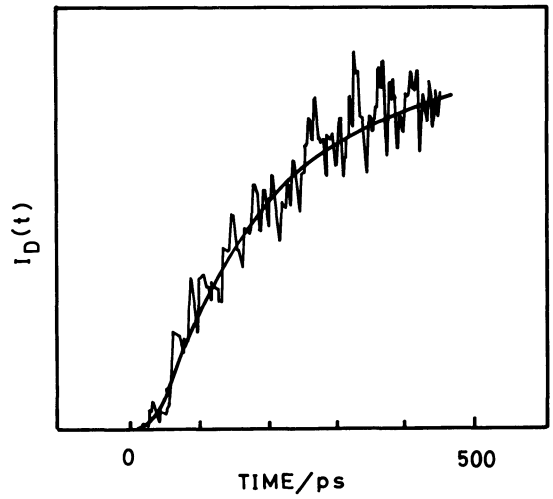

Fig. 3. Rise curve of excimer fluorescence of DNCB at −37°C.
The solid line shows the curve simulated by the function of $I_D(t) = \exp(-t/63\ \mathrm{ns}) - \exp(-t/0.16\ \mathrm{ns})$.

The dynamic process of excimer formation is well confirmed by time-resolved measurements for monomer and excimer fluorescence. Figure 3 shows a rise curve of excimer emission of DNCB in the picosecond time region. The measurements were carried out at various temperatures and the rise-time constants were determined by a simulation method. The decay-time constants were also obtained by the single photon counting technique in the nanosecond region. For the monomer fluorescence, the decay curve should be given as a double exponential decay function, but it could not be confirmed by the picosecond time-resolving measurements because of the weak signal intensities. Decay times for the monomer emission in the nanosecond region are the same as those of excimer emission in the observed temperature range. This fact shows that the association and dissociation rate constants of the excimer are fairly large compared with the other rate constants. Thus, the dynamic equilibrium between the excited monomer state and the excimer state is achieved before deactivation to the ground state. The observed rise- and decay- time constants are summarized in Fig. 4.

Discussion

The naphthyl groups of DNCB come face to face with each other without a deformation of the aromatic rings, as shown in Fig. 5. The pair of naphthyl groups can be expected to form an intramolecular excimer since the aromatic rings can achieve an arrangement similar to the sandwich-type conformation. However, the interaction between two naphthyl groups in the ground state is too weak to make a dimeric complex which would give a different absorption spectrum from an isolated naphthalene unit.[14] Furthermore, the monomer fluorescence spectrum of DNCB is similar to that of 2-ethylnaphthalene. From these facts, it can be concluded that the excited state immediately after photoexcitation is the monomer state and the intramolecular excimer is formed from this excited state by some dynamic processes accompanied by conformational changes of the cyclobutane ring.

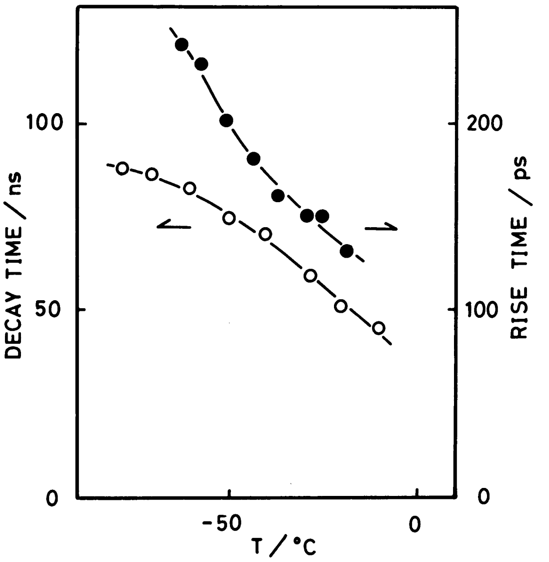

Fig. 4. Temperature dependence of rise and decay time constants.

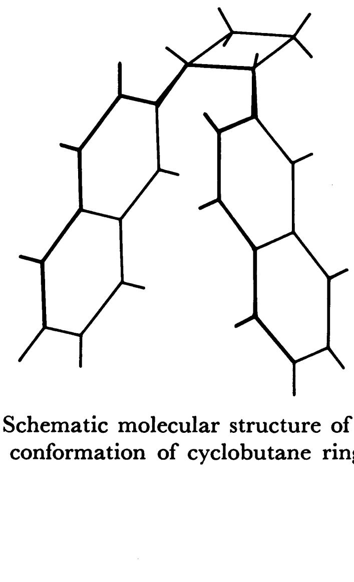

Fig. 5. Schematic molecular structure of DNCB at the planar conformation of cyclobutane ring.

We can obtain the excimer-formation rate constant by time-resolving measurements. The kinetic scheme of this system, and the notation of rate parameters are written as follows.

$$\begin{array}{lll} \mathrm{M} + h\nu \longrightarrow \mathrm{M}^* & & \\ \mathrm{M}^* \longrightarrow \mathrm{M} + h\nu_1 & & k_{01}^{\mathrm{f}} \\ \mathrm{M}^* \longrightarrow \mathrm{M} & & k_{01}^{\mathrm{n}} \\ \mathrm{M}^* \longrightarrow \mathrm{D}^* & & k_{21} \\ \mathrm{D}^* \longrightarrow \mathrm{M}^* & & k_{12} \\ \mathrm{D}^* \longrightarrow \mathrm{M} + h\nu_2 & & k_{02}^{\mathrm{f}} \\ \mathrm{D}^* \longrightarrow \mathrm{M} & & k_{02}^{\mathrm{n}} \end{array}$$

where M and M* represent the naphthyl group in the ground state and the excited state, respectively, and D* is the intramolecular excimer. In the present system, the dynamic equilibrium conditions[15] are satisfied: k_{21}, $k_{12} \gg k_{01}$, k_{02}, where $k_{01}=k_{01}^{\mathrm{f}}+k_{01}^{\mathrm{n}}$, and $k_{02}=k_{02}^{\mathrm{f}}+k_{02}^{\mathrm{n}}$. The rate constants, k_{01} and k_{02}, for the naphthyl groups have previously been reported to be of the order of $10^7\,\mathrm{s}^{-1}$.[16] Judging from the fast rise times of excimer emission and its slow decay, the rate constants k_{21} and k_{12} are larger than k_{01} and k_{02} by a factor of at least 100. Under dynamic equilibrium conditions, the following equations are used.

$$\lambda_2 = k_{21} + k_{12}$$
$$\Phi_{\mathrm{M}} = k_{01}^{\mathrm{f}} k_{12} / \lambda_1 \lambda_2$$

where λ_1 and λ_2 are the decay time constant and rise time constant, respectively, in the excimer response function,

$$I_{\mathrm{D}}(t) = \exp(-\lambda_1 t) - \exp(-\lambda_2 t).$$

The value of k_{01}^{f} was determined by measurements of the fluorescence quantum yield and lifetime for 2-ethylnaphthalene in the same temperature range: $k_{01}^{\mathrm{f}}=4.2-4.4\times10^6\,\mathrm{s}^{-1}$. From the data, λ_1, λ_2, Φ_{M}, and k_{01}^{f}, the excimer formation and dissociation rate constants, k_{21} and k_{12} can be determined. Errors in this calculation come mainly from the simulated values of λ_2, and these are of the order of several per cent. The Arrhenius plots of thus-obtained k_{21} and k_{12} are shown in Fig. 6. From the slopes of these plots, the activation energy of the excimer formation process, E_{21} was found to be 5.0 kJ/mol, and that of the dissociation process, E_{12} was 8.4 kJ/mol (with an error of about ±0.5 kJ/mol). Then, the formation- and dissociation-rate constants are expressed by,

$$k_{21} = 5.1\times10^{10}\exp(-5.0\times10^3/RT)$$
$$k_{12} = 1.6\times10^{11}\exp(-8.4\times10^3/RT)$$

where R is the gas constant. The enthalpy change for the excimer formation in DNCB is given as the difference between E_{21} and E_{12}: $\Delta H=-3.4\,\mathrm{kJ/mol}$. This value is much smaller than the reported ΔH value

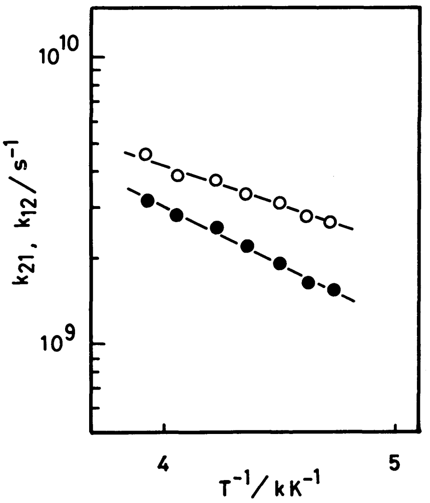

Fig. 6. Arrhenius plots of k_{21}(○) and k_{12}(●).

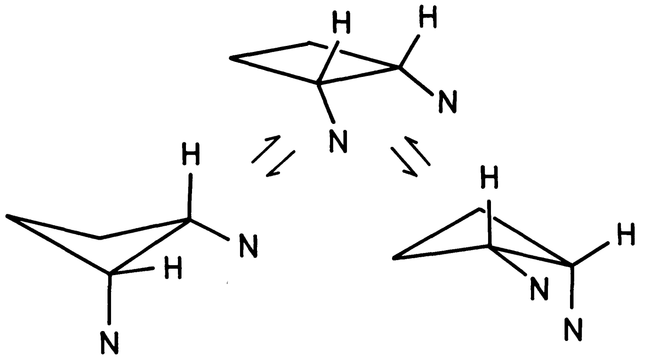

Fig. 7. Bending motion of cyclobutane ring. N: 2-Naphthyl.

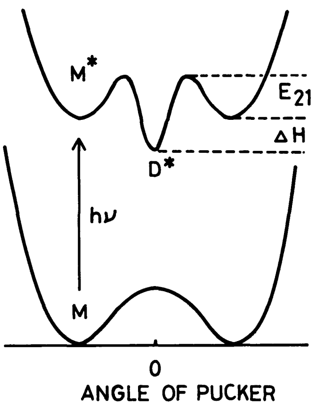

Fig. 8. Schematic potential energy diagram of DNCB.

for the stable excimer of 2-ethylnaphthalene: −18 kJ/mol.[3,17] Thus, the intramolecular excimer of DNCB has a very weak binding energy and exists only in the low-temperature region in contrast to the stable excimers formed in various dinaphthylalkanes.[16]

The excimer formation and dissociation processes seem to correspond with the bending motion of the cyclobutane ring between puckered forms, as shown in Fig. 7. Two naphthalene rings of DNCB can take an overlapped arrangement at the planar form of cyclobutane ring as shown in Fig. 5, which is attained in the course of the bending motion. The planar conformation has been said to be in a little higher energy state, *ca.* 6.2 kJ/mol than the puckered forms studied by Raman spectroscopy.[18] The overlapping arrangement at the planar form of the cyclobutane ring is not a parallel-sandwich arrangement with respect to the naphthyl groups. Assuming the angle, N–C–H, to be 110°, and the distances, C(aliphatic)–C(aliphatic)=0.155 nm, C(aliphatic)–C(aromatic)= 0.152 nm, and C(aromatic)–C(aromatic)=0.139 nm, the planes of naphthalene rings come face to face with each other at an angle, *ca.* 50°. This means their C(aliphatic)–C(aromatic) in-plane axes are inclined at an angle *ca.* 50°, and the distance between the two naphthalene rings is estimated to be 0.28 nm and 0.67 nm for the nearest and farthest aromatic carbon atoms, respectively. The instability of the excimer state is due to this structural restriction which prevents the naphthalene rings from forming the stable parallel sandwich conformation at the distance of 0.3—0.4 nm. The transition rate of the two puckered forms has been assumed to be considerably fast because of the low barrier energy for the ring inversion. In the present work, it is clear that the rate of bending motion is in the order of 10^9 s^{-1}, thus the conformational lifetime of a puckered form is less than a few hundred picoseconds.

According to the above discussion, the schematic potential energy diagram is illustrated in Fig. 8. The photophysical properties of this unstable excimer are noted: 1) small enthalpy gain for the formation process, 2) large dissociation rate to the excited monomer state even in low temperatures, 3) increase of radiationless dissipation to the ground state at high temperatures. Similar properties have been observed for the unsymmetrical naphthalene excimers formed in 1-(1-naphthyl)-3-(2-naphthyl)propane, whose binding energy was found to be 8.8 kJ/mol.[19] These characteristics seem to be common to the unstable intramolecular excimers. It has often been reported that unstable excimers give somewhat blue shifted fluorescence spectra compared with the stable excimer. But, DNCB shows the same excimer emission band as the stable excimer in spite of its instability. The wavelength of excimer fluorescence should be determined by the difference between the excited state electronic energy and the ground state energy of the excimer geometry. If the ground state energy becomes higher than that of the stable excimer, it is possible that the unstable excimer shows longer wavelength emission than that of the stable excimer. In the present case, the cyclobutane ring at the planar conformation forces the naphthyl groups to have a higher energy geometry both in the ground state and in the excimer state. Therefore, the emission band of excimers seems to be unsuitable as a measure of instability.

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