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Effect of Conformation on Ring Opening of Cis and Trans Dimers of Acenaphthylene in the Triplet State. Direct Detection of Hydrocarbon Biradical, 1,1′-Biacenaphthene-2,2′-diyl[1]

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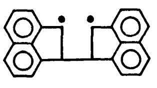
Triplet sensitized photodecomposition of cis and trans dimers of acenaphthylene (c-D and t-D) has been studied in benzene by means of a nanosecond laser flash photolysis. An aromatic hydrocarbon biradical, 1,1′-biacenaphthene-2,2′-diyl (**1**) was found as an intermediate for the decomposition of triplet t-D to acenaphthylene monomers. The rate of bond opening was directly measured to be $8.3\times10^6\ s^{-1}$ at 20 °C. The temperature dependence of the rate yields the frequency factor $2.8\times10^7\ s^{-1}$ and activation energy 3.1 kJ mol^{-1}. The lifetime of **1** is 330 ns; this is insensitive to temperature changes (6—64 °C). Oxygen quenches **1** with the rate constant of $9\times10^9\ M^{-1}\ s^{-1}$ (1 M=1 mol dm^{-3}). On the other hand, the triplet state of c-D did not show any evidence of the presence of **1** as an intermediate. The difference of ring opening mechanisms between the two isomers is interpreted in terms of different steric hindrances between two acenaphthene rings. The triplet-triplet (T-T) absorption spectra of both dimers resemble each other. No characteristic absorption due to intramolecular triplet excimer of naphthalene was observed even for c-D.

Direct detection of unstable biradicals has been made in the Norrish type II reactions of alkyl phenyl ketones by means of laser photolysis methods.[2,3] Such studies are very important to elucidate reaction mechanisms, *i.e.*, to investigate channels of deactivation of a precursor in the excited state as well as behaviors in the biradical itself.[4]

Takamuku and Schnabel[5] reported the observation of biradical, **2**, produced through ring cleavage in the triplet state of r-1,c-2-bis(methoxycarbonyl)-t-3,t-4-di(1-naphthyl)cyclobutane. The spectrum of **2** drew our attention to the spectrum which had been observed in the triplet photosensitization of trans dimer of acenaphthylene during the course of our study about behavior of the triplet states containing acenaphthene units. We report here direct detection of a pure hydrocarbon biradical, **1**, formed through triplet sensitization of t-D and the influence of cis and trans conformations on the cleavage of a cyclobutane ring of acenaphthylene dimers, as studied by the laser flash photolysis. In addition, we show T-T absorption spectra of both dimers and compare them with the spectrum of acenaphthene.



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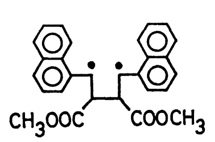

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Experimental

Materials. The cis and trans dimers of acenaphthylene (c-D and t-D) were synthesized by photodimerization. Acenaphthylene monomer (M) as a starting material was purchased from Wako Pure Chemical Ind. and recrystallized once from ethanol. Procedures of synthesis and purification were essentially the same as the methods described by Nerbonne and Weiss[6] except for a slight modification noted below. A light source was a 450-W Hg-lamp (Ushio, UM-455) with a water-cooled quartz jacket. A few sealed glass tubes containing *ca.* 70 ml of acenaphthylene solution were immersed in a thermostated water bath at 25 °C and irradiated through a side window of the bath. The thick glass window and the tubes cut off the light less than 340 nm. In the preparation of c-D, cyclohexane was used as a solvent in the place of hexane in Ref. 6 and solutions of M were bubbled by oxygen before sealing. Purities of the dimers were checked by UV absorption[7,8a] and emission spectra[9] measured with a spectrophotometer (Hitachi Model 200-10) and a spectrophotofluorimeter (Hitachi Model MPF-2A), respectively.

Acenaphthene (ACN) as a reference to an unit chromophor of the dimers was purified by triple recrystallization from methanol. The zone-refined benzophenone (BP) or the G. R. grade acetophenone (AP) was used as a triplet sensitizer. Methylcyclohexane and isopentane for a mixed glass solvent at 77 K were purified by the usual methods. The spectrograde benzene (Dotite) was used as a solvent in steady illumination and flash photolysis experiments.

The Nanosecond Flash Photolysis. The solutions of each dimer containing a sensitizer were degassed by several freeze-pump-thaw cycles. The nanosecond flash photolysis was done at 347 nm excitation using a ruby laser described elsewhere.[10] The laser beam excites the sensitizer but does not excite the dimers. Transient absorption spectra in the 340—600 nm range were measured at room temperature. For kinetic measurements, temperature control of a sample was carried out by circulating thermostated water in a quartz Dewar vessel equipped with a thermocouple.

Steady State Illumination. Both solutions of c-D and t-D containing BP were illuminated steadily with 365 nm light for isolation of decomposed products. The 365 nm light was obtained from a 100-W high-pressure Hg-lamp (Toshiba SHL-100UV) using a combination of glass lenses and a filter (Toshiba UV-D1C). After condensation of illuminated solutions with an evaporator, products were separated and identified by the aid of a TLC technique and a UV-VIS absorption measurement.

Results and Discussion

Steady State Illumination. Continuous irradiation with the 365 nm light gave rise to pale-yellow coloration of both dimer solutions. This coloration arises from gradual increase of the characteristic absorption band of M in the visible region. The relative rate of such change, as monitored at the absorption band, was faster for t-D than for c-D. Examination of the R_f

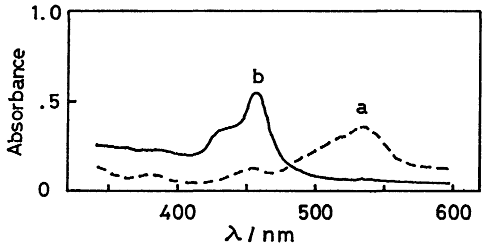


Fig. 1. Transient absorption spectra observed for cis dimer of acenaphthylene (5.0×10^{-3} M) in benzene containing benzophenone (4.0×10^{-3} M) as a sensitizer.
a: 30 and b: 130 ns after the start of laser oscillation.

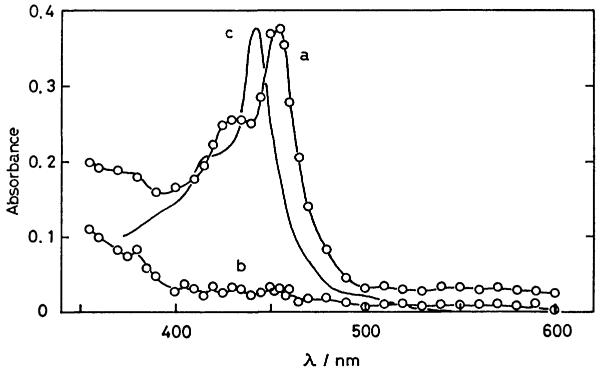


Fig. 2. Transient absorption spectra for cis dimer of acenaphthylene (5.0×10^{-3} M) [a and b] and for acenaphthene (1.0×10^{-2} M) [c] in benzene using acetophenone (1.0×10^{-2} M) as a sensitizer.
a: 250 ns, b: 3 μs, and c: 1 μs after the start of laser oscillation.

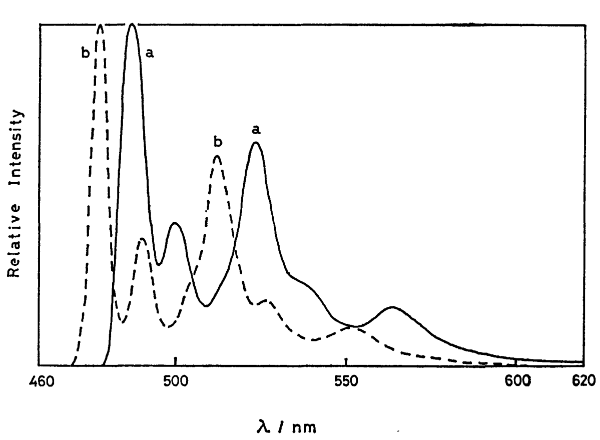


Fig. 3. Phosphorescence spectra measured for c-D [a] and ACN [b] in methylcyclohexane–isopentane matrix at 77 K (uncorrected for spectral response).

value of TLC and the UV absorption spectrum showed recovery of M for each solution. Products other than M, except for the starting materials, were unrecognized on a plate of TLC developed by the mixture of benzene and cyclohexane (1:3 in volume). It was thus confirmed that both of the dimers sensitized to the triplet state cause cycloreversion to acenaphthylene monomers.

Benzophenone (or Acetophenone)——Cis Dimer in Benzene. Figure 1 shows transient absorption spectra in the BP(4.0×10^{-3} M)–c-D (5.0×10^{-3} M) system obtained by the nanosecond flash photolysis. Similar spectra for the AP (1.0×10^{-2} M)–c-D (5.0×10^{-3} M) system is given in Fig. 2 together with the T-T absorption of ACN for the purpose of comparison. The absorption at 530 nm in Fig. 1a is attributable to triplet benzophenone (^{3}BP)[11] formed immediately after excitation. The ^{3}BP decays rapidly with the rate parameter of 1.7×10^7 s^{-1} under the present concentration of c-D. Since c-D has the lowest triplet state energy ($E_T^{(c)}=20.6\times10^3$ cm^{-1}), lower than that of BP ($E_T^{(BP)}=24.25\times10^3$ cm^{-1}),[12] the T-T energy transfer to c-D will dominate deactivation of ^{3}BP. The $E_T^{(c)}$ value was estimated from the 0-0 band of phosphorescence measured in methylcyclohexane–isopentane matrix at 77 K (Fig. 3a). A new band with maximum at 455 nm (Fig. 1b) grows up with a rate identical to the decay rate of ^{3}BP. After reaching its maximum intensity, this band disappears with a life of *ca.* 2 μs and no other specific absorption is observed. Decay time of this band was shortened by air saturation. The absorption spectrum is quite similar to that in Fig. 2a observed by replacing BP with AP ($E_T^{(AP)}=25.75\times10^3$ cm^{-1})[12] as a sensitizer. Namely, this transient is independent of a sensitizer. The band 1b is also similar in position and shape to the T-T absorption of ACN as a reference (Fig. 2c), although the maximum of the former band is slightly red-shifted, from 422 nm of the latter band to 455 nm. These observations allow us to assign both absorptions with the maxima at 455 nm (Figs. 1b and 2a) are to be attributed to the triplet state cis-dimer, ^{3}(c-D).

Decay rate of the band at 455 nm tends to become faster with each run. The sample solutions were also tinted with yellow by many shots of laser pulses. The UV-VIS absorption measurements confirmed the presence of M in these photolyzed solutions. This corresponds to recovery of M by the steady state illumination mentioned above. Therefore, it is considered that the acceleration of decay rate arises from quenching by M molecules accumulated gradually by each flash photolysis. The T-T energy transfer from ^{3}(c-D) to M by diffusional encounter may be responsible for the quenching, because the triplet energy of M, $E_T^{(M)}$, has been estimated to be 15000—16500 cm^{-1},[13] much lower than that of ^{3}(c-D). The plot of reciprocal lifetimes of ^{3}(c-D) against the number of experimental runs (25 points), in analogy to the Stern-Volmer plot, gave a good linear relation. Then, the intrinsic lifetime of ^{3}(c-D) was estimated, by the least square method, to be 2.2 μs at 20 °C from the extrapolation to the first experiment. An Arrhenius plot for the decay rate determined by this procedure as a function of temperature fits a straight line (Fig. 7c) yielding activation energy, $E_a^{(c)}=(25\pm3)$ kJ mol^{-1}, and the frequency factor, $A^{(c)}=(1.36\pm0.08)\times10^{10}$ s^{-1}, for 6 points between 9 and 58 °C.

Electronic Interaction between Naphthalene Rings of c-D. The electronic interaction between two naphthalene rings of c-D in the triplet state is important, because conformation of naphthalene rings of c-D (dihedral angle between the two rings≈60°)[9] is supposed to

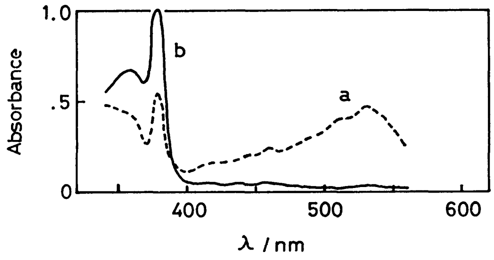


Fig. 4. Transient absorption spectra observed for trans dimer of acenaphthylene ($\approx 2\times10^{-3}$ M) in benzene containing benzophenone (4.0×10^{-3} M) as a sensitizer.
a: 40 and b: 230 ns after the start of laser oscillation.

be similar to that of 1,2-di-(1-naphthyl)ethane (DNE), which exhibits the phosphorescence and absorption of intramolecular triplet excimer of naphthalene.[14]

Let us first compare the phosphorescence spectrum of c-D with that of ACN in a rigid glass at 77 K (Fig. 3). The spectral shape of c-D (3a) is very similar to that of ACN (3b). No broad band characteristic of the triplet excimer[14,15] is observed around 520—500 nm. The 0-0 band of c-D is located at 486 nm, showing a red-shift compared with that of ACN. This red-shift and wavelength position are common to naphthalene dimers stable in the ground state such as an intramolecular sandwich dimer of 1,3-di(1-naphthyl)propane[16] and a dimer in poly(2-vinylnaphthalene).[17] They have the 0-0 bands at 485 nm and 482 nm, respectively. Phosphorescence features noted above indicate that at 77 K, c-D can not take a disposition similar to that of the triplet excimer, although some weak electronic interactions like those in the stable dimers are present between the naphthalene rings of ^{3}(c-D).

Next, we should notice the T-T absorption of c-D. The spectrum of ^{3}(c-D) is composed of the main band around 455 nm and a weak absorption tail in the longer wavelength region (530—600 nm). Since the two naphthalene rings in c-D and in DNE dispose in a similar manner, the transient absorption spectrum of c-D is expected at room temperature to involve a definite absorption band due to triplet excimer at 470 nm, like that observed in DNE.[14] However, the spectrum in Fig. 1b or 2a exhibits no additional absorption band around 470 nm other than the contribution of the red side slope of the main band. Kinetic measurements revealed further that both the main and the weak absorption band decay with approximately identical lifetimes up to 3 μs after excitation. Figures 2a and 2b represent this spectral change with time; the spectrum of ^{3}(c-D) decays monotonously without any spectral change. That is to say, the c-D does not show any distinct absorption around 470 nm due to the triplet excimer of naphthalene, although DNE does show such an absorption. Therefore, we consider that owing to structural rigidity, it is impossible for the two naphthalene rings of c-D, even at room temperature, to take a conformation favorable for exhibiting a distinguished absorption due to triplet excimer.

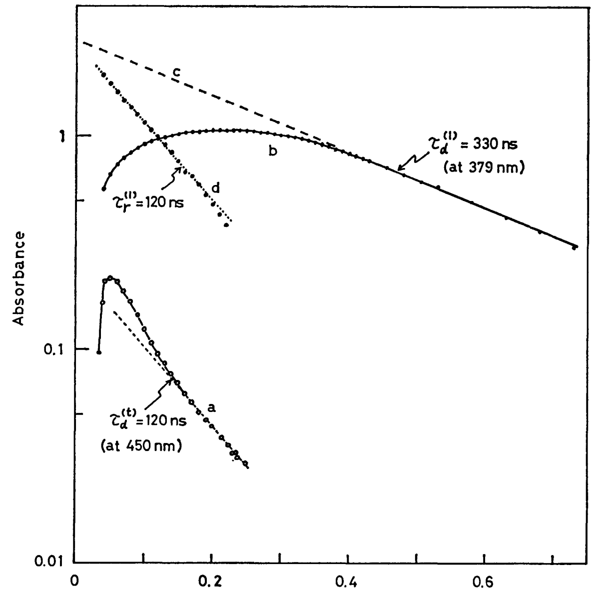


Fig. 5. Rise and decay profiles of transient absorptions monitored at 450 nm [a] and 379 nm [b].
Owing to overlap of ^{3}BP absorption, the linearity of [a] is wrong. [c]: the extrapolation of decay in Curve b. [d]: (Curve c — Curve b) *vs.* t plot. This slope derives the rise time of **1**.

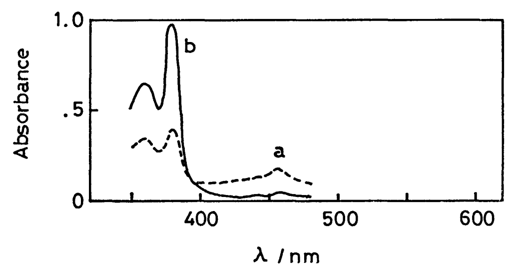
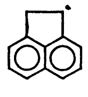


Fig. 6. Transient absorption spectra for the trans dimer (2.0×10^{-3} M) in benzene with acetophenone (1.0×10^{-2} M) as a sensitizer.
a: 40 and b: 170 ns after the start of laser oscillation.

Benzophenone (or Acetophenone)——Trans Dimer in Benzene. Figure 4 shows time-dependent absorption spectra in the BP (4.0×10^{-3} M)-t-D ($\approx 2\times10^{-3}$ M) system. The spectrum at 40 ns (4a) consists of a band around 530 nm (^{3}BP), a weak band around 450 nm, and a sharp peak at 379 nm. The first and second bands decay rapidly in the initial time domain, but the band at 379 nm grows (4b). The rise time (120 ns) monitored at 379 nm was identical to the decay time observed at 450 nm. After reaching the maximum intensity, the 379 nm band decreases with the lapse of time, obeying the first-order decay kinetics. Its rate was not affected by photolysis numbers, in contrast to the decay of ^{3}(c-D). The decay time is 330 ns. Time dependences for 379 and 450 nm absorptions are illustrated in Fig. 5.

Intermediacy of the triplet t-D, ^{3}(t-D), is ambiguous in Fig. 4, since the expected absorption of ^{3}(t-D) is masked by the absorption of ^{3}BP in the 400—460 nm region. To clarify the spectrum of ^{3}(t-D), we chose AP as a sensitizer, because the extinction coefficient of ^{3}AP is rather low in the wavelength range greater than 400 nm.[18] Figure 6 represents transient spectra measured in such a system. A well-defined absorption band of ^{3}(t-D) is observed with maximum at 455 nm in the early time after excitation. It resembles well the spectra of ^{3}(c-D) in Figs. 1b and 2a, which demonstrates no large difference in the triplet electronic states of both dimers. Decay of this band is accompanied by remarkable growth of the 379 nm band, which is identical to the spectrum of Fig. 4b. It is thus clear that ^{3}(t-D) is a precursor generating the transient with the 379 nm absorption band.

*Identification of Biradical **1** and Its Properties.* We still have to assign the spectrum around 379 nm. The spectrum is quite similar to that of **2**[5] in both shape and position. The decay of this band obeys the first-order kinetics. Its lifetime (330 ns) is close to that of **2** (225 ns in acetonitrile).[5] As mentioned previously, t-D causes cycloreversion to the corresponding monomers, just like r-1,c-2-bis(methoxycarbonyl)-t-3,t-4-di(1-naphthyl)cyclobutane does. Since the biradical **2** is formed through one bond breaking of the cyclobutane ring of the latter, the present transient is supposed to be a transient formed in a similar fashion. Then, the species with 379 nm band is presumed to be biradical **1**. The similarity of the conjugate system of **1** and **2** is a reasonable way to interpret the similarity of their spectra. In fact, acenaphthene radical (**3**) corresponding to a half of **1** has been reported to possess an absorption in the identical wavelength region (320—400 nm)[19] and also 1-ethylnaphthalene-α-yl (**4**) shows an absorption spectrum similar to that of **1** in the near wavelength position.[20] Furthermore, the spectrum observed here differs from spectra of a group of hydrocarbon biradicals such as 2,3-dihydrophenalene-1,3-diyl (**5**) and 7,8,9,10-tetrahydrocyclohepta[*de*]naphthalene-7,10-diyl (**6**) measured by Muller *et al.*[21] and Gisin *et al.*,[22] respectively.



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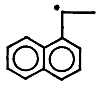

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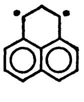

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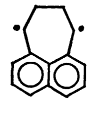

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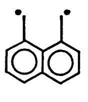

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The above statement implys that the present intermediate keeps the acenaphthene structure but not 1,8-diethylnaphthalene-α,α′-diyl (**7**) structure in the bond scission of a cyclobutane ring; namely, the bond scission will occur between 1- and 1′-carbons, but not between 1- and 2-carbons. Hence, the spectrum in question can safely be assigned to be due to biradical **1**.

Dissolved oxygen quenches **1** with a bimolecular rate constant of $0.9\times10^{10}\ \mathrm{M^{-1}\ s^{-1}}$ in benzene at 19 °C.[23] This value is comparable with $2.1\times10^{10}\ \mathrm{M^{-1}\ s^{-1}}$ for **2** in acetonitrile[5] and $1.3\times10^{10}\ \mathrm{M^{-1}\ s^{-1}}$ for **6** in methanol.[22] This profound effect of oxygen has been known as a characteristic behavior for 1,4-biradicals in the triplet spin state produced from alkyl phenyl ketones by the type II reactions.[2,4] A preliminary result indicates that diethyl mercury, a compound involving a heavy atom, quenches **1** effectively with the rate constant of $3.7\times10^{7}\ \mathrm{M^{-1}\ s^{-1}}$. This finding would not contradict the assumption that **1** is a triplet biradical. The decay time of **1** was little influenced by temperature changes from 6 to 64 °C.[24] Inverse of the rise time of **1**[25] fits the Arrhenius equation of parameters, $E_a^{(t)}=3.1\pm0.2$ kJ mol^{-1} and $A^{(t)}=(2.8\pm0.4)\times10^{7}\ \mathrm{s^{-1}}$.

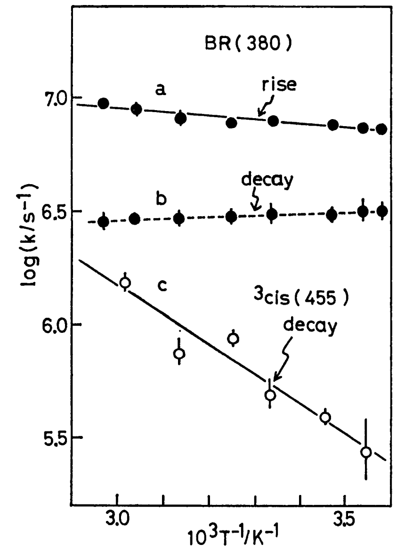


Fig. 7. Arrhenius plots for rise and decay rates of biradical **1** (BR) and for decay rate of triplet cis dimer (^{3}cis). Errors are indicated by bars. The numbers in parentheses denote the absorption wavelengths monitored.

TABLE 1. RISE (τ_r) AND DECAY (τ_d) TIMES OF TRANSIENT MONITORED AT EACH ABSORPTION MAXIMUM (λ_{max}) AT 20 °C

Transient	λ_{max}/nm	τ_r/ns	τ_d/ns
^{3}cis	455		2.2×10^3
^{3}trans	455		120
BR **1**	379	120	330
			65 (in air)

TABLE 2. ARRHENIUS PARAMETERS OBTAINED FOR THE DECAY RATE OF TRIPLET *cis* DIMER AND FOR THE RISE AND DECAY RATES OF BIRADICAL **1**
(temperature range: 6—60 °C)

	A/s^{-1}	E_a/kJ mol^{-1}
^{3}cis decay	1.36×10^{10}	25
1 rise	2.8×10^{7}	3.1
1 decay	1.9×10^{6}	−1.2

Arrhenius plots are shown in Fig. 7. Rate constants and Arrhenius parameters are collected in Tables 1 and 2, respectively.

Reaction Scheme. Reaction scheme of the triplet-sensitized ring opening of acenaphthylene dimers can be represented as Fig. 8.

The triplet-sensitized t-D causes a bond scission

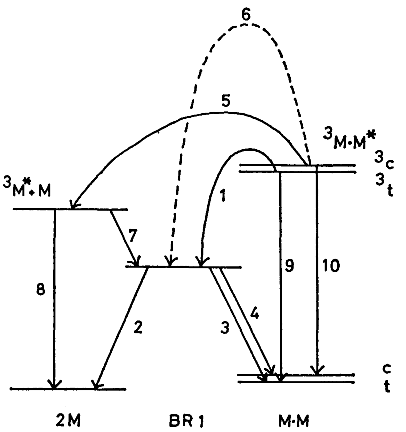
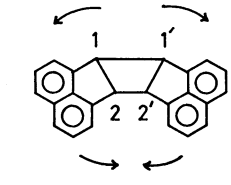


Fig. 8. Reaction scheme of cis and trans dimers of acenaphthylene sensitized to the triplet state.
BR **1** refers to biradical **1**, M acenaphthylene monomer, M-M the dimer of acenaphthylene, and c and t indicate the cis and the trans dimer, respectively. The process of direct decomposition from ^{3}c to 2M is omitted. Processes, 1, 5, and 6 are illustrated by curves to emphasize potential barriers.

(Process 1) to generate **1**, which subsequently undergoes the second bond cleavage leading to production of two acenaphthylene monomers, 2M (Process 2). Processes 3 and 4 going back to the ground states of t-D and c-D, respectively, should compete with Process 2, because **1** has been assumed as a common intermediate for the photodimerization of acenaphthylene (Process 7 followed by Processes 3 and 4).[8b,c] The rise time of **1**, $\tau_r^{(1)}$, corresponds to the decay time of ^{3}(t-D), $\tau_d^{(t)}$, which depends on the rates of both Processes 1 and 9. The deactivation to the ground state in ^{3}(t-D), Process 9, would not differ so much from the corresponding one in ^{3}ACN, for the electronic state of ^{3}(t-D) does not differ so much from that of ^{3}ACN. Since the decay time of ^{3}ACN, $\tau_d^{(\mathrm{ACN})}$ (>16 μs),[26] is considerably longer than $\tau_r^{(1)}$ (120 ns), contribution of Process 9 would be negligible to the decay of ^{3}(t-D). Namely, the inverse of $\tau_r^{(1)}$ gives the rate constant of primary bond opening (Process 1). Thus, the Arrhenius parameters, $E_a^{(t)}$ and $A^{(t)}$, obtained from Fig. 7a belong to this process of biradical formation. The small activation energy and moderate frequency factor reflect the ease of the reaction 1. Moreover, it is worth noting that the $E_a^{(t)}$ value (260 cm^{-1}) is very close to the frequency energy (280 cm^{-1}) of vibrational progression in ^{1}L$_a$← ^{1}A absorption spectrum and the frequency (269 cm^{-1}) in the Raman spectrum characteristic to t-D.[9] The bond opening of ^{3}(t-D) may be promoted by the thermal excitation of these modes.

On the other hand, the c-D sensitized to the triplet state dissociates to monomers with no production of **1** as an intermediate, *i.e.*, Process 6 was not found. Some possible mechanisms are as follows. Since $E_T^{(M)}$ is 15000—16500 cm^{-1},[13] $E_T^{(c)}$ 20600 cm^{-1}, and the ground state of c-D lies near the state of a pair of monomers (2M),[9] then the energy level of the state, ^{3}M*+M, is lower than that of ^{3}(c-D). Accordingly, two channels for decomposition are energetically possible: one is a pathway generating ^{3}M*+M (Process 5) and another a direct cycloreversion to 2M. According to the spin conservation rule, the spin-allowed Process 5 may be more favorable than the spin-forbidden direct decomposition to 2M. At the present stage of investigation, however, we can not decide clearly which process is dominant. Moreover, Process 10 (deactivation to the ground state) competing with the decomposition process is involved in the total decay of ^{3}(c-D), $\tau_d^{(c)}$. Its contribution to $\tau_d^{(c)}$ is larger than that of Process 9 to $\tau_d^{(t)}$, as judged from their lifetimes: $\tau_d^{(c)}$ 2.2 μs, $\tau_d^{(t)}$ 0.12 μs, and τ_d^{ACN} 16 μs, which is regarded as an approximate value to the reciprocal rates for Processes 9 and 10. Under these circumstances, temperature dependence of $\tau_d^{(c)}$ is swayed by relative contribution of the above competing processes. This suggests that the Arrhenius plot for the decay of ^{3}(c-D) would not become linear. Nevertheless, the present result showed that the plot becomes approximately linear (Fig. 7c). It is probably due to the narrowness of the temperature range. Therefore, the observed values of $E_a^{(c)}$ and $A^{(c)}$ do not directly reflect the temperature change of a certain ring opening reaction process. However, ^{3}(c-D) decays rather slowly compared with ^{3}(t-D); Process 5 proceeds more slowly than Process 1. If frequency factors for these two processes are nearly equal, an activation energy for Process 5 will be higher than $E_a^{(t)}$. This estimation relates to the next discussion.

Reactivity Difference between Cis and Trans Dimers. The striking difference in triplet reactivities between cis and trans dimers can be interpreted in terms of the difference in steric hindrances between two ACN rings, as follows. At least one bond of the cyclobutane ring of c-D or t-D must be stretched prior to bond scission. Stretching of C_1–C_1' bond in the directions



indicated by the arrows moves ACN rings in the directions indicated by arrows and gives rise to changes in the relative disposition of two ACN rings. In the case of c-D, the edges of the two ACN rings on the side of the C_2–C_2' bond are brought close to each other, whereas the other sides of the ACN rings separate. The very high potential barrier resulting from repulsion between two ACN rings should be overcome in order that the bond opening may proceed through such deformation. It seems impossible that c-D can cleave one bond in such a manner as to generate **1** (Process 6 in Fig. 8). It will be rather easy to break two bonds, C_1–C_1' and C_2–C_2', simultaneously, because such a high potential barrier is removed, although a fairly high potential barrier still remains for c-D to open the two bonds. In the case of t-D, the high potential barrier resulting from repulsion between ACN rings is absent and only one bond breaking is necessary to generate **1**. Therefore, it is considered that Process 1 proceeds very smoothly.

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23) The rate constant value was estimated by the Stern-Volmer equation $\tau^{-1}=\tau_0^{-1}+k_q[O_2]$, where $\tau=65$ ns, $\tau_0=330$ ns, and $[O_2]=1.4\times10^{-3}$ M. The concentration of dissolved oxygen was derived from data in the following reference; A. G. Loomis, "International Critical Tables of Numerical Data. Physics, Chemistry, and Technology," ed by E. W. Washburn *et al.*, McGraw-Hill, New York (1928), Vol. III, p. 261.

24) A least square fit to an Arrhenius plot gave a negative activation energy, $E_a=-1.2\pm0.2$ kJ mol^{-1} and a frequency factor, $A=(1.9\pm0.1)\times10^6$ s^{-1} with a relatively poor correlation factor, 0.91. In order to examine whether this small negative activation energy is meaningful or not, we are now investigating the effect of temperature over a wider range.

25) Uncorrected for small contribution of the decay rate of ^{3}BP.

26) Under the present experimental conditions, ^{3}ACN decayed according to the nearly complete second-order kinetics, probably due to T-T annihilation. Apparent decay time was *ca.* 4.4 μs in the initial stage of time and *ca.* 16 μs in the later stage. The latter value is given as $\tau_d^{(ACN)}$ in the text.