

Photocycloaddition of 4-Dimethylaminostyrene with 1-Vinylpyrene or Styrene

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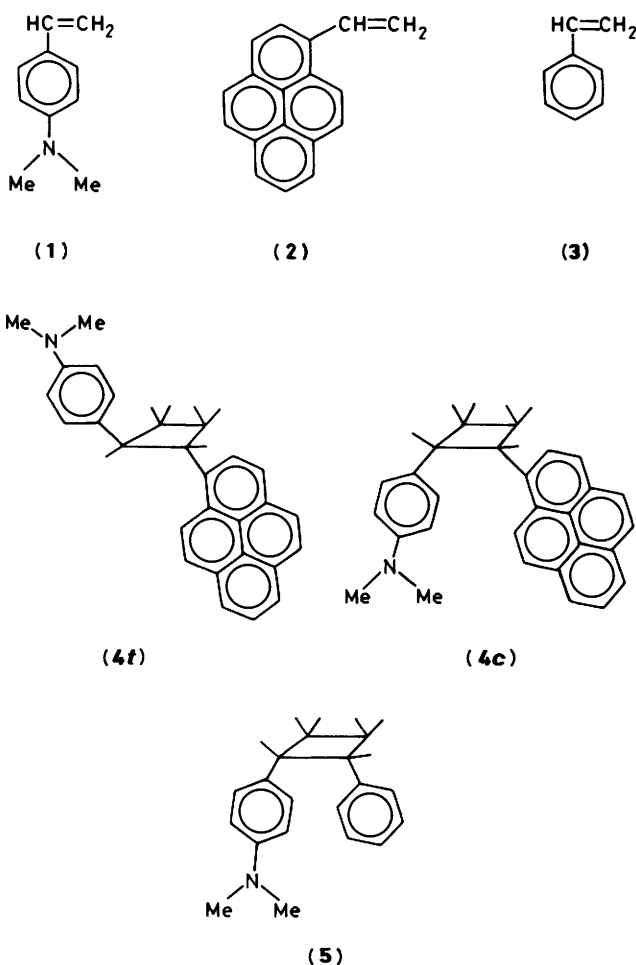
Photocycloaddition reactions of 4-dimethylaminostyrene (1) as an electron donor with 1-vinylpyrene (2) or styrene (3) as electron acceptors were studied. In non-polar solvents, photoirradiation of (1) with (2) gave *trans*- and *cis*-1-(4-dimethylaminophenyl)-2-pyren-1-ylcyclobutane (4*t* and 4*c*), whereas photoreaction of (1) with (3) gave only *cis*-1-(4-dimethylaminophenyl)-2-phenylcyclobutane (5). The yield of these cycloadducts decreased with increasing solvent polarity, and in polar solvents mainly the copolymer was produced. Transient intermediates were studied by nanosecond ruby laser photolysis of the system (1) + (2). The transient absorption spectrum in the non-polar solvent benzene was ascribed to the exciplex type, while in the polar solvent acetonitrile the spectrum of free cation and anion radicals was observed. These facts imply that photochemical cycloaddition of these systems occurred *via* an exciplex as the intermediate. The formation of *cis*- and *trans*-cycloadducts is discussed in terms of the reactivity of the exciplex state and the conformation of the exciplex.

Since the first report of exciplexes,¹ many photochemical reactions have been presumed to occur through exciplexes as intermediates.† For example, it has been proposed that photoinduced [2 + 2] cycloadditions, such as naphthalene-acrylonitrile,² cyanophenanthrene-methylstyrene,³ cyanonaphthalene-olefin,⁴ and methoxybenzene-cyano-olefin⁵ pass through exciplex intermediates. However, it is difficult to prove experimentally that the reactions proceed *via* exciplexes, because several transients such as the emissive state, ion pairs, and free ions may participate in a bimolecular deactivation process of photoexcited molecules.⁶

We now report the photocycloaddition of 4-dimethylaminostyrene (1) as an electron donor with 1-vinylpyrene (2) or styrene (3) as electron acceptors. The donor-acceptor pair of *NN*-dimethylaniline and pyrene is a typical exciplex system. The quantum yield of exciplex emission of *NN*-dimethylaniline with pyrene is high⁷ and the dynamic behaviour of this exciplex system has been thoroughly studied. The present system of (1) and (2) shows exciplex emission and gives some photoproducts such as *trans*- and *cis*-cycloadducts by photoirradiation, whereas the system of (1) with (3) gives no exciplex emission and produces only a *cis*-cycloadduct by photoexcitation. This difference is related to the reactivity of the exciplex states and the conformation of the exciplexes. In this study, the solvent effect on the photoproducts and transient absorption spectra were studied and the role of exciplexes in the photocycloaddition is discussed.

Results and Discussion

Photocycloaddition of (1) with (2).—Photoexcitation of (2) in the presence of (1) in non-polar solvents such as benzene produces a new emission band around 520 nm, as shown in Figure 1. The emission band is broad and structureless, but the quantum yield of this new emission is not as high (ϕ 0.10 in benzene) as that of *NN*-dimethylaniline with pyrene (ϕ 0.48 in hexane).⁷ This new emission band is ascribed to exciplex emission. The emission intensity decreases, accompanying the red-shift of spectral maximum as the polarity of the solvent increases. The free energy change for exciplex formation⁸ is satisfied for the pair (1) and (2), since the oxidation potential of (1) is 0.28 V (*versus* Ag-0.01N-Ag⁺) and the reduction potential



of (2) is -2.48 V (*versus* Ag-0.01N-Ag⁺). The Stern-Volmer plot for the fluorescence quenching of (2) (in benzene $\tau_0 = 51$ ns, in acetonitrile $\tau_0 = 61$ ns) by (1) in solution at room temperature gives a diffusion-controlled rate constant *ca.* 10^{10} l mol⁻¹ s⁻¹ for all solvents used in this work.

† In this paper, the term 'exciplex' is equivalent to 'heteroexcimer'.

Photoreaction^a of (1) with (2) or (3)

(1)	(2)	(3)	Solvent ^b	ϕ_{ex}^c	τ_{ex}^d/ns	Product (%) ^e			
						Concentration (mM)	(4 <i>f</i>)	(4 <i>c</i>)	(5)
10	0.05		Benzene	0.10	55	28.4	4.0		2.0
10	0.05		Benzene ^f	0.019	7.4	4.0	~ 0		~ 0
10	0.05		Diethyl ether	0.11	29	78.2	3.5		16.4
10	0.05		THF	0.054	64	22.2	1.7		13.1
10	0.05		MEK	0.003	23	~ 0	~ 0		10.8
10	0.05		MeCN	~ 0		~ 0	~ 0		32.0
68		240	Benzene					14.4	1.4
68		240	Diethyl ether					13.9	1.6
68		240	THF					14.3	9.7
68		240	MEK					4.0	31.1
68		240	MeCN					0.5	38.1

^a Photoirradiation time and conditions are in the text. ^b Abbreviations are in the Experimental section. ^c Quantum yield of exciplex emission. ^d Lifetime of exciplex emission. ^e % is based on the total amount of (2) for the case of reaction of (1) with (2), and based on (1) for the case of reaction of (1) with (3). ^f With O₂, unknown products 12.1%.

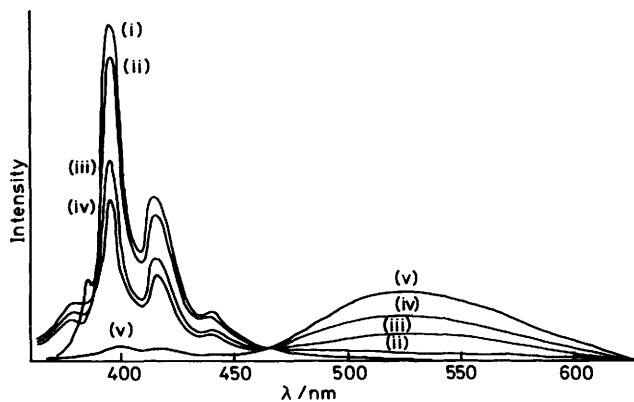


Figure 1. Fluorescence quenching and exciplex emission of (2) [$5.0 \times 10^{-5}M$ except (v)] by addition of (1) in benzene at 297 K. (i), $0M$ -(1); (ii), $1.0 \times 10^{-3}M$ -(1); (iii), $5.0 \times 10^{-3}M$ -(1); (iv), $1.0 \times 10^{-2}M$ -(1); and (v), $1.0 \times 10^{-1}M$ -(1) and $5.0 \times 10^{-4}M$ -(2)

A degassed solution of $0.05mM$ -(2) with $10mM$ -(1) was photoirradiated in various solvents by a 300 W high-pressure mercury lamp fitted with a UV-35 filter at 297 K for 3 h. Photoexcitation was applied selectively to (2). The photoproducts in benzene as solvent consist of two cycloadducts and a small amount of polymer. The cycloadducts were separated by liquid chromatography and the structures were determined as *trans*- and *cis*-1-(4-dimethylaminophenyl)-2-pyren-1-ylcyclobutane (4*t* and *c*) by mass, i.r., and n.m.r. spectra. In the polar solvent acetonitrile, the cycloadduct formation was suppressed and only the polymer was obtained in these experimental conditions. The solvent effect on the photoproducts is shown in the Table.

In this experiment, the concentration of (2) was lowered to the analytical limit to prevent the formation of cyclobutane dimers of (2);* in the concentration range in the Table, neither excimer emission of (2) nor the dimer of (2) was obtained. When the concentration of (1) is $> 100mM$, the *trans*-cyclobutane dimer of (1) was also produced. Especially in polar solvents such as acetonitrile, appreciable amounts of the dimer of (1) were produced. This dimer is considered to be produced from the cation radical of (1).⁹ Under the conditions of the Table, however, the amount of this dimer is negligibly small.

The Table shows that larger amounts of cycloadducts are produced in the solvents in which strong exciplex emission is

observed. In acetonitrile, neither exciplex emission nor any cycloadduct was obtained, and appreciable amounts of polymer were produced; in diethyl ether the highest exciplex quantum yield and highest yield of photoproducts were obtained. Here the yield of photoproduct is calculated on the basis of the total amount of (2) and this was limited by the decrease of the reactants as the reaction proceeded.

It is often considered that an efficient photochemical reaction gives weak or no fluorescence emission since the radiative transition is overwhelmed by the efficient reaction process. However, in the present system of (1) and (2), both reaction and exciplex emission quantum yields are not high enough to compete with each other, and therefore both exciplex reaction and exciplex emission are observed.† Incidentally, the pair *NN*-dimethylaniline and pyrene is known to form a very emissive exciplex.⁷

The fact that the reaction yield of photocycloaddition is parallel to the quantum yield of exciplex emission strongly suggests that the exciplex is an intermediate in this cycloaddition. To confirm this assumption, the quenching effect of oxygen was examined. A non-degassed sample in benzene solvent gave only a slight amount of photocycloadduct as shown in the Table. Further, an experiment in which the oxygen concentration was properly adjusted was carried out, i.e., the oxygen concentration was varied by changing the ratio of oxygen to nitrogen and the mixed gas was introduced into the reaction cell, and then the cycloaddition rate and the exciplex emission intensity were measured at the same time. The cycloaddition rate decreased as the concentration of O₂ increased with decreasing exciplex emission intensity as shown in Figure 2: the relative cycloadduct yield based on the total amount of (2) is proportional to the quantum yield of the exciplex emission. This relationship suggests that the exciplex is the intermediate in cycloadduct formation.

Addition of some amines such as pyridine or triethylamine to this system quenched the exciplex emission, but induced some side reactions, hence the quenching of the exciplex by such quenchers was not successful.¹⁰

The cycloadduct produced (Table) is mostly the *trans*-type (4*t*). This adduct (4*t*) is not produced by the photoisomerization of (4*c*) as the main photoreaction of (4*c*) is cleavage to (1) and

* In fact, photoirradiation of a benzene solution of (2) ($1.0 \times 10^{-3}M$) shows appreciable excimer emission around 485 nm and gives the *cis*-dimer of (2).

† In benzene, $\phi_{(4t) + (4c)}$ is ca. 0.015 for 50% quenching of ¹(2)* with (1).

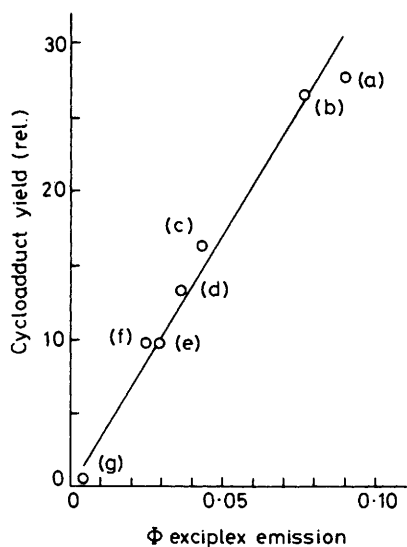


Figure 2. Relationship between the relative yield of (4t) + (4c) and the absolute quantum yield of exciplex emission in benzene solvent at 297 K. (1) 1.0×10^{-2} M; (2) 8.0×10^{-5} M; (a), $P(\text{O}_2)$ 0 Torr; (b), $P(\text{O}_2)$ 18.5 Torr; (c), $P(\text{O}_2)$ 36.2 Torr; (d), $P(\text{O}_2)$ 69.1 Torr; (e), $P(\text{O}_2)$ 99.1 Torr; (f), $P(\text{O}_2)$ 127 Torr; and (g) $P(\text{O}_2)$ 760 Torr

(2), and the quantum yield of photoisomerization from (4c) to (4t) is negligibly small.

For the polymer obtained in benzene solvent, it was found by i.r. and elemental analysis that it is a copolymer of (1) and (2). This is also supported by the fact that the polymer shows strong intramolecular exciplex emission in non-polar benzene solvent. Here, the concentration of the initiating species of polymerization is very low (ca. 1/300 of that of cycloadducts) according to the estimate based on the molecular weight of the copolymer ($M_w 10^{3-4}$).

Direct measurements of intermediates were made by nano-second laser photolysis. Figure 3 (upper half) shows the transient absorption in acetonitrile obtained 70 ns after an exciting pulse at room temperature. Photoexcitation was by a 347 nm light pulse and (2) was mainly excited. The absorption bands, 640, 537, and 425 nm (435 nm in benzene), of this spectrum are attributed to the cation radical of (1), the anion radical of (2), and the excited triplet state of (2), respectively, by comparison with the reference spectra shown in Figure 3 (lower half). The absorption bands of Figure 3 (upper half) are sharp and have lifetimes longer than 1 μ s. Therefore, these absorptions at 640 and 537 nm are assigned to the free cation radical and anion radical, respectively, and they are deactivated by the recombination process and chemical reactions. On the other hand, Figure 3 (lower half) which is obtained in benzene solvent 70 ns after an exciting pulse at room temperature, shows a broad absorption band at ca. 530 nm with a shoulder at ca. 640 nm,¹¹ and a sharp band at 435 nm which is ascribed to the triplet state of (2). The lifetime of this broad band is ca. 55 ns and agrees with the emission lifetime of the exciplex. Hence this absorption is assigned to that of the exciplex. Moreover, the measurements of transient photoconductivity indicated that free ions are produced for the system of (2) with (1) in acetonitrile solution, whereas in benzene solution no photocurrent was observed. Therefore, it is concluded that in acetonitrile the high polarity of the solvent produces free ion radicals, while in benzene only an exciplex-type transient species is formed.¹²

The reaction proceeds as shown in the Scheme. In non-polar solvents, the quenching of the excited singlet of (2) by (1)

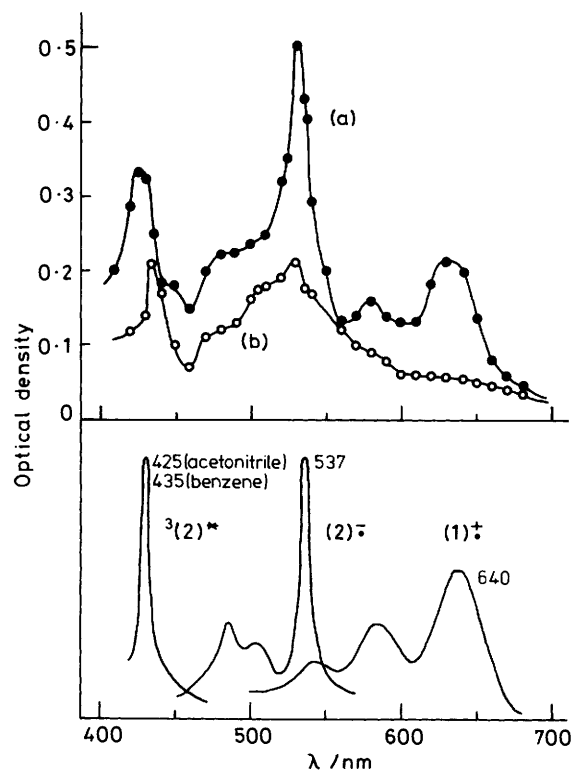
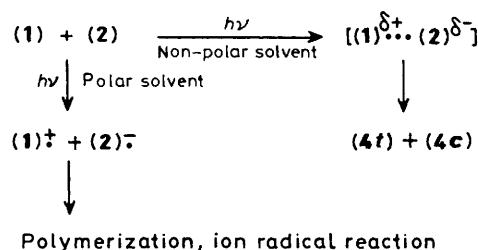


Figure 3. Transient absorption spectra (upper half) and the reference spectra of (1)^{•+}, (2)^{•-}, and ³(2)* (lower half). The transient spectra were measured at 297 K in acetonitrile (a) and in benzene (b) at 70 ns after excitation: (1), 1.0×10^{-3} M; (2), 5.0×10^{-5} M. The reference spectra of (1)^{•+} and (2)^{•-} were measured by γ -ray irradiation at 77 K, and spectrum of ³(2)* was measured by laser photolysis at room temperature



Scheme.

produces an exciplex which gives cycloadducts, whereas in polar solvents photodissociation to free ion radicals is dominant and these free ion radicals initiate polymerization and ion radical reactions. Careful examination of the photoproducts in acetonitrile solvent shows the *trans*-cyclobutane dimer of (1). However, dimerization initiated by ion radicals is not as efficient as the cycloaddition of (1) with (2).

In the photocycloaddition of (1) with (2), most of the cycloadduct produced is of the *trans*-type (4t). In general, the most stable structure of the aromatic exciplex is said to be the sandwich type,¹³ and in many cases this type of products has been obtained³ (see later). In the present system, photoisomerization from (4c) to (4t) is discounted and cycloaddition *via* the excited triplet state of (2) is also improbable from the fact that, in acetonitrile solvent, no cycloadducts can be found irrespective of the excited triplet state formation of (2).

The presumed mechanism for (4t) formation is as follows. The

conformational requirements for exciplex formation are not as strict as that for the excimer. It has been pointed out that some molecules whose rigid framework prevents close approach between donor and acceptor moieties show exciplex emission.¹⁴ The *trans*-cyclobutane (**4t**) also shows intramolecular exciplex emission in tetrahydrofuran solvent at room temperature. In the present system, it is possible that bond formation at the vinyl group occurs preferentially when the exciplex conformation is nearly in the *trans*-form.

Photocycloaddition of (1) with (3).—Styrene (**3**) quenches the fluorescence of (**1**) (in hexane $\tau_0 = 5.6$ ns, in acetonitrile $\tau_0 = 4.4$ ns) with a diffusion-controlled rate constant: 2.8×10^9 in benzene and 2.0×10^{10} l mol⁻¹ s⁻¹ in acetonitrile. The possibility of *S-S* energy transfer is excluded by considering their energy levels. The free enthalpy change of photoinduced electron transfer is exothermic by >30 kcal mol⁻¹ on the basis of Weller's equation.⁸ Therefore, the quenching mechanism of this system is regarded as electron transfer, and exciplex formation is expected in non-polar solvents. However, the exciplex emission of this system could not be observed and no transient species could be found by nanosecond laser photolysis in benzene solvent. On the other hand, in acetonitrile solvent the formation of the free cation radical of (**1**) and the free anion radical of (**3**) was confirmed by their transient absorption.

Photoirradiation of the degassed solution of (**1**) with (**3**) for 2 h by a 300 W high-pressure mercury lamp fitted with a UV-D36C filter produces a cycloadduct, *cis*-1-(4-dimethylaminophenyl)-2-phenylcyclobutane (**5**) as shown in the Table. The cyclobutane is of the *cis*-type only and no other cycloadduct could be found. The solvent effect on the product is also shown in the Table. The tendency is the same as that of the system of (**1**) with (**2**). In the solvents of low polarity, mainly the cycloadduct is produced, and as the solvent polarity increases, the amount of cycloadduct decreases with the increase of polymer yield. The formation of free ion radicals in acetonitrile has been confirmed by laser photolysis and these free ion radicals initiate radical reactions: in fact they give small amounts of dimers and polymer. However, the dimers of these ion radical reactions are produced in too small amounts to be analysed in these experimental conditions. For the polymer, which is produced by radical polymerization, the amount of initiating species is estimated to be very small (*ca.* 1/400 of that of the cycloadduct in benzene).

In this manner, the reaction of this system resembles that of (**1**) with (**2**), except that the cycloadduct produced is of the *cis*-type. The formation of a *cis*-type cyclobutane seems to reflect the conformation of the exciplex intermediate, though the existence of an exciplex could not be found by spectroscopic methods. Presumably, the reactivity of this intermediate is very high and the exciplex emission process cannot compete with cyclobutane formation. It seems that the time resolution of our laser photolysis (14 ns pulse width) is not sufficient to detect short lived intermediates.

On comparing the two systems, it is proposed that the reactivity of exciplex intermediates determines the configuration of the cycloadduct product. The long lifetime of the exciplex of (**1**) with (**2**) or the large π system of (**2**) allows a wide variety of conformations and leads to a *trans*-type cyclobutane, whereas for the reaction of (**1**) with (**3**), the short lifetime or the overlap of small π rings limits the conformations of the exciplex and leads to a *cis*-type cyclobutane. Many photoreactions that have been reported to proceed *via* exciplex intermediates are non-emissive, presumably because high reactivity of the exciplex intermediates prevents the exciplex emission. The case of reaction system of (**1**) with (**3**) seems to belong to this type of reaction.

Conclusions.—In the case of (**1**) with (**2**), much evidence shows that the reaction passes through an exciplex state although the main photocycloadduct is of the *trans*-type. The formation of a *trans*-type cycloadduct was explained by the following mechanism. The exciplex of (**1**) with (**2**) has a loose conformation and cycloaddition occurs preferentially in an exciplex conformation close to the *trans*-conformation. In the case of (**1**) with (**3**), the fact that a *cis*-cycloadduct is efficiently produced suggests that it is derived from an exciplex-type intermediate, although there is no spectroscopic evidence. In this system the reactivity of the exciplex is probably too high to allow exciplex emission and conformational change of the exciplex, and this gives the *cis*-type of cycloadduct.

Experimental

Materials.—4-Dimethylaminostyrene (**1**) was prepared from 4-dimethylaminobenzaldehyde¹⁵ and was purified by distillation.

1-Vinylpyrene was prepared from pyrene-1-carbaldehyde by a Wittig reaction and was purified by silica gel column chromatography. Special care was taken to eliminate pyrene which was an impurity in pyrene-1-carbaldehyde.

Styrene was dried and purified by distillation under reduced pressure. Benzene, diethyl ether, tetrahydrofuran (THF), and methyl ethyl ketone (MEK) were dried and purified by distillation. Acetonitrile was refluxed over P₂O₅ several times and was fractionally distilled. 2-Chlorobutane and 2-methyl-tetrahydrofuran for γ -ray irradiation were dried by molecular sieves and then distilled prior to use.

Identification of Cycloadducts.—A degassed solution of (**1**) (67 mg) with (**2**) (13 mg) in benzene (2 ml) was photoirradiated for 3 h by a 300 W high-pressure mercury lamp (Toshiba) fitted with a UV-35 (Toshiba) filter. The cycloadducts produced in this system were collected by chromatography (Waters) on silica gel column eluting with CH₂Cl₂-hexane (1:9). The *cis*-cyclobutane has a larger retention time than the *trans*-cyclobutane. The conformation of (**4t**) and (**4c**) was determined by n.m.r. chemical shifts.^{8,16} *trans*-1-(4-Dimethylaminophenyl)-2-pyren-1-ylcyclobutane (**4t**) has m.p. 86–88 °C (Found: C, 89.6; H, 6.9. C₂₈H₂₅N requires C, 89.6; H, 6.7%); ν_{\max} (KBr) 3 050w, 2 950m, 2 860m, 1 620s, 1 520vs, 1 480w, 1 440m, 1 350br, 1 160m, 950m, 840s, 820vs, 760m, 700m, 420m, and 410m cm⁻¹; δ_{H} (90 MHz; C₆D₆; Me₄Si) 1.96–2.42 (4 H, m, CH₂), 2.52 (6 H, s, CH₃), 3.68–4.08 (1 H, m, CH), 4.24–4.64 (1 H, m, CH), 6.52–7.32 (4 H, m, aromatic), and 7.58–8.20 (9 H, m, aromatic); m/z 375 (100%, M⁺), 347 (9, M⁺ - C₂H₄), 228 [7, (2)⁺], and 147 [9, (1)⁺]. *cis*-1-(4-Dimethylaminophenyl)-2-pyren-1-ylcyclobutane (**4c**) was an oil (Found: C, 89.8; H, 6.8%); δ_{H} (90 MHz; C₆D₆; Me₄Si) 2.10 (6 H, s, CH₃), 2.28–2.72 (4 H, m, CH₂), 3.96–4.32 (1 H, m, CH), 4.85–4.96 (1 H, m, CH), 5.98–7.00 (4 H, m, aromatic), and 7.52–8.28 (9 H, m, aromatic); m/z 375 (42%, M⁺), 347 (21, M⁺ - C₂H₄), 228 [66, (2)⁺], and 147 [100, (1)⁺]. A degassed solution of (**1**) (20 mg) with (**3**) (50 mg) in benzene (2 ml) was photoirradiated by a 300 W high-pressure mercury lamp fitted with a UV-D36C (Toshiba) filter for 3 h. The *cis*-cyclobutane was obtained by chromatography as above. *cis*-1-(4-Dimethylaminophenyl)-2-phenylcyclobutane (**5**) had m.p. 48–49 °C (Found: C, 86.3; H, 8.45. C₁₈H₂₁N requires C, 86.0; H, 8.4%); ν_{\max} (KBr) 2 950s, 1 610s, 1 520s, 1 440m, 1 340br, 1 210m, 1 160w, 1 060w, 940m, 810vs, 720m, 690s, and 530m cm⁻¹; δ_{H} (90 MHz; C₆D₆; Me₄Si) 2.12–2.40 (4 H, m, CH₂), 2.43 (6 H, s, CH₃), 3.68–3.92 (2 H, m, CH), 6.32–6.96 (4 H, m, aromatic), and 6.92–7.15 (5 H, m, aromatic); m/z 251 (6%, M⁺), 223 (1, M⁺ - C₂H₄), 147 [100, (1)⁺], and 104 [3, (3)⁺]. The *cis*-conformation of (**5**) is determined by the comparison of n.m.r. chemical shift of (**5**) [δ 2.30 (CH₂), 2.43 (CH₃), 3.82 (CH), and 6.64 (aromatic)] with

that of the dimers of (1) [*cis*-dimer of (1); δ 2.46 (CH₂), 2.44 (CH₃), 3.88 (CH), and 6.74 (aromatic), whereas *trans*-dimer of (1); δ 2.14 (CH₂), 2.56 (CH₃), 3.50 (CH), and 6.92 (aromatic)], where numericals are the central values of n.m.r. signal pattern.⁸

Spectroscopic Measurements.—Absorption spectra were measured by a Shimadzu UV-200S spectrophotometer. Fluorescence spectra were measured by a Shimadzu RF-501 spectrofluorophotometer. The absolute emission quantum yields were measured by quinine sulphate as a standard.¹⁷ The lifetime of fluorescence was determined by the single-photon counting method (Ortec Inc.).

Transient absorptions were measured by nanosecond laser photolysis method. Photoexcitation was made by an NEC SLG2009 Q-switched giant pulse ruby laser. The 347 nm light pulse obtained by a KDP frequency doubler has 10 mJ pulse energy and 14 ns pulse duration. All samples for laser photolysis were degassed by the freeze-pump-thaw method in Pyrex ampoule fitted with a 1 cm quartz cell.

Reference spectra of (1)^{•+} and (2)^{•-} were obtained by γ -ray irradiation at 77 K in 2-chlorobutane and in 2-methyltetrahydrofuran,¹⁸ respectively.

Cyclic Voltammetry.—Electrochemical potentials were measured by cyclic voltammetry in MeCN versus Ag-0.01N-Ag⁺ as a reference electrode.

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