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Laser Photolysis Studies on [2+2]-Photocycloreversion and Photoisomerization Reactions of *trans*- and *cis*-1,2-Di(1-pyrenyl)cyclobutane Dimers through Radical Ion Intermediates

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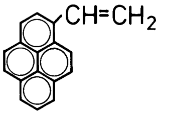
Transient radical ion intermediates of [2+2]-photocycloreversion and photoisomerization reactions of the 1-vinylpyrene (**1**) cyclobutane dimers, *trans*- and *cis*-1,2-di(1-pyrenyl)cyclobutanes (**2t** and **2c**, respectively), were studied by nanosecond laser photolysis measurements; the reaction quantum yields were determined by photoproduct analysis. The excited singlet state of dimers **2t** and **2c** was quenched by an electron acceptor, 1,4-dicyanobenzene, with a diffusion-controlled rate in a polar acetonitrile solvent. The transient absorption spectra of the dimers in the system showed the formation of a dimer radical cation of pyrene chromophores, whose positive charge was delocalized in the two pyrene rings. The dimers were cleaved to form **1** through the dimer radical cation. By contrast, the formation of a dimer radical anion could not be observed in quenching by an electron donor, *N*,*N*-dimethyl-*p*-toluidine. The cleavage yield of the dimers from the anionic species was low. The decrease in the electron density in the cyclobutane bond in the cationic state promotes the cycloreversion reaction of dimers. In the absence of an electron donor or acceptor in the nonpolar benzene solvent, the direct photocleavage of **2t** and **2c** to **1** through the singlet excited state occurred efficiently, whereas in polar acetonitrile the cleavage was reduced to half by solvation of the excited states. A photocleavage of dimers also occurred in their triplet states.

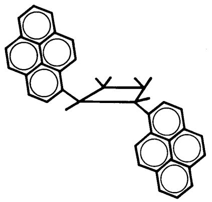
The fragmentation reactions of cyclobutane compounds into two olefins, and of oxetane into a carbonyl group and an olefin, have been considered to be good prototypes of [2+2]-cycloreversion reactions.[1-17] If two bonds of the cyclobutane ring are broken simultaneously according to the Woodward–Hoffmann rule, the cleavage reaction proceeds in one step without any transient intermediate.[2] In this case, the stereoselective cycloreversion of cyclobutanes, similar to the case of cycloaddition of olefins, is allowed in their photoexcited states. A photoinduced [2+2]-cycloreversion reaction of cyclobutanes has occasionally been used as the simplest case for theoretical studies of the principle of orbital symmetry conservation.[3,4]

Recently, many reports concerning photocycloreversion reaction have been devoted to two fields. The photocleavage of pyrimidine dimers of DNA is of biological interest.[1,14] UV-Irradiation of DNA produces pyrimidine dimers; this damaged DNA is photoreactivated by the cycloreversion of the dimers caused by a photoreactivating enzyme. Secondly, chemically stored energy in the strained molecules is important from the standpoint of solar-energy storage.[10-13] For this purpose, the valence isomerizations of norbornadiene to quadricyclene and cage compounds have been extensively studied in this field.

As for the recent mechanistic studies concerning the photocycloreversion of the cyclobutane ring, many transient intermediates have been reported to exist.[1,7-17] 1,4-Diradical intermediates are occasionally found in the pyrolysis or photocleavage via the excited triplet state of cyclobutanes.[7-9,11,15,18] Photochemically produced excited complexes, such as excimers and exciplexes, are also reported to initiate cleavage.[11-17] The cycloreversions via the radical cation or anions are mainly studied by using gamma-ray irradiation and pulse radiolysis.[15] The behavior of the cyclobutane radical cations in the cycloreversion reaction has also been studied by theoretical calculations as well as by chemically induced magnetic polarization (CIDNP) experiments.[19,20]



(1)



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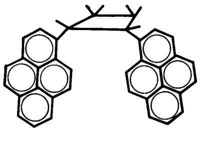


(2c)

In the present work, we studied the radical cation and anion formation of cyclobutane compounds by nanosecond laser photolysis, and tried to understand the transient intermediates which participate in the cleavage and isomerization reactions via the ionic states. The two isomers of the 1-vinylpyrene (**1**) dimers, *trans*- and *cis*-1,2-di(1-pyrenyl)cyclobutanes (**2t** and **2c**, respectively), have two pyrenyl (Py) groups in the vicinal position of a cyclobutane ring. The chromophore Py is well-known for excimer and dimer radical cation formations:[21-23] In this report, the term "dimer radical ion" is used for the dimeric radical ion whose positive or negative charge delocalizes between two chromophores, whereas the term "radical ion of dimer" is used for the radical ion of one chromophore in cyclobutanes.[23-29] By the measurement of laser photolysis, the "dimer radical ions" and "radical ion of dimers" of **2t** and **2c** were well distinguishable with the transient absorption spectra. Besides the laser photolysis measurements, the reaction quantum yields of photoinduced cycloreversion and isomerization were determined by product analysis, and are discussed with regard to the transient intermediates observed in the transient absorption spectra.

Experimental

Chemicals. 1-Vinylpyrene **1** was synthesized from 1-pyrenecarbaldehyde by a Wittig reaction. Purification was made by recrystallization and silica-gel column chromatography with hexane–dichloromethane (5:1, v/v) as the eluent. Care was taken to eliminate pyrene, which was an impurity in 1-pyrenecarbaldehyde. Pyrene (Py, Tokyo Kasei Kogyo Co.) was purified twice by recrystallization and once by column chromatography. 1,4-Dicyanobenzene (DCNB, Wako Pure Chem. Ind.) and benzophenone (BP, Wako) were purified three times by recrystallization. *N*,*N*-Dimethyl-*p*-toluidine (DMT, Wako) was purified by distillation under reduced pressure prior to use.

Benzene (Wako) and 2-chlorobutane (Tokyo Kasei) were dried over $CaCl_2$ and purified by distillation. Acetonitrile (MeCN, Wako) was dried by refluxing over P_2O_5 several times and was fractionally distilled. 2-Methyltetrahydrofuran (MTHF, Tokyo Kasei) was filtered using an Al_2O_3 column and then dried. Purification was achieved by distillation under N_2 and subsequent vacuum distillation.

1-Vinylpyrene **1** cyclobutane dimers, **2t** and **2c**, were photochemically produced: The photodimerization of **1** in a MeCN solution produces *trans*- and *cis*-cyclobutane dimers.[30] Photoirradiation of a degassed MeCN solution of **1** (0.027 mol dm^{-3}) in a Pyrex tube by a 300-W high-pressure mercury lamp (Toshiba) for 3 h at room temperature gave both dimers. The products were fractionated by liquid chromatography (Waters, 3000 type) on a silica-gel column (Micro PORASIL) by eluting with CH_2Cl_2–hexane (4:100, v/v). The cis dimer has a larger retention time than the trans dimer. The conformation of **2t** and **2c** was determined by NMR chemical shifts.[31,32]

***trans*-1,2-Di(1-pyrenyl)cyclobutane 2t:** Mp 162—164 °C; ^1H NMR (90 MHz; C_6D_6; Me_4Si) δ=2.00—2.49 (4H, m, CH_2), 4.68—5.03 (2H, m, CH), and 7.58—8.37 (18H, m, aromatic); MS *m*/*z* 456 (10 %, M^+), 428 (2, $M^+-C_2H_4$), and 228 [100, $\mathbf{1}^+$].

***cis*-1,2-Di(1-pyrenyl)cyclobutane 2c:** Mp 81—83 °C; IR (KBr) 3050 m, 2930 m, 2850 w, 1600 m, 1580 w, 1490 w, 1430 w, 1410 w, 1180 s, 840 vs, 750 s, 710 s, 695 s, 675 m, and 495 m cm^{-1}; ^1H NMR (90 MHz; C_6D_6; Me_4Si) δ=2.48—2.90 (4H, m, CH_2), 4.98—5.24 (2H, m, CH), and 7.38—8.22 (18H, m, aromatic); MS *m*/*z* 456 (0.5%, M^+), 428 (0.1, $M^+-C_2H_4$), and 228 [100, $\mathbf{1}^+$].

Cyclobutane dimers were purified by liquid chromatography prior to use; the purity of both dimer was found to be more than 99%. Care was taken to prevent the dimers from thermal or photochemical decomposition.

Quantum Yield Measurements of Photoreactions. The quantum yields of the cycloreversion and isomerization of dimers were determined by photoirradiation under the monochromatic light of a spectrofluorophotometer. A 5-cm^3 sample solution of the dimers (5.0×10^{-5} mol dm^{-3}) in a 1-cm quartz cell was freed from oxygen by N_2 bubbling for 15 min. The samples were photoexcited in a temperature-controlled (297 K) sample chamber of an RF-501 spectrofluorophotometer (Shimadzu). The number of photons of the monochromatic Xe lamp measured by potassium ferrioxalate actinometry[33,34] was 2.0×10^{-9} E s^{-1} at 330 nm (slit width: 19 nm). The Py chromophore was selectively photoexcited at 330 nm, and the system with a DMT additive was photoexcited at 350 nm, since DMT has an absorption tail at 330 nm. For a system of triplet photosensitization, BP was selectively excited at 375 nm. After photoirradiation, the samples were analyzed immediately by liquid chromatography. In all measurements, the photoreaction yield was limited to less than 30% and the absorption of the exciting light by the products was corrected. For all systems, the contribution of thermal reactions, which was practically negligible, was corrected for by a blank experiment. The values of the determined reaction quantum yield were reproducible within ±5%.

Optical Measurements. All sample for the absorption and emission measurements were degassed ($<10^{-5}$ mmHg, 1 mmHg=133.322 Pa) by repeated freeze-pump-thaw cycles in a Pyrex ampoule fitted with a 1-cm quartz cell. The absorption spectra were measured by a UV-200S spectrophotometer (Shimadzu) at a 2-nm slit width. The emission spectra were obtained with an RF-501 spectrofluorophotometer (Shimadzu), whose spectral response was calibrated using a standard tungsten lamp. The quantum yield of emission was determined relative to that of quinine sulfate in sulfuric acid.[35]

The transient absorption was obtained by a nanosecond ruby laser photolysis apparatus, as described elsewhere.[36] The measurements were made at 297 K. The exciting laser light pulse at 347.1 nm has a 10-mJ pulse energy and a 14-ns pulse duration. Samples for the laser photolysis were freed from oxygen by N_2 bubbling for 15 min. The optical density of all samples at 347.1 nm was adjusted to be nearly the same (ca. 1.0) in order to attain homogeneous excitation.

The reference absorption spectra of the radical ions were measured by gamma-ray irradiation from a ^{60}Co source (2×10^6 rad h^{-1}) using a degassed 1-mm quartz cell in glass matrices at 77 K. Radical cations and radical anions were produced in glass matrices of 2-chlorobutane and MTHF, respectively.[37]

Results

Absorption and Emission of Dimers. The absorption-band shape of the chromophore Py is sensitive to the environmental conditions.[38] The cyclobutane dimers, **2t** and **2c**, have the Py groups in the vicinal position of the cyclobutane ring. The absorption spectra thus reflect the degree of the ground-state interaction between two neighboring Py chromophores.

Figure 1 shows the absorption spectra of dimers obtained in the MeCN solvent at 297 K and normalized at 290 nm. The absorption bands at around 290—360 nm are ascribed to the S_2—S_0 transition of the Py chromophore.[22] In Fig. 1, *trans*-dimer **2t** shows practically the same band shape as does that of reference 1-ethylpyrene (EPy); that is, two neighboring Py chromophores at the trans position of cyclobutane ring show no evidence of interaction in the shape of the absorption bands. However, the spectrum of *cis*-dimer **2c** is different from that of **2t**, indicating the existence of an interaction between two Py groups. In the spectrum of **2c**, the vibrational structure becomes less clear: The ratios of the absorption peak to valley for **2c** were smaller than those of **2t**. The molar extinction coefficient of **2t** at the 348.0 nm peak was ca. 8×10^4, whereas that of **2c**

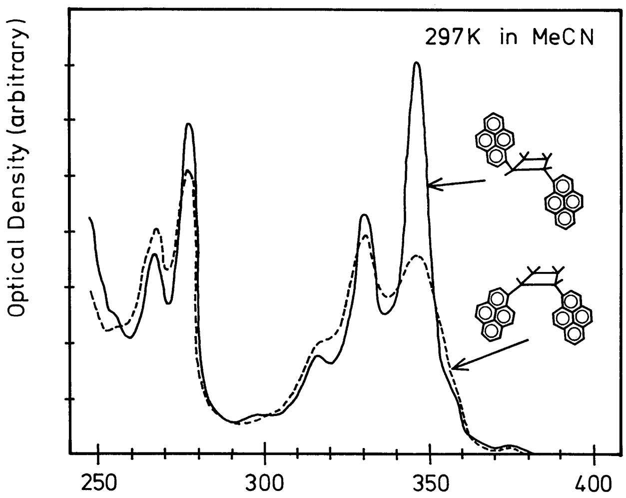


Fig. 1. Absorption spectra of 1-vinylpyrene **1** cyclobutane dimers (**2t**: solid line, and **2c**: broken line) measured in MeCN solvent at 297 K. The spectra were normalized at 290 nm.

was decreased to ca. 3×10^4. This shows that the distance of two Py chromophores of **2t** is too far to interact in the ground state, while for **2c** two Py groups take a sandwich-like conformation and interact with each other. This interaction of chromophores induced broadening of the absorption band with no peak shift, but with a slight hypochromicity.

As for the emission of the dimers, it was very weak due to intramolecular quenching in solution: The emission quantum yield of the intramolecular excimer of **2c** was less than 0.002 at 297 K in benzene solvent; the clear excimer emission of **2t** could not be observed, as has been reported for the emission of tetraphenylcyclobutanes.[11] The pure emission spectra of dimers in solution were difficult to measure due to the contamination of **1**, which shows strong fluorescence and was easily produced by photocleavage, even under the weak exciting light of a spectrofluorophotometer.[16,30] The excited state of the dimers is deactivated by the cleavage reaction and the emission is considerably quenched.

Photoreaction Quantum Yield of Dimers. Table 1 shows the absolute reaction quantum yields of the photoinduced cycloreversion and isomerization of dimers **2t** and **2c**, in several conditions. The O_2-freed sample solutions in the temperature-controlled sample chamber of a spectrofluorophotometer at 297 K were photoirradiated by monochromatic Xe light for a few minutes; the products were then analyzed immediately by liquid chromatography. The Py chromophore was selectively excited by 330 nm light and 1-vinylpyrene **1** was exclusively produced by the [2+2]-cycloreversion of the dimers. Together with the photocleavage reaction, the photoisomerization reaction from *cis*- to *trans*- and *trans* to *cis*-cyclobutane also occurred. Table 1 shows the values of the quantum yields of the cycloreversion and isomerization in nonpolar benzene and polar MeCN solvents. An electron donor, *N*,*N*-dimethyl-*p*-toluidine (DMT), as an additive produces radical anions of **2t** and **2c**, whereas the additive electron acceptor, 1,4-dicyanobenzene (DCNB), produces radical cations of the dimers.[39,40] The concentrations of DMT (1.0×10^{-2} mol dm^{-3}) and DCNB (1.0×10^{-2} mol dm^{-3}) were enough to quench the excited state of Py within 10 ns. An additive, benzophenone (BP, 2.5×10^{-2} mol dm^{-3}), was used as a triplet sensitizer; in this case, BP was selectively photoexcited at 375 nm. The triplet energies of Py and BP are 201 kJ mol^{-1},[33] and 290 kJ mol^{-1},[33] respectively. In this energy relationship, the triplet energy transfer from ^{3}BP* to Py is expected to be diffusion-controlled. In this sensitized system, the reaction quantum yields include both the intersystem crossing efficiency of ^{1}BP* to ^{3}BP* and the triplet energy transfer quantum efficiency from ^{3}BP* to Py. However, both efficiencies are expected to be quantitative at this concentration of Py and, therefore, the values in Table 1 are equivalent to the reaction quantum yields of ^{3}**2t*** and ^{3}**2c***.

Reference Absorption Spectra. For an interpretation of the transient spectra in laser photolysis, reference absorption spectra were obtained by gamma-ray ionization[37] at 77 K in rigid matrices (2-chlorobutane and MTHF) and by laser photolysis at 297 K in solution.

Figure 2 shows two T–T ([I] and [II]) and six radical ion ([III]—[VIII]) absorption spectra with their peak wavelengths. The three spectra obtained at 297 K ([I]—[III]) were measured by the laser photolysis in liquid solvents, whereas five radical ion spectra obtained at

Table 1. Photocycloreversion and Photoisomerization Quantum Yields of Cyclobutane Dimers

Solvent/Additive	Photocycloreversion		Photoisomerization	
	2t	**2c**	**2t**	**2c**
MeCN/DMT[a]	0.033	0.046	0.005	0.033
MeCN/DCNB[b]	0.073	0.061	<0.001	0.071
Benzene	0.15	0.17	0.025	0.080
MeCN	0.093	0.077	0.007	0.033
MeCN/BP[c]	0.060	0.12	0.007	0.099

a) *N*,*N*-Dimethyl-*p*-toluidine (DMT, 1.0×10^{-2} mol dm^{-3}) was added as an electron donor. b) 1,4-Dicyanobenzene (DCNB, 1.0×10^{-2} mol dm^{-3}) was added as an electron acceptor. c) Benzophenone (BP, 2.5×10^{-2} mol dm^{-3}) was added as a triplet sensitizer, and was selectively photoexcited.

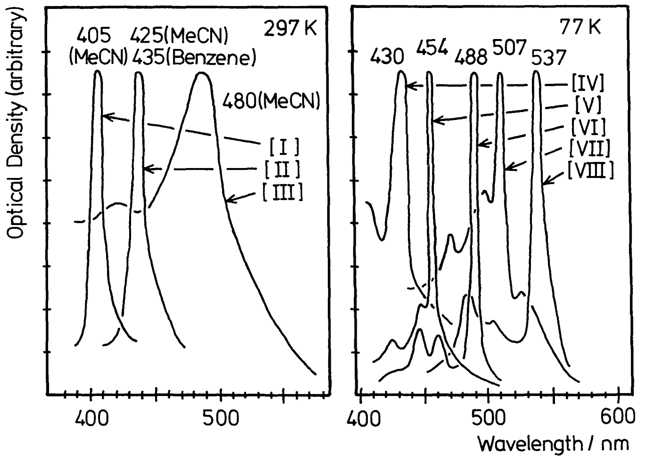


Fig. 2. Absorption spectra of triplet states and radical ions with the peak wavelengths. Spectra [I]—[III] were measured by the laser photolysis at 297 K. Spectra [IV]—[VIII] were obtained by the gamma-ray irradiation in rigid matrices at 77 K. [I]: ^{3}Py*, [II]: ^{3}**1***, [III]: DMT$^{+\cdot}$, [IV]: DCNB$^{-\cdot}$, [V]: Py$^{+\cdot}$, [VI]: Py$^{-\cdot}$, [VII]: **1**$^{+\cdot}$, and [VIII]: **1**$^{-\cdot}$.

77 K ([IV]—[VIII]) were measured by gamma-ray irradiation in rigid matrices. The radical ions and triplet states of the Py chromophore had sharp absorption bands at both temperatures, and the substitution by a vinyl group appreciably induced the red-shift of the peaks. For example, ^{3}Py* has an absorption peak at 405 nm, whereas ^{3}**1*** has a peak at 425 nm in the MeCN solvent. Hence, we can distinguish the Py triplet state (405 nm) formed in the cyclobutanes from the triplet state of **1** (425 nm) which is the product of photocleavage.

Figure 3 shows the absorption spectra of the radical ions of **2t** and **2c** produced by gamma-ray irradiation in rigid matrices at 77 K. The irradiation in the 2-chlorobutane matrix produces the radical cation of the solute, whereas in the MTHF matrix the radical anion is formed. Figures 3 [A] and [C] show the absorption spectra of **2t**$^{+\cdot}$ and **2c**$^{+\cdot}$, respectively. They show almost the same characteristics: Both have a broad peak at around 480 nm, which is quite different from that of Py$^{+\cdot}$ (454 nm). The absorption band shown in spectra [A] and [C] resembles that of intramolecular Py$_2^{+\cdot}$ in shape as well as in position. Such an absorption band

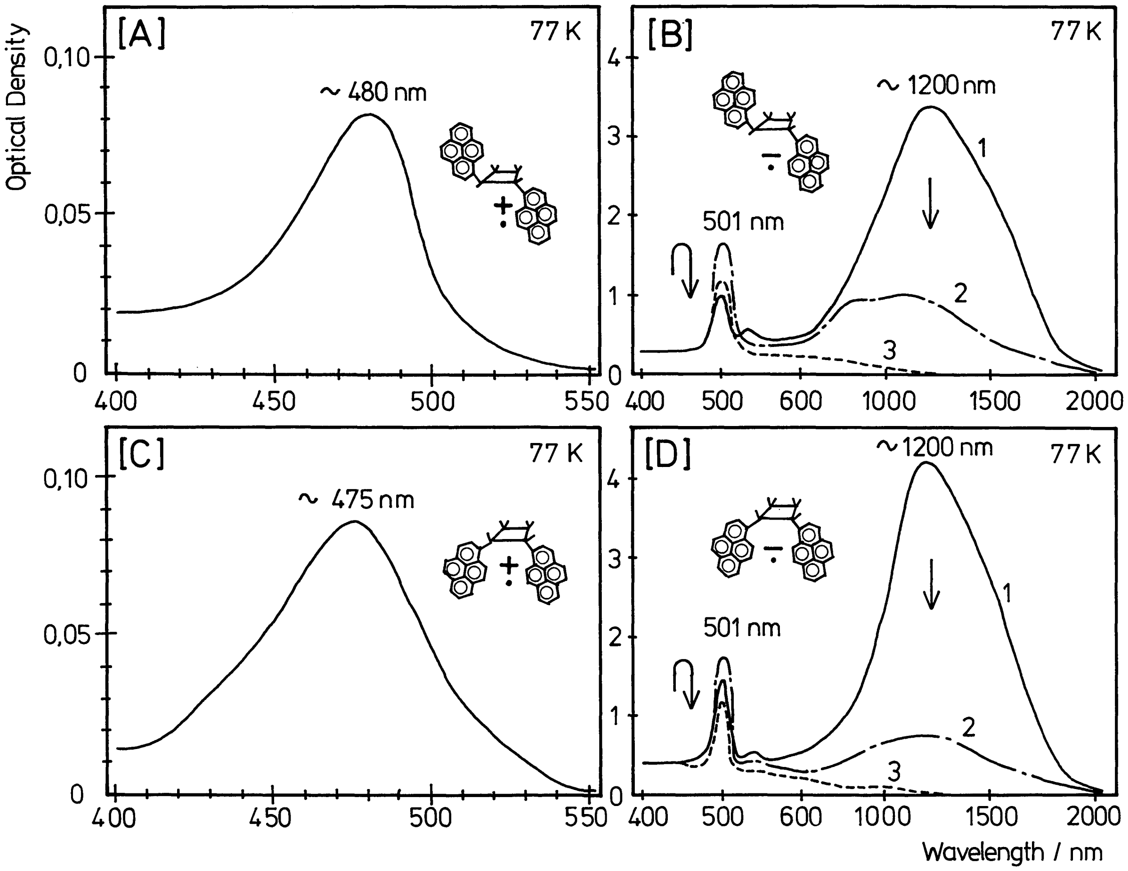


Fig. 3. Absorption spectra of radical ions of 1-vinylpyrene **1** cyclobutane dimers (**2t**: [A] and [B], and **2c**: [C] and [D]) with the peak wavelengths. Spectra were obtained by the gamma-ray irradiation in rigid matrices at 77 K. Immediately after irradiation (spectra No. 1), after warming (spectra No. 2), and after further warming (spectra No. 3). [A]: **2t**$^{+\cdot}$, [C]: **2c**$^{+\cdot}$, [B]: **2t**$^{-\cdot}$, and [D]: **2c**$^{-\cdot}$.

was observed for poly(1-vinylpyrene) or for the dimer models.[41] Therefore, these spectra are ascribed to the dimer radical cation of the intramolecular Py ($\mathrm{Py}_2^{\cdot+}$) whose positive charge is delocalized between two py rings. The absorption spectrum of intramolecular $\mathrm{Py}_2^{\cdot+}$ is less clear in vibrational structure compared to that of the dimer radical cation formed intermolecularly from pyrene.[23]

Radical anions of **2t** and **2c** were produced in MTHF at 77 K and the absorption spectra are shown in Fig. 3 [B] and [D], respectively. Both spectra are almost identical and the curves numbered 1 were taken immediately after gamma-ray irradiation. Two absorption bands are recognized in the spectra: The band at 501 nm is ascribed to the radical anion of Py ($\mathrm{Py}^{\cdot-}$) formed in the dimers, and the band at around 1200 nm is assigned to the absorption of trapped electrons.[42] A slight warming of the MTHF matrix increased the band intensity at 501 nm, as shown in spectra No. 2; further warming decreased the absorption (spectra No. 3). The initial increase of this band is explained by a recapturing of trapped electrons to Py chromophores. This absorption band at 501 nm is very sharp compared with that of broad $\mathrm{Py}_2^{\cdot+}$, and is similar to $\mathrm{Py}^{\cdot-}$ (488 nm) in Fig. 2. The small spectral shift and the sharp band shape show the weaker interaction of Py chromophores in the anionic states of **2t** and **2c** than do those in the cationic states.[28,29]

Laser Photolysis Measurements. Nanosecond ruby-laser photolysis was carried out in order to study the transient intermediates of photocleavage reactions. Figure 4 shows the transient absorption spectra of dimers in benzene and MeCN solutions at 297 K. As shown in spectra [A] and [B], only $^3\mathbf{1}^*$ can be recognized by the photolysis of dimers in the benzene solvent. The transient absorption immediately after laser excitation (<50 ns) was hardly measured due to the overlap of the emission and the absorption of Py excimer could not be observed.[43] In the polar solvent MeCN, the spectra were the same as those in benzene, except for the shift of the abosrption maximum of $^3\mathbf{1}^*$ from 435 nm to 425 nm, which is due to the solvent effect as shown in the reference absorption spectra of Fig. 2. As shown in Fig. 4 [C] and [D], the addition of DMT as an electron donor to the dimers in MeCN solvent produced several transient species, which are ascribed to $^3\mathbf{1}^*$ (425 nm), $\mathrm{DMT}^{\cdot+}$ (470 nm), $\mathbf{1}^{\cdot-}$ (500 nm), and $\mathrm{Py}^{\cdot-}$ (530 nm). Since DMT has an absorption tail at 347.1 nm, the concentration of DMT in these systems was lowered to 1.0×10^{-3} mol dm^{-3}, which was a tenth of the concentration for the steady-state measurements of Table 1. Next, the effect of an electron acceptor DCNB was examined; the results are shown in spectra [E] and [F], where a strong absorption band of $\mathrm{Py}_2^{\cdot+}$ was found at around 480 nm. The concentration of DCNB in these systems was the same as that for the steady-state experiment of Table 1, and the absorption of $\mathrm{DCNB}^{\cdot-}$ appeared at 430 nm, overlapping with that of $^3\mathbf{1}^*$. In the figures, the dimer radical cations of **2t** and **2c** gave almost the same spectra.

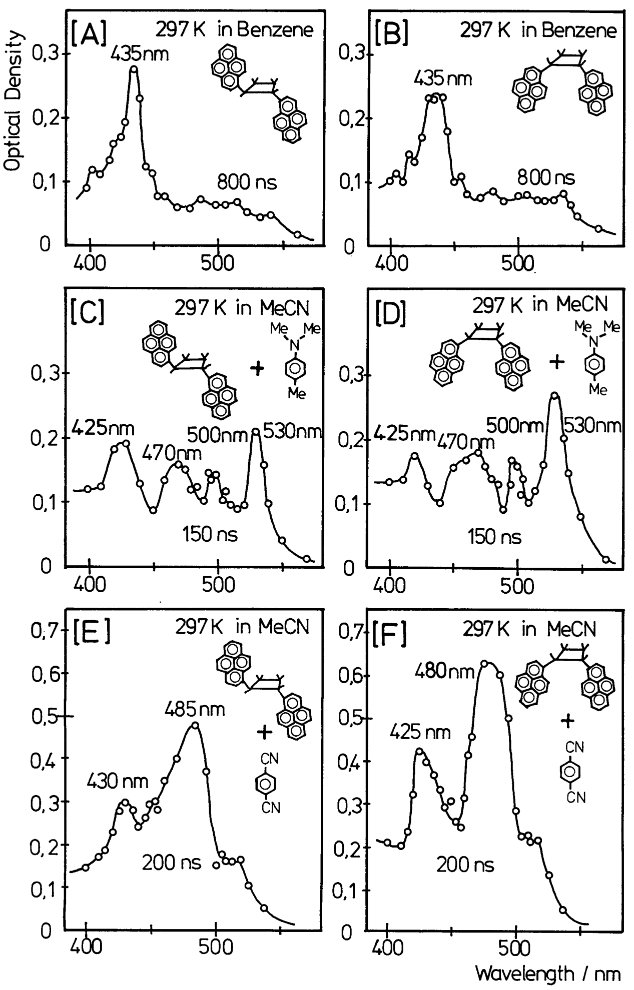


Fig. 4. Transient absorption spectra of 1-vinylpyrene **1** cyclobutane dimers **2t** ([A], [C], and [E]) and **2c** ([B], [D], and [F]) measured by the laser photolysis in benzene ([A] and [B]) or MeCN ([C], [D], [E], and [F]) solvent at 297 K. [A]: **2t** obtained at 800 ns after excitation, [C]: **2t** with DMT at 150 ns, [E]: **2t** with DCNB at 200 ns, [B]: **2c** at 800 ns, [D]: **2c** with DMT at 150 ns, and [F]: **2c** with DCNB at 200 ns. [DMT]= 1.0×10^{-3} mol dm^{-3}, and [DCNB]=1.0×10^{-2} mol dm^{-3}.

Table 2. Observed Transient Intermediates by Laser Photolysis Measurements

Solvent/Additive	**2t**	**2c**
MeCN/DMT[a)]	$^3\mathbf{1}^*$, $\mathrm{Py}^{\cdot-}$, $\mathbf{1}^{\cdot-}$, $\mathrm{DMT}^{\cdot+}$	$^3\mathbf{1}^*$, $\mathrm{Py}^{\cdot-}$, $\mathbf{1}^{\cdot-}$, $\mathrm{DMT}^{\cdot+}$
MeCN/DCNB[b)]	($^3\mathbf{1}^*$)[c)], $\mathrm{Py}_2^{\cdot+}$, $\mathrm{DCNB}^{\cdot-}$	($^3\mathbf{1}^*$)[c)], $\mathrm{Py}^{\cdot+}$, $\mathrm{DCNB}^{\cdot-}$
Benzene	$^3\mathbf{1}^*$	$^3\mathbf{1}^*$

a) *N*,*N*-Dimethyl-*p*-toluidine (DMT, 1.0×10^{-3} mol dm^{-3}) was added. b) 1,4-Dicyanobenzene (DCNB, 1.0×10^{-2} mol dm^{-3}) was added. c) Absorption band of $^3\mathbf{1}^*$ overlapps with that of $\mathrm{DCNB}^{\cdot-}$.

Table 2 summarizes the transient species observed in Fig. 4. In every system, the formation of $^3\mathbf{1}^*$ was recognized but $^{3}\mathrm{Py}^{*}$ could not be found in the time range of our measurements. In a system with an additive, DCNB, the absorption of the dimer radical cation ($\mathrm{Py_2^{+\cdot}}$) was observed, whereas in the system with DMT, there was no noticeable evidence of dimer radical anion ($\mathrm{Py_2^{-\cdot}}$) formation.

Discussion

Figure 1 shows a broader absorption band shape of **2c** than that of **2t**, indicating that two neighboring Py chromophores interact in the cis position of the cyclobutane ring. This interaction in the ground state was not found for the cyclobutanes having naphthyl groups. The absorption spectra of *trans*- and *cis*-1,2-di(2-naphthyl)cyclobutanes resemble those of 2-ethylnaphthalene.[44] The Py ring seems to be large enough to interact in the cis position of cyclobutane. The trans dimer **2t** showed almost the same absorption spectrum as that of EPy; that is, the Py chromophores in the trans position of cyclobutane are too far to interact. By contrast, as for the cyclobutane which has an electron donor and an acceptor in the trans position, a chromophore interaction was found in the absorption spectrum; the absorption bands of the Py chromophore for the *trans*-cycloadduct of *trans*-1-(4-dimethylaminophenyl)-2-(1-pyrenyl)cyclobutane were slightly different from that of EPy.[16] The interaction distance of the electron donor–acceptor pair seems to be long enough to reach in the trans position of the cyclobutane ring in the ground state.

Photocycloreversion of Dimers via Ionic Intermediates. The cycloreversion and isomerization of dimers, **2t** and **2c**, via the ionic intermediates were examined by the addition of an electron donor DMT or an electron acceptor DCNB to the solution. The chromophore pairs of DMT–Py and of Py–DCNB are known to form exciplexes in nonpolar solvents; their photophysical characteristics have been extensively studied.[39,40] In such polar solvents as MeCN, an electron transfer from a donor to an acceptor is followed by photodissociation into solvated free radical ions; in this case, electron transfer from DMT to Py produces $\mathrm{DMT^{+\cdot}}$ and $\mathrm{Py^{-\cdot}}$ and that from Py to DCNB produce $\mathrm{Py^{+\cdot}}$ and $\mathrm{DCNB^{-\cdot}}$.

Spectra [C] and [D] of Fig. 4 show the transient absorption obtained 150 ns after excitation in an MeCN solvent at 297 K. Photoexcited **2t** and **2c** were quenched by DMT to give the four transient absorption bands. As shown in the figures, the two dimers show similar spectra. In these systems, the concentration of DMT was lowered to one tenth of that in the quantum yield measurements, as mentioned before. By dilution, the electron-transfer quenching of dimers by DMT becomes slightly insufficient. The formations of $^{3}\mathbf{1}^{*}$ (425 nm) and $\mathbf{1}^{-\cdot}$ (500 nm), as shown in the spectra, are considered to be caused by this low DMT concentration. The quenching by DMT cannot effectively compete with the direct photocleavage which produces **1**. Then, successive photoabsorption of the same exciting laser pulse tail by product **1** forms $^{1}\mathbf{1}^{*}$, which is converted to $^{3}\mathbf{1}^{*}$ by intersystem crossing; and $\mathbf{1}^{-\cdot}$ was produced by an electron transfer from DMT to $^{1}\mathbf{1}^{*}$. The fact that the lifetime of $^{3}\mathbf{1}^{*}$ did not change with the concentration of DMT indicates that the quenching of $^{3}\mathbf{1}^{*}$ by DMT is negligible.

The $\mathrm{Py^{-\cdot}}$ can be recognized at 530 nm in transient spectra [C] and [D]. The absorption band shape and the peak wavelength of the $\mathrm{Py^{-\cdot}}$ are in accord with those obtained by gamma-ray irradiation, as shown in Figs. 3 [B] and [D]. This $\mathrm{Py^{-\cdot}}$, whose charge is localized to one Py ring, is produced by electron transfer quenching of $^{1}\mathbf{2t}^{*}$ and $^{1}\mathbf{2c}^{*}$ with DMT. In the present study, no absorption band which can be ascribed to $\mathrm{Py_2^{-\cdot}}$ could be found. As for the formation of the aromatic dimer radical anion, there has been no report,[25] except for a special case.[26] The charge resonance energy in the dimer radical anion seems to be weaker than that of the dimer radical cation. The results that the lifetime of the $\mathrm{Py^{-\cdot}}$ is in the microsecond order and that it decays mostly by the recombination with $\mathrm{DMT^{+\cdot}}$ (470 nm) indicate that the fraction of the cleavage of dimers through the $\mathrm{Py^{-\cdot}}$ is not so large.

Table 1 shows that the quantum yields of photocleavage of dimers through the quenching by DMT are low (0.033 for **2t** and 0.046 for **2c**). This is because $\mathbf{2t}^{-\cdot}$ and $\mathbf{2c}^{-\cdot}$ are deactivated by the recombination with $\mathrm{DMT^{+\cdot}}$ and their cleavage is not a major process. On the other hand, the cleavage quantum yields of dimers quenched by DCNB are higher (0.073 for **2t** and 0.061 for **2c**) than the systems of the DMT additive. In the transient absorption spectra as shown in Figs. 4 [E] and [F], the strong absorption of $\mathrm{Py_2^{+\cdot}}$ (ca. 480 nm), which was identified by the reference spectra of Figs. 3 [A] and [C], was found as a main band, and this $\mathrm{Py_2^{+\cdot}}$ seems to be cleaved. In Figs. 4 [E] and [F], the small absorption band of $^{3}\mathbf{1}^{*}$ can also be recognized through it overlaps with that of $\mathrm{DCNB^{-\cdot}}$ (430 nm), but it is not a major product.

It is interesting that the photocleavage via $\mathbf{2t}^{+\cdot}$ and $\mathbf{2c}^{+\cdot}$, whose positive charge is delocalized to $\mathrm{Py_2^{+\cdot}}$, is more efficient than that via $\mathbf{2t}^{-\cdot}$ and $\mathbf{2c}^{-\cdot}$, whose negative charge is localized to $\mathrm{Py^{-\cdot}}$. Ledwith et al. proposed that an open-chain type radical cation of *trans*-1,2-di(9-carbazolyl)cyclobutane (DCzB) participates in the cycloaddition reaction.[45] The laser photolysis experiments of the DCzB showed that the two carbazole (Cz) chromophores in the trans position of the cyclobutane ring give the absorption of the dimer radical cation ($\mathrm{Cz_2^{+\cdot}}$).[27] In our system of $\mathbf{2t}^{+\cdot}$, the formation of the dimer radical cation has been confirmed, as mentioned above. Recently, a theoretical calculation and experiments concerning CIDNP have suggested the existence of a "long-bonded cyclobutane" structure:[19,20] The one bond of a radical cation cyclobutane ring becomes long by the deficiency of the electron density.

The finding that the cleavage quantum yields of $\mathbf{2t}^{+\cdot}$ and $\mathbf{2c}^{+\cdot}$ are larger than those of $\mathbf{2t}^{-\cdot}$ and $\mathbf{2c}^{-\cdot}$ is in agreement with the reactivity tendency of the "long-bonded cyclobutane" structure. The decrease in the electron density in the cyclobutane bond is considered to promote the cleavage reaction.

As for the isomerization reactions of dimers via ionic intermediates, the isomerization from **2c** to **2t** was found to be favorable. This is considered to be caused by the steric factor of the cyclobutane ring.

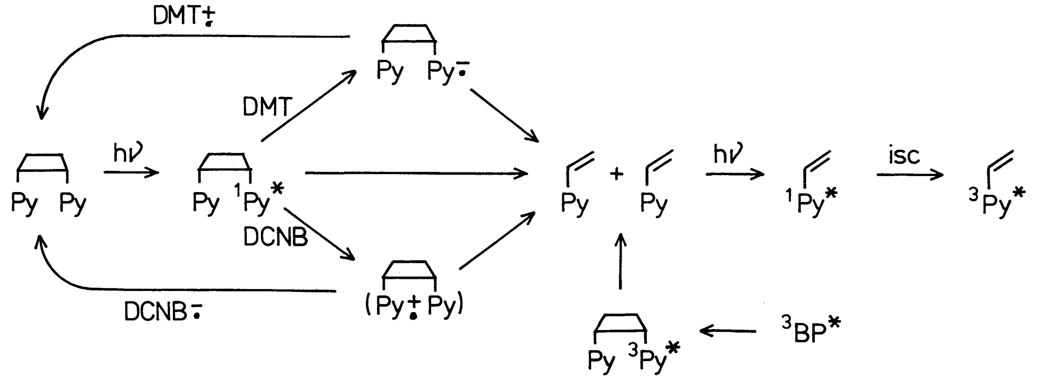
Photocycloreversion of Dimers from Singlet and Triplet Excited States. As shown in Table 1, the reaction quantum yields of cycloreversion and isomerization of **2t** and **2c** without an additive in the nonpolar benzene solvent are larger than those in the polar MeCN solvent. The polar excited singlet state of cyclobutanes seems to be stabilized in a polar MeCN solvent by solvation, and deactivation processes become dominant. Similar solvent effects could also be seen in our previous study.[16] As for the effects of different configurations of **2t** and **2c**, the quantum yields of cycloreversion of both dimers were nearly the same, whereas those of isomerization were larger for **2c** than for **2t**. The latter seems to be due to the "cis effect" of the Py chromophores.[1,8] The "cis effect" occurs due to a strain of the cyclobutane ring when the cyclobutane ring is substituted by large chromophores, or when the cyclobutane ring is a part of a bi- or polycycle. The photocleavage reaction in the latter case has often been reported to proceed by a chain mechanism.[13,14] In the present system, however, the effect is not so large. Furthermore, the quantum yields of cycloreversion for **2t** and **2c** are nearly the same. It seems that a cycloreversion in the excited state is effective for the large Py chromophore in the trans position of cyclobutane, as well as in the cis position.

The cycloreversion and isomerization from the excited triplet state of dimers, **2t** and **2c**, were observed by the use of triplet sensitizer of benzophenone (BP) as shown in Table 1. As mentioned before, these quantum yields in Table 1 are regarded as being the quantum yield of cleavage or isomerization of the dimers from their triplet state. They show that the dimer **2c** has a higher reactivity of cycloreversion and isomerization compared with that for **2t**. In triplet sensitized photocycloreversion, a diradical intermediate is most popular.[9,15] Probably, this is also ascribed to the cis effect.

In laser photolysis measurements, the transient absorption spectra of [A] and [B] in Fig. 4 gave only the band of $^{3}\mathbf{1}^{*}$. This formation of $^{3}\mathbf{1}^{*}$ was recognized in all transient spectra as shown in Table 2, and further the system which gave a large cleavage quantum yield showed stronger absorption of $^{3}\mathbf{1}^{*}$. These facts suggest that $^{3}\mathbf{1}^{*}$ is formed through a two step photo-excitation process.[16] The exciting laser light of our laser photolysis has a pulse duration of 14 ns. If the rate of cycloreversion is fast enough, the photoproduct **1** can be excited again by the same exciting light pulse tail, and then the produced $^{1}\mathbf{1}^{*}$ converts to $^{3}\mathbf{1}^{*}$. Overlapping of the fluorescence in the short time region (<50 ns) after the excitation hindered the observation of short-lived transient species, such as an excimer or zwitterion in the systems of Figs. 4 [A] and [B]. As for the anthracene dimer, the excimer was proposed as the transient intermediate of the cycloreversion.[11] Similarly, the excimer intermediate may participate in the cycloreversion of **2t** and **2c** in consideration of the fact that the chromophore Py easily forms the excimer.[21,22] As for the cyclobutane compounds, the most stable conformation of a cis cyclobutane ring is considered to be in a puckered form. The planar form, where two aromatic rings take the nearest conformation, has a slightly higher energy state, ca. 6.3 kJ mol^{-1} than the puckered form.[46] Furthermore, two aromatic rings cannot take a parallel-sandwich arrangement, even in the planar form of cyclobutane by the framework of cyclobutane ring.[44] Therefore, the excimer formed in cyclobutane compounds is unstable, and this is probably one of the reasons for the weak excimer emission and short lifetime.

Conclusion

The transient states of photocycloreversion and isomerization reactions of 1-vinylpyrene **1** cyclobutane



Scheme 1.

dimers, **2t** and **2c**, were discussed from the absorption spectra of laser photolysis and by the reaction quantum yields under the steady-state photoirradiation. The results are summarized in the Scheme. An efficient cycloreversion of dimers was found from their singlet and triplet states, though the solvation of the excited state by a polar solvent decreased the cycloreversion yields. The intramolecular dimer radical cation formation was observed for the dimers and the $\mathbf{2t}^{+\cdot}$ and $\mathbf{2c}^{+\cdot}$ were found to cleave in a yield comparable to that of direct photocleavage. An electron deficiency in the dimers is considered to be responsible for the cleavage. No formation of the dimer radical anion was observed. The cleavage of $\mathbf{2t}^{-\cdot}$ and $\mathbf{2c}^{-\cdot}$ to **1** was inefficient.

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