Photoinduced [2 + 2] Cycloreversion Reactions of 1-Vinylpyrene–4-Dimethylaminostyrene Cycloadducts

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The reaction quantum yields of the photoinduced [2 + 2] cycloreversion of the cycloadducts *trans*- and *cis*-1-(4-dimethylaminophenyl)-2-pyren-1-ylcyclobutane (**3t** and **c**) were determined and the transient absorption spectra were analysed with a nanosecond laser photolysis. In the non-polar solvent benzene, photocycloreversion of cycloadducts occurred efficiently, whereas in polar acetonitrile the quantum yield of the photocleavage reaction decreased remarkably. Transient spectroscopy revealed the photocleavage route of the cyclobutane ring *via* an intramolecular exciplex state in a non-polar solvent. In the polar solvent, this exciplex state was stabilized as an ion-pair which was largely deactivated by intramolecular charge recombination.

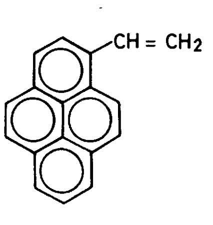
Cycloreversion of cyclobutane compounds, which is a reverse process of cycloaddition of two olefins, is initiated thermally or photochemically.[1] In recent years, cycloreversion reactions have been extensively studied from the point of view of solar energy conversion[2–6] and photoreactivation of damaged DNA.[7,8] When the two bonds of the cyclobutane ring break simultaneously according to the Woodward–Hoffmann rule,[9] cycloreversion proceeds in one step *via* a concerted mechanism. Recently, however, much evidence has shown that cyclobutanes cleave by two steps through a transient intermediate. For the cyclobutane pyrolysis reactions, the 1,4-diradical is the most popular candidate of the intermediates.[10–12] In this case, the experimental value of the activation energy for the cleavage of the cyclobutane ring is very similar to the calculated one for the diradical formation.[1,13,14] The diradical intermediate is also found in the photochemical cycloreversion of cyclobutanes.[15,16] Photochemically produced diradicals have been directly observed by transient spectroscopy, where the diradicals were produced *via* the excited triplet state.[17–19]

On the other hand, ionic species have also been proposed to be the intermediates in cyclobutane cleavage.[1–8,10] In photochemistry, electron transfer is one of the most popular reactions of the excited molecules. Ionic states, such as exciplexes and ion radicals, are expected to play an important role in photoinduced cycloreversions in the same way as in photochemical cycloadditions.[20] For example, redox-photosensitized cyclobutane cleavage reactions have been studied by Pac *et al.*[21] who emphasized the importance of through-bond interaction in the transient complex. Transient ionic species in photo- and radiation-induced cycloreversions have been studied by Takamuku *et al.*,[22] who proposed that the mode of cycloreversion is determined by the stability of the transient intermediates.

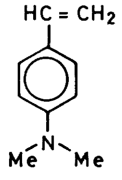
In this paper, cycloadducts of 1-vinylpyrene (**1**) and 4-dimethylaminostyrene (**2**) are studied to examine the reactivity of photoinduced cycloreversion. The absolute quantum yields of photocleavage of cyclobutanes were determined in several solvents which have different polarity, and the transient intermediates were analysed by nanosecond laser photolysis. Cycloadducts of (**1**) and (**2**) have pyrene (Py) and *NN*-dimethylaniline (DMA) chromophores in the same molecule at neighbouring positions. The exciplex behaviour of this chromophore pair has been extensively studied.[23] Hence, it is interesting to study the intramolecular exciplex behaviour as an intermediate of photocleavage for these cycloadducts.

Results

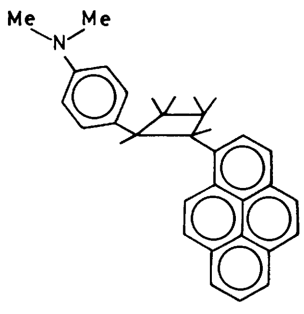
Cycloadducts, *trans*- and *cis*-1-(4-dimethylaminophenyl)-2-pyren-1-ylcyclobutane (**3t** and **c**), were produced by photocycloaddition of (**1**) and (**2**).[24]



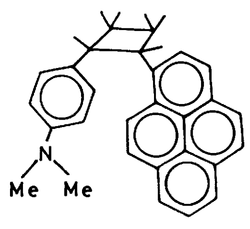
(**1**)



(**2**)



(**3t**)



(**3c**)

Absorption Spectra.—The cycloadducts have two neighbouring chromophores. If these two chromophores interact with each other in the ground state, some change in the absorption spectrum from the isolated chromophores would be expected. Figure 1 shows the absorption spectra of (**3t** and **c**) obtained in the acetonitrile solvent. These spectra are normalized at *ca.* 290 nm to allow better comparison of their band shapes. The absorption bands around 290—360 nm originate mostly from the S_2–S_0 absorption of the Py chromophore, and the absorption of the DMA moiety overlaps with that of the Py chromophore. However, the absorption around 320—380 nm has almost no contribution from the DMA chromophore since the large molar extinction coefficient of Py overcomes that of DMA, and the difference in the band

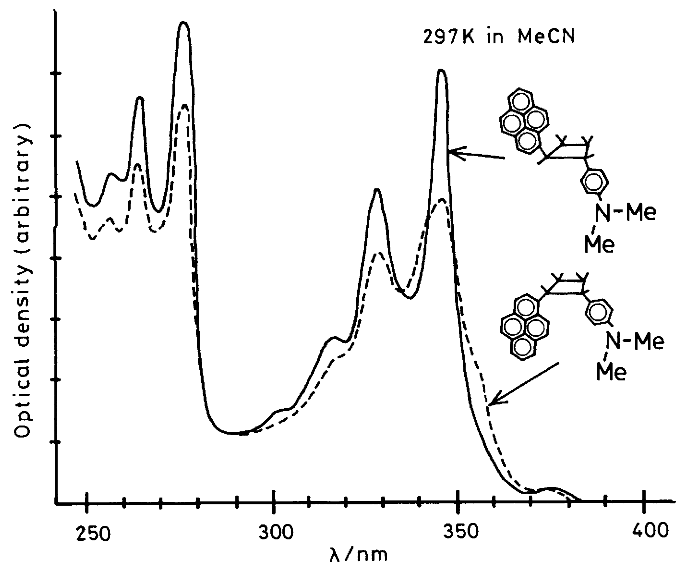


Figure 1. Absorption spectra of the cycloadducts (**3t** and **c**) measured in MeCN solvent at 297 K. These spectra were normalized at *ca.* 290 nm

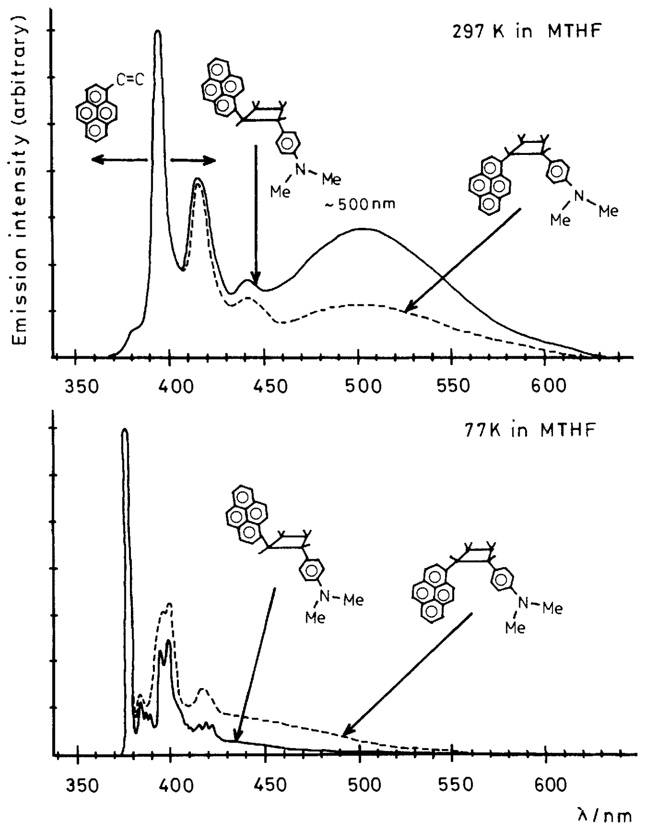


Figure 2. Emission spectra of the cycloadducts (**3t** and **c**). These spectra were normalized at the peak of the shortest wavelength. Upper spectra were measured in an MTHF solvent at 297 K. The emission bands at *ca.* 400 nm were ascribed to the emission from $^{1}(\mathbf{1})^{*}$ which was produced by the exciting light of the spectrofluorophotometer. Lower spectra were measured in the MTHF rigid matrix at 77 K

shape can be discussed in comparison with that of 1-ethylpyrene (EPy) as a standard.

The band shape of (**3t**) showed a small difference from that of EPy: the amplitude of the vibrational structure of (**3t**) is somewhat smaller than that of EPy. This difference could not be found for the *trans*-cyclobutane dimer of (**1**) (*trans*-homodimer), and it seems that the interaction between an electron donor (DMA) and an acceptor (Py) is stronger than that of two Py in the *trans*-homodimer in the ground state.

On the other hand, (**3c**) gave a very different spectrum from EPy and (**3t**), indicating the existence of a strong interaction between Py and DMA chromophores. In the spectrum of (**3c**), the vibrational structure is less clear. The distance of the two chromophores for the *trans*-cycloadduct is too far to interact in the ground state, while for the *cis*-cycloadduct, the Py and DMA groups take a conformation close to the sandwich type and interact with each other. The effect of chromophore interaction on the absorption spectrum appears only in the amplitude of the vibrational structure, and no peak shift of absorption maxima is found. The absorption spectra were also examined in non-polar benzene and in polar MeCN, but no noticeable change was observed for either solvent.

Emission Spectra.—Pure emission spectra of the cycloadducts were not obtained since (**1**) was easily formed by the photocleavage of the cycloadducts during the measurements of emission spectra. Intense emission from (**1**) appeared even at the first scan by a spectrofluorophotometer and became overwhelmingly strong as the scan proceeded.

Figure 2 shows the emission spectra of the cycloadducts, (**3t** and **c**). Though these spectra were obtained from the first scan of the spectrofluorophotometer, emission from (**1**) had already appeared. In Figure 2, the spectra were normalized at the peak of the shortest wavelength and hence an exact comparison of the emission intensity of (**3t**) with that of (**3c**) cannot be made. In the upper emission spectra of cycloadducts in Figure 2, which was measured in 2-methyltetrahydrofuran (MTHF) at 297 K, a broad structureless band is recognized at *ca.* 500 nm. This band is ascribed to the emission of Py–DMA exciplex.[23] In MTHF, the quantum yield of the exciplex emission for (**3t**) looks larger than that for (**3c**) but, since the photocleavage of (**3c**) is faster than that of (**3t**), real quantum yields of exciplex emission may be in the reverse order: the quantum yield of the exciplex emission for both cyclobutanes is *ca.* 0.03. In benzene or MeCN, the exciplex emission quantum yields of (**3t** and **c**) were low, <0.003, and an obvious emission peak could not be observed. Note that the exciplex emission is observed even in the *trans*-form of cycloadduct (**3t**). The conformational requirement of exciplex emission seems loose,[25] and the exciplex for (**3t**) is formed between rather remote Py and DMA chromophores.

In the rigid matrix of MTHF at 77 K, exciplex emission of cycloadducts was also detected as shown in the lower half of Figure 2. Hence it seems that some part of the exciplex is produced without dynamic processes of conformational change. In MTHF at 77 K, a clear emission maximum could not be found, and the exciplex emission shifted to a wavelength shorter than that at 297 K. The measurement of the exact emission quantum yield at 77 K was hard because of the optical complexity resulting from the use of a Dewar cell. However, it is recognized that the *cis*-cycloadduct (**3c**) has much more intense exciplex emission than (**3t**). This result for (**3c**) is expected from the molecular structure upon the suppression of photocleavage.

Quantum Yields of Cycloreversion and Isomerization.—The degree of intramolecular chromophore interaction of cyclobutanes in the ground and in the excited states was estimated by absorption and emission spectroscopy, respectively, as mentioned above. We then obtained the absolute quantum yield of photoinduced cycloreversion reactions. Samples in the chamber of a spectrofluorophotometer were photoirradiated for a few minutes and were immediately analysed by liquid

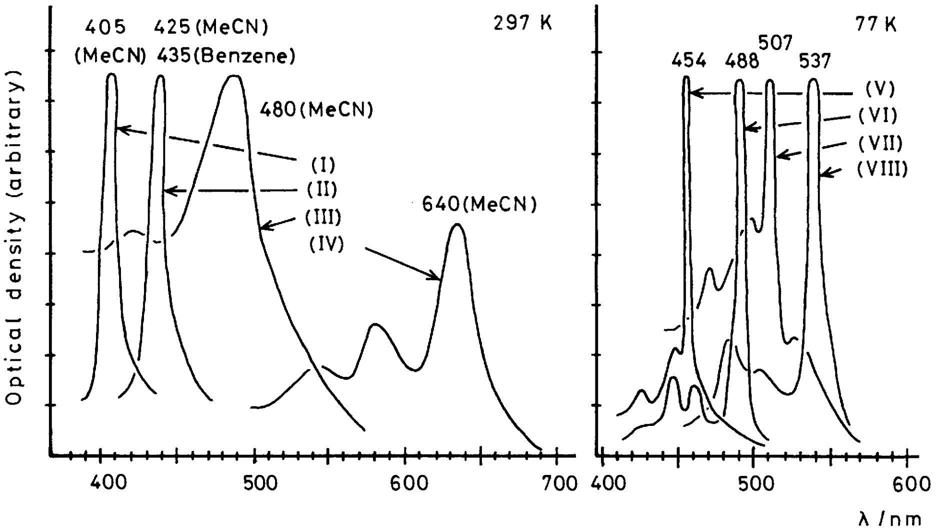


Figure 3. Reference absorption spectra of triplet states and ion radicals. Spectra (I)—(IV) were measured by the laser photolysis method at 297 K, and (V)—(VIII) were measured by γ-ray irradiation in rigid matrices at 77 K. (I) ^{3}Py*, (II) ^{3}(1)*, (III) DMT$^{+\bullet}$, (IV) (2)$^{+\bullet}$, (V) Py$^{+\bullet}$, (VI) Py$^{-\bullet}$, (VII) (1)$^{+\bullet}$, and (VIII) (1)$^{-\bullet}$

Table 1. Quantum yields of photocycloreversion and photoisomerization reactions of cycloadducts

	Photocycloreversion		Photoisomerization	
Solvent	(3t)	(3c)	(3t)	(3c)
Benzene	0.12	0.17	<0.001	0.017
MTHF	0.11	0.13	<0.001	<0.001
MeCN	0.009	0.067	<0.001	<0.001

chromatography. Photoexcitation was on the Py chromophore selectively. In the course of the measurements for the cleavage reactions of (3c), a more photoisomerization of cyclobutane to give the conversion (3c) into (3t) was detected in benzene. All the results for the cycloreversion and isomerization quantum yields are given in Table 1. The solvent effect on photoreaction of cyclobutanes was examined in non-polar benzene and polar MeCN. MTHF, which is a good solvent for exciplex emission, was also examined. In every system, cycloreversion was overwhelmingly faster than isomerization, and the products (1) and (2) were preferentially produced by [2 + 2] cycloreversion.

Reference Absorption Spectra.—Cycloreversion reactions of cyclobutanes were investigated by nanosecond laser photolysis and transient species were detected as described later. Some reference absorption spectra of triplet states and ion radicals are given for comparison. Some reference spectra for ion radicals were obtained by radiation-induced ionization,[26] and the other reference spectra for ion radicals and all those for the triplet states were measured by laser photolysis.

Figure 3 shows some reference absorption spectra at the wavelength of absorption maxima.[27–30] The spectra obtained at 297 K were measured by laser photolysis, whereas those at 77 K were measured by γ-ray irradiation in rigid matrices.[26] The absorption spectra of *NN*-dimethyl-*p*-toluidine cation radical (DMT$^{+\bullet}$) and (2)$^{+\bullet}$ measured by laser photolysis agree with the spectra obtained by γ-ray irradiation at 77 K, except for the sharpness of the absorption band and slight shift of absorption maxima. These reference spectra clearly show that the vinyl group causes an appreciable shift of the absorption maxima. Therefore, we can easily distinguish ion radicals formed from the cyclobutanes from those of vinyl monomers which are produced by photocleavage of the cyclobutanes.

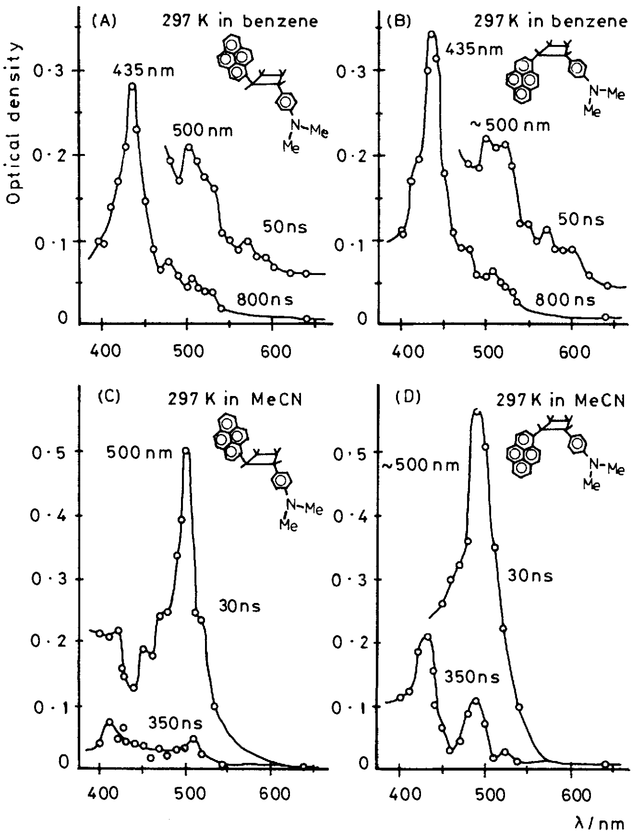


Figure 4. The transient absorption spectra of the cycloadducts (3t and c) measured by the laser photolysis method in benzene or MeCN solvent at 297 K. (A) (3t) at 50 and 800 ns after excitation, (B) (3c) at 50 and 800 ns, (C) (3t) at 30 and 350 ns, and (D) (3c) at 30 and 350 ns

Transient Spectroscopy.—Laser photolysis is a useful method for determining the transient intermediates of photochemical reactions.[31] The photocleavage reaction of the cycloadducts was investigated by ruby laser photolysis.

Figure 4 shows the transient absorption spectra of the cycloadducts. These cycloadducts of (**3t** and **c**) have a donor and an acceptor chromophore in one molecule, and solvent polarity effects were examined in non-polar benzene and polar MeCN solvents. In benzene, the cycloadducts gave a clear absorption of ^{3}(**1**)* *at 800 ns after* laser excitation. In the short time region after excitation (50 ns), however, only weak absorption at *ca.* 500 nm was detected as shown in spectra (A) and (B). This species can be ascribed to the absorption of Py$^{-\bullet}$; the existence of cationic species could not be observed owing to both the overlap of strong emission at the shorter-wavelength range and the overlapping of the spectrum with that of Py$^{-\bullet}$. In polar MeCN, weak emission of the samples enabled the measurement of the shorter-wavelength range at a shorter time after laser excitation. The results are shown in spectra (C) and (D). In polar MeCN, Py$^{-\bullet}$ is clearly absorbed with an absorption peak at *ca.* 500 nm. The peak shift of the absorption maxima from the reference Py$^{-\bullet}$ at 488 nm in Figure 3 is due to the difference in the measurement conditions. No distinguishable absorption peak of DMA$^{+\bullet}$ could be found, and this absorption band is considered to overlap with that of Py$^{-\bullet}$.[32] As shown in Figure 4, the lifetime of each ionic species is rather short, and the lifetime of the 435 nm species agrees with that of ^{3}(**1**)*.

Table 2 summarizes the transient species observed in Figure 4. In every system, the formation of ^{3}(**1**)* was detected but ^{3}Py* could not be found. The absorption of Py$^{-\bullet}$ showed different behaviour in benzene and MeCN. In MeCN, strong absorption was found, whereas in benzene, the absorption band was weak and not sharp. The absorption band of DMA$^{+\bullet}$ could not be observed in either solvent by the overlap of emission and strong absorption of Py$^{-\bullet}$, though DMA$^{+\bullet}$ is expected to exist.

The lifetime of the ionic species Py$^{-\bullet}$ is *ca.* 45 and 20 ns in benzene and MeCN, respectively, in agreement with the exciplex emission lifetime.

Discussion

The interaction between the chromophores of cycloadducts in the ground state is detected in the absorption spectra in Figure 1. In these intramolecular donor–acceptor systems, there is a weak interaction even in the *trans*-cyclobutane (**3t**). Chromophores DMA and Py seem to interact slightly at this distance, whereas in (**3c**) a strong interaction could be seen.

Exciplex emission from cycloadducts was observed as shown in Figure 2. However, the emission quantum yield was not so large even in MTHF solvent compared with the strong exciplex emission in intermolecular[23] or interpolymer[33] systems, and in benzene or MeCN the emission peak could not be observed. In MTHF, the quantum yield of the exciplex emission for (**3t**) looks larger than that for (**3c**), but this figure is apparent since the rate of photocleavage is fast and the emission spectrum of ^{1}(**1**)* overlaps with that of exciplex emission. Exciplex emission was also detected even in a rigid matrix at 77 K: some part of these exciplexes are considered to be formed without conformational change of cyclobutane, and the stronger emission of (**3c**) than that of (**3t**) indicates a more sandwich-like structure of the two chromophores in (**3c**) than in (**3t**).

As for the transient species in the laser photolysis (Figure 4), the formation of ^{3}(**1**)* is considered to be through a two-step photoexcitation at this stage of investigation. The absorption intensity of ^{3}(**1**)* is roughly proportional to the second power of the pulse intensity. Furthermore, the higher the quantum yield of photocleavage in the steady-state excitation, the stronger the absorption intensity of ^{3}(**1**)* in laser photolysis. The exciting light in our laser photolysis has a pulse duration of 14 ns. It is considered that the photocleaved product (**1**) is produced by the leading part of an exciting light pulse and then product (**1**) can be excited by the tailing part of the exciting light pulse. This is two-step photoexcitation which needs two photons, and is observed only when the reaction has a large quantum yield.

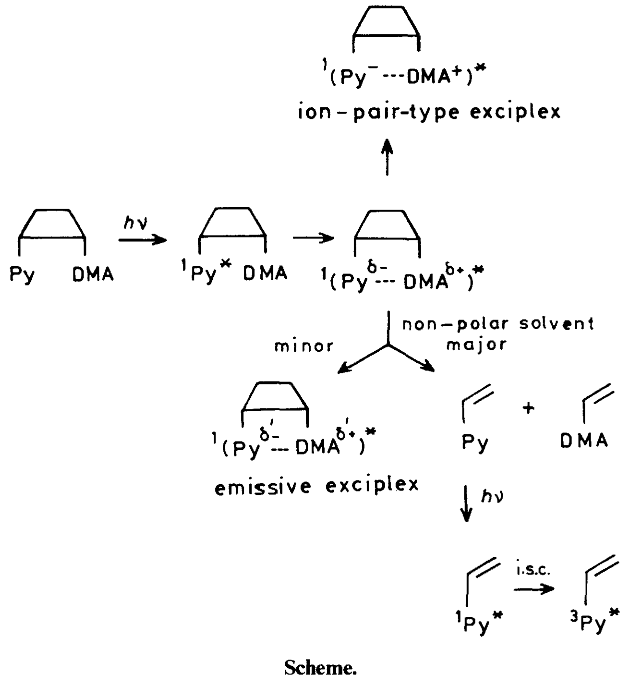
Table 2. Transient species observed by nanosecond laser photolysis measurement

Solvent	(**3t**)	(**3c**)
Benzene	^{3}(**1**)* (strong), Py$^{-\bullet}$ (weak)	^{3}(**1**)* (strong), Py$^{-\bullet}$ (weak)
MeCN	^{3}(**1**)* (weak), Py$^{-\bullet}$ (strong)	^{3}(**1**)* (weak), Py$^{-\bullet}$ (strong)

The efficiency of photocleavage of these cycloadducts showed a marked effect of solvent polarity. In non-polar benzene, the quantum yields of cycloreversion were large and a strong transient absorption of ^{3}(**1**)* with the small absorption of Py$^{-\bullet}$ was obtained, whereas in polar MeCN, the cycloreversion reaction became slower and the absorption of Py$^{-\bullet}$ was large in transient absorption. The transient species at *ca.* 500 nm in benzene solvent can probably be ascribed to the remaining exciplex which has not been cleaved: the main part of the exciplex dissociates to (**1**) and (**2**). A large and sharp absorption of Py$^{-\bullet}$ in MeCN suggests the formation of an ion-pair-like exciplex state rather than a normal type of exciplex: the high polarity of MeCN enables the formation of this type of exciplex. The low quantum yields of photocleavage in the MeCN solvent indicate that this ion-pair-like exciplex deactivates mostly by charge recombination. In this system, however, ^{3}Py* formed by geminate charge recombination was not found.

The quantum yield of photocycloreversion in MTHF was also examined as shown in Table 1. MTHF is a good solvent for the exciplex emission, and in this case appreciable emission was observed as shown in Figure 2. However, the quantum yield of photocleavage in MTHF was slightly lower than that in benzene. This means that emission does not compete with photocleavage, because the quantum yield of the exciplex emission is still low even in MTHF.

As for the mechanism of photocleavage (see Scheme), electron transfer from DMA to the neighbouring Py chromophore is



Scheme.

expected to be fast enough to compete with the concerted photocleavage process which has no electron transfer, since chromophores need not move in a large scale for the electron transfer at this intramolecular donor–acceptor distance. The exciplex state produced cleaves immediately in non-polar solvents and a small part of the exciplex forms a stable emissive exciplex which can be detected by transient spectroscopy. In polar MeCN, the polar structure of the exciplex is solvated by solvent molecules and the complete electron transfer from DMA to Py produces an ion-pair-type exciplex. This solvated ion-pair type of exciplex is deactivated effectively by back-electron transfer from $Py^{-\bullet}$ to the neighbouring $DMA^{+\bullet}$, and the quantum yield of photocleavage is low.

In all systems, contrary to our expectation, large differences between *trans*- and *cis*-cyclobutane could not be found. These two isomers show similar reaction quantum yields and transient absorption spectra. Probably the strong interaction between a donor and an acceptor chromophore obscures the structural difference between *trans*- and *cis*-cyclobutanes.

Experimental

Materials.—4-Dimethylaminostyrene (**2**) was prepared from 4-dimethylaminobenzaldehyde[34] and was purified by distillation under reduced pressure. 1-Vinylpyrene (**1**) was prepared from pyrene-1-carbaldehyde by a Wittig reaction and was purified by silica gel column chromatography.

Pyrene (Py) (Tokyo Kasei Kogyo) was purified by recrystallization and column chromatography. *NN*-Dimethyl-*p*-toluidine (DMT) (Wako) was purified by distillation under reduced pressure.

Benzene (Wako) and 2-chlorobutane (Tokyo Kasei Kogyo) were dried and distilled. Acetonitrile (Wako) was refluxed over P_2O_5 several times and was fractionally distilled. 2-Methyltetrahydrofuran (MTHF) (Tokyo Kasei Kogyo) was dried and purified by vacuum distillation.

Cyclobutanes.—Two cycloadducts, *trans*- and *cis*-1-(4-dimethylaminophenyl)-2-pyren-1-ylcyclobutane (**3t** and **c**), respectively were prepared photochemically from the corresponding vinyl monomers as described elsewhere.[24,35] All compounds are identified by n.m.r., mass, and i.r. spectroscopy and by elemental analysis. The cyclobutanes were purified by liquid chromatography (Waters) on a silica gel column prior to use. Care was taken to avoid thermal or photochemical decomposition.

The *trans*-cyclobutane dimer of (**1**) was prepared by the photoirradiation of (**1**) and is described elsewhere.[36]

Quantum Yields of Photoreactions.—The sample solution of cyclobutanes (5.0×10^{-5} mol l^{-1}) in a 1 cm quartz cell was freed from oxygen by N_2 bubbling for 15 min. Photoirradiation was made in a sample chamber of RF-501 (Shimadzu) spectrofluorophotometer for a few minutes. The light intensity was measured by potassium ferrioxalate actinometry.[37,38] The photon intensity was measured as 2.0×10^{-9} E s^{-1} at 330 nm when the slit was set at 19 nm. Photoexcitation was done at 330 nm by the Py chromophore. Photoirradiated samples were immediately analysed by liquid chromatography using a u.v. detector monitored at 254 nm. The molar extinction coefficient at 254 nm for each compound was corrected. In all measurements, the conversion of photocycloreversion was limited to $<30\%$ and the effect of exciting light absorption by the products was corrected. Thermal reactions, which were practically negligible, were corrected by blank experiments in all systems. The values of reaction quantum yield were reproducible to within $\pm 5\%$ on repeated runs.

Optical Measurements.—All samples for absorption and emission measurements were degassed by repeated freeze–thaw cycles. Absorption spectra were measured by a UV-200S (Shimadzu) spectrophotometer with a 2 nm slit width. Emission spectra were measured by a RF-501 (Shimadzu) spectrofluorophotometer whose spectral response was calibrated by a standard tungsten lamp. The quantum yield of emission was determined relative to that of quinine sulphate in sulphuric acid.[39]

Samples for laser photolysis were freed of oxygen by N_2 bubbling for 15 min. The optical density of all samples at 347.1 nm was adjusted to be almost the same in a 1 cm quartz cell. Measurements were made at 297 K by exciting the Py group. The exciting light pulse at 347.1 nm has 10 mJ pulse energy and 14 ns pulse duration: the precise description of the laser photolysis apparatus is given elsewhere.[30].

Reference absorption spectra of $^3Py^*$ and ^{3}(**1**)* were measured by laser photolysis at 297 K. The optical density of the degassed solution of Py or (**1**) in a 1 cm quartz cell was 1.5 at 347.1 nm. The produced $^3Py^*$ had a lifetime of 4.0 μs in MeCN, and ^{3}(**1**)* had lifetimes of 8.3 and 17 μs in MeCN and benzene, respectively. The ion radical absorption spectra of $DMT^{+\bullet}$ and $(\mathbf{2})^{+\bullet}$ were also measured by laser photolysis at 297 K. The photoexcitation of DMT or (**2**) in polar MeCN induced photoionization. The decay curve of these ion radicals consisted of several components of lifetimes from 0.5 to 100 μs. The ion radical absorption spectra of $Py^{+\bullet}$, $Py^{-\bullet}$, $(\mathbf{1})^{+\bullet}$, and $(\mathbf{1})^{-\bullet}$ were measured by γ-ray irradiation method. γ-Rays from a ^{60}Co source (2×10^6 rad h^{-1}) was irradiated on the samples for a certain time. Measurements were made with a degassed 1 mm quartz cell in glass matrices at 77 K. Cation radicals were produced in a glass matrix of 2-chlorobutane, and anion radicals were produced in a glass matrix of MTHF.[26]

Acknowledgements

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