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Photochemistry of Amino-Linked Bichromophoric Anthracenes. Efficient Cyclomerization of 9-(1-Naphthylmethylaminomethyl)anthracene and Adiabatic Cycloreversion of the Cyclomer

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The spectral and photochemical properties of the title compound **1** and bis(9-anthrylmethyl)amine (**2**) have been investigated. The fluorescence spectrum of **1** in methylcyclohexane showed an emission from the locally excited state of the anthracene part and a weak broad emission at 410—550 nm from the intramolecular exciplex. The fluorescence quantum yields of **1** and **2** decreased along with an increase in the solvent polarity. Both **1** and **2** underwent intramolecular [4+4] cycloaddition. The quantum yield of the cyclomerization of **1** was 0.24 in acidic methanol, while in MeCN the reaction was completely quenched by an intramolecular electron transfer from the amino group to the excited anthracene moiety. Excitation of the cyclomer from **1** at 285 nm brought about fluorescene from both the locally excited anthracene and the exciplex state, indicating that adiabatic cycloreversion took place on the S_1 potential surface. To investigate the conformations, the crystal structures of **1** and **2** were determined and PM3 calculations were performed for **1**–H^+. The calculations indicate that a conformer in which the two chromophores are located close to each other has a higher energy then other stable conformers.

The photophysics and photochemistry of non-conjugated bichromophoric systems have been investigated from the viewpoint of understanding interaction between two chromophores. For example, bisanthracene derivatives having various linkages are known to undergo intramolecular [4+4] cycloaddition (cyclomerization) and/or to exhibit emission from the intramolecular excimer state.[1—3] Although two chromophores linked by a long chain tether can interact with each other in the excited state,[1] it was reported that a three-atom link facilitates a sandwich-type overlap of two aromatic rings.[4] In spite of the potential reactivity to cyclomerization, studies on bichromophoric compounds having 9-anthryl and 1-naphthyl groups have been very limited.[5—7] We recently reported that anthracene–naphthalene bichromophoric compounds linked by a three-carbon chain underwent cyclomerization from the excited singlet state, competing with dimerization of the anthracene moieties.[5] The efficiency of cyclomerization was affected by the substituents on the carbon chain through a conformational change and/or an alteration of the quantum yield of the intersystem crossing to the unreactive triplet state. As for other tethers consisting of three atoms, compounds having an ester linkage, such as $AnCOOCH_2Nap$ (An = 9-anthryl, Nap = 1-naphthyl), gave only the corresponding anthracene dimer,[6] while an ether chain, CH_2–O–CH_2, facilitated cyclomerization, compared with the trimethylene linkage.[7] Such an influence of the structure of the linkage on the photochemistry prompted us to study the photochemical behavior of amino-linked systems. In this paper we describe the photochemistry of new bichromophoric anthracenes **1** and **2** having a CH_2–NH–CH_2 linkage, and discuss the effects of the reaction media and protonation at the amino nitrogen on the cyclomerization. An adiabatic cycloreversion of the cyclomers was also investigated in order to obtain information about the electronic nature of the exciplex and the locally excited state of **1** and **2** (Chart 1).

Results and Discussion

Absorption and Fluorescence Spectra. **1** and **2** were synthesized by a $NaBH_3CN$ reduction of the corresponding imines, which were obtained by acid-catalyzed condensation of 9-anthracenecarboxyaldehyde and the appropriate amine. The spectral data and elemental microanalysis were as expected for **1** and **2**.

The UV-vis spectrum of **1** in methylcyclohexane (MCH) showed an absorption band in 320—390 nm with a well-resolved structure, which is closely similar to that of the monochromophoric **3**, and an absorption due to the naphthalene part in 270—300 nm. Bisanthracene derivative **2**

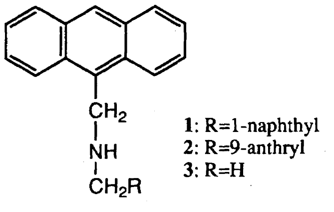


Chart 1.

also showed an absorption spectrum typical of anthracene, although the maximum of the 0–0 band was red-shifted by 3 nm compared with that of **3**. These spectral features indicate that there are no important interactions between the two chromophores in the ground state for both **1** and **2**. An alteration of the solvent to MeCN did not cause a significant variation in the spectra of **1**—**3**, while in acidic aqueous methanol (0.1 mol dm^{-3} HCl in MeOH–H_2O 9 : 1 v/v) the absorption bands were shifted to the red by ca. 2 nm, and were slightly broadened.

Figure 1 shows the fluorescence spectrum of **1** in MCH at 295 K. Besides monomer-type emission from the locally excited state of the anthracene moiety (LE), a weak broad emission was observed at 410—550 nm (λ_{max} ca. 450 nm), which was assigned to fluorescence from an intramolecular exciplex (EX). The EX emission maximum was similar to that reported for $AnCH_2OCH_2Nap$ (455 nm) or $An(CH_2)_3Nap$ (450—470 nm).[7] The fluorescence quantum yield of **1** decreased without any significant change in the spectral shape as the solvent polarity increased (0.17 in MCH, 0.069 in dioxane, 0.013 in THF, and 0.007 in MeCN).[8] This trend is explained by intramolecular quenching via electron transfer from the amino group to the excited anthracene, as reported for several 9-aminoalkylanthracenes in MeCN or aqueous solutions.[9] On the other hand, in acidic aqueous methanol **1** showed a strong LE and a weak EX (420—550 nm) emissions. Along with an increase in temperature from 286 to 318 K, the ratio of EX to LE slightly increased, although the total intensity decreased. This temperature dependence indicates that there is a substantial activation barrier for exciplex formation accompanying a conformational change. When the naphthalene part was excited (excitation wavelength 280 nm), the shape of the spectrum was the same as that observed upon excitation of the anthracene part, and no emission from the naphthalene was detected, indicating that a fast intramolecular energy transfer took place from the S_1 state of the naphthalene part to the anthracene moiety.

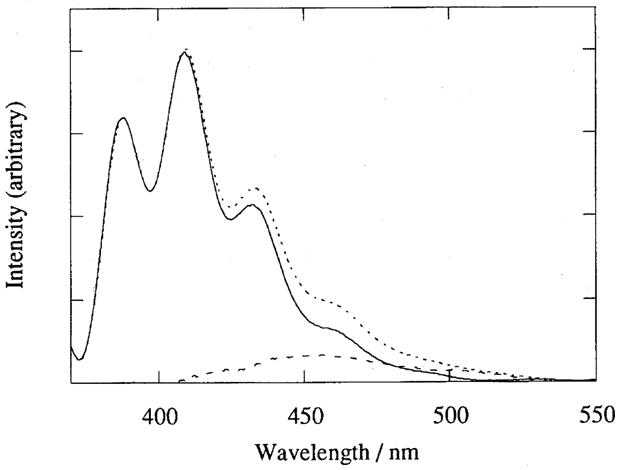
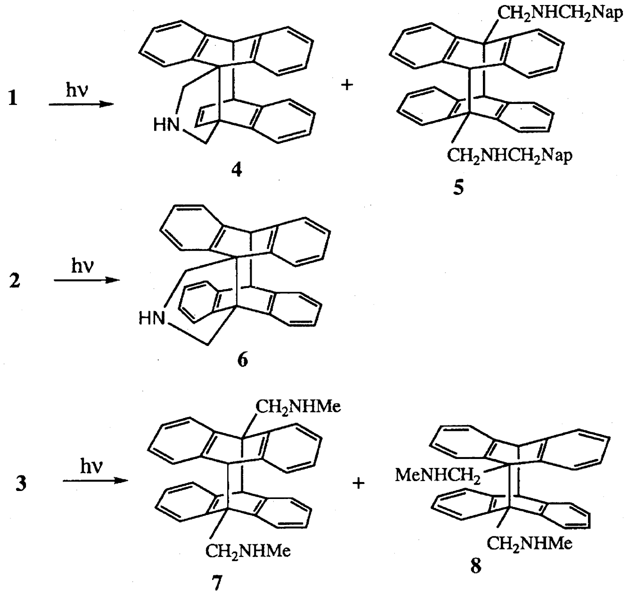


Fig. 1. Fluorescence spectra of **1** and **3** on excitation at 366 nm in MCH at 295 K. ·····: **1**, —: **3**, - - -: exciplex emission derived from subtraction of the spectrum of **3** from that of **1** normalized at 390 nm.

Table 1 lists the fluorescence quantum yields of **1**—**3** together with those of other bichromophoric compounds for a comparison. In MCH the fluorescence quantum yields of **1** and **2** were intermediate between those of the corresponding bichromophoric compounds linked by a CH_2OCH_2 tether and by a trimethylene chain, while the efficiencies of the cyclomerization were similar to those of the latter. The fluorescence spectrum of **2** in MCH showed only a monomer-type emission. The absence of excimer fluorescence from **2** in spite of the occurrence of cyclomerization (vide infra) suggests that the excimer might be short-lived and non-emissive.

Photoreactions of 1—3. When a solution of **1** (8.5×10^{-3} mol dm^{-3}) in degassed benzene was irradiated ($\lambda > 330$ nm) at ca. 20 °C, cyclomer **4** and an anthracene dimer **5** were formed in a ratio of 64 : 36 (Scheme 1). The structure of **4** was determined by NMR spectrometry. The chemical shifts and coupling constants of the bridgehead and olefin protons were closely similar to the reported values for the related anthracene–naphthalene cyclomers.[5] The ^{13}C NMR spectrum showed 26 signals, indicating that all of the carbon atoms were nonequivalent. The regiochemistry of **5** was determined as being head-to-tail on the basis of the chemical shift of the bridgehead protons ($\delta = 3.65$).[10] It was reported that $An(CH_2)_3Nap$ also gave both the head-to-tail anthracene dimer and the cyclomer.[6,11] In the case of **2**, cyclomer **6** was obtained as the sole product without a concomitant formation of the corresponding dimer under the same conditions. Products **4**—**6** were stable in a benzene solution at room temperature. The irradiation of **3** (0.014 mol dm^{-3}) gave head-to-tail dimer **7** and head-to-head dimer **8** in a ratio of 2 : 1. Upon removing the solvent under reduced pressure around 30 °C, **8** underwent thermal cycloreversion to give monomer **3**, while **7** was stable under this condition.

Upon the irradiation of **1** or **2** in MCH in the presence of biacetyl as the triplet sensitizer, no cyclomer was formed and



Scheme 1.

Table 1. Quantum Yields of Fluorescence and Cyclomerization in Various Solvents

	MCH			MeCN		HCl–MeOH[a]		
	Φ_{fl}	(Φ_{ex})	Φ_{cyc}[b]	Φ_{fl}	Φ_{cyc}[b]	Φ_{fl}	(Φ_{ex})	Φ_{cyc}[b]
$AnCH_2NHCH_2Nap$ (**1**)	0.16	(0.015)	0.007	0.007	0	0.30	(0.02)	0.24
$AnCH_2CH_2CH_2Nap$	0.44	(0.02)[c]	0.007[c]					
$AnCH_2OCH_2Nap$	0.078	(0.037)[c]	0.078[c]					
$AnCH_2NHCH_2An$ (**2**)	0.16		0.17	0.015	0.055	0.05		0.028[d]
$AnCH_2CH_2CH_2An$	0.47[e]		0.14[e]					
$AnCH_2OCH_2An$	0.03[e]		0.32[e]					
$AnCH_2NHCH_3$ (**3**)	0.11		—	0.02	—	0.53		—

a) 0.1 mol dm^{-3} HCl in $MeOH–H_2O$ (9 : 1 v/v). b) Irradiated with 366 nm light. c) Ref. 7. d) In 0.05 mol dm^{-3} $HCl/EtOH–H_2O$ (19 : 1 v/v). e) Ref. 1.

the starting material was recovered. Considering the triplet energy of biacetyl (235 kJ mol^{-1}), the excited energy is transferred selectively to the anthracene moiety (E_T 175 kJ mol^{-1}) rather than to the 1-naphthyl group (E_T 250 kJ mol^{-1}).[12] These facts indicate that cyclomerization of **1** and **2** proceeded from the excited singlet state and that the locally excited triplet state of the anthracene part was unreactive. It was reported for other non-conjugated bichromophoric anthracenes that the cyclomerization took place from the excited singlet state via an exciplex (or excimer) state,[1] while involvement of the excited triplet state was suggested for carbonyl-conjugated anthracenes, such as $AnCOCH_2CH_2An$.[13]

The quantum yields of the cyclomerization of **1** and **2** were examined in various solvents at lower concentrations (7×10^{-4}—1.2×10^{-3} mol dm^{-3}) so that dimerization of **1** was negligibly slow. As can be seen in Table 1, the reactivity of **1** or **2** in MCH was lower than that of the corresponding compound having a $CH_2–O–CH_2$ link, and was similar to that of the trimethylene-tethered analog. The advantage of the $CH_2–O–CH_2$ link is due to the lower energy barrier for rotation around C–O bonds in comparison with C–C bonds.[1] The observed moderate reactivities of **1** and **2** can be easily understood by considering that the $CH_2–NH–CH_2$ linkage is less flexible than $CH_2–O–CH_2$ and that electron-transfer quenching might be operating to some extent. In MeCN, the consumption of **1** was much slower and cyclomer **4** was not formed at all, though a small amount of dimer **5** was detected. The quantum yield of cyclomerization for **2** was lower than that of in MCH. These results indicated that the cyclomerization was also quenched by an intramolecular electron-transfer in polar solvents.

In acidic media where the amino nitrogen was protonated, the photolysis of **1** gave **4** efficiently. To our knowledge, the quantum yield of 0.24 was the highest for the cyclomerization of singly-bridged anthracene–naphthalene bichromophoric systems. Tazuke and Watanabe reported that for tetraethyl [3](1,4)naphthaleno[3](9,10)anthracenophane-2,2,15,15-tetracarboxylate the quantum yield of cyclomerization was 0.31.[14] In this compound the two chromophores are fixed close to each other in a face-to-face orientation by means of a cyclophane structure; also, its absorption band is largely red-shifted compared to a single anthracene chromophore due to a strong interchromophore interaction,[14] which is in contrast to that of **1**. Unexpectedly, the quantum yield of the cyclomerization of **2** in acidic alcohol was lower than that of in MCH. Because of the very low solubility of **2** in acidic methanol, ethanol was used as the solvent. The quantum yield of the monomer fluorescence was also low, and no EX emission was observed. An unnoticed deactivation process may occur from the LE and/or the EX states. Protonation at the amino nitrogen also influenced the photodimerization of **3**. The quantum yield of dimerization of **3** in C_6D_6 (0.01 mol dm^{-3}) was 0.032 as a sum of the formation of **7** and **8**. On the other hand, irradiation of **3**·HCl in D_2O at the same concentration gave only the head-to-tail dimer **7**·2HCl with a quantum yield of 0.072. The regioselectivity can be attributed to a Coulombic repulsion between the positively charged ammonium groups. The increase in the quantum yields of both fluorescence and dimerization on protonation suggested that even in non-polar solvents, such as MCH and C_6H_6, the intramolecular electron-transfer had some contribution to the deactivation of the excited state.

Although a photochemical reaction of **1** and **2** in the solid state was also attempted, no product was detected in the differential IR or ^1H NMR spectra.

Conformational Analysis. According to Becker,[2] the photochemical behavior of chain-linked bisanthracene derivatives is greatly affected by the conformation of the tether. The molecular structures of **1** and **2** in the ground state were examined by means of an X-ray structure analysis and semiempirical MO calculations. The crystal structure of **1** was isomorphic with $AnCH_2CH_2CH_2Nap$.[5] Although two adjacent naphthalene rings related by an inversion center showed π–π stacking, no such interaction was observed between anthracene moieties. The crystal of **2** contains benzene as a solvent of crystallization in a 1 : 2 stoichiometry of C_6H_6 : **2**. The benzene molecule lies on an inversion center and interacts with adjacent anthracenes in a face-to-edge fashion. As can be seen in Fig. 2, the $An–CH_2–NH–CH_2$ moiety in **1** adopts a *gauche* conformation, while the $Nap–CH_2–NH–CH_2$ is *trans*. In the case of **2** one $An–CH_2–NH–CH_2$ part is also in a *gauche* conformation. The lack of reactivity of **1** and **2** in the solid state can be understood based on the crystal structures. Two chromophores in a molecule are located far from each other, and intermolecular face-to-face stacking is not attained between

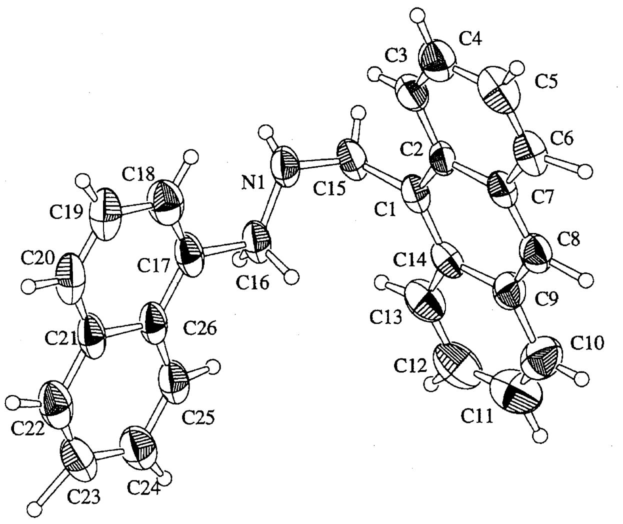


Fig. 2. ORTEP diagram[23] of **1** with the atom numbering. The anisotropic ellipsoids for non-H atoms enclose 30% probability.

two anthracenes in the adjacent molecules. A noticeable conformational feature of **1** is almost an eclipse orientation of the naphthyl group to the C16–N bond; i.e. the torsion angle of N–C16–C17–C18 is close to 0°. This conformation, however, might be stabilized due to intermolecular forces, because the structure optimization of molecule **1** by the PM3[15] method gave a larger torsion angle (−67.9°) with the conformation of the other parts remaining almost unchanged. For **1**–H$^+$, optimized structures were obtained including other possible conformers by MO calculations. As can be seen in Table 2, the *trans*, *trans* form (tt) was more stable by only 1.0 kcal mol^{-1} than the *gauche*, *trans* (gt) or tg conformers. In these three conformers, the distances between C1 (9-position of the anthracene) and C17 (1-position of the naphthalene) are large, and an overlap of the two aromatic rings cannot be attained. In an optimized structure with a g$^-$g$^+$ conformation, the two aromatic rings are located close to each other, although not exactly parallel. The ΔH_f value of this conformer was calculated to be much higher than that of other conformers (Table 2). In these calculations the solvation effect was not taken into account, and the folded conformation with the ammonium part placed in outer sphere might be stabilized in polar solvents. It is suggested, however, that the population of the g$^-$g$^+$ conformer should be small in the ground state, which agrees with the results of the UV spectroscopy.

Table 2. Some Torsion Angles and C1–C17 and Inter-Ring Distances (Å) for Conformers of **1** and **1**–H$^+$ [a)]

Compound Conformation Methods	**1** gt X-Ray	**1**–H$^+$ gt PM3	**1**–H$^+$ tg PM3	**1**–H$^+$ tt PM3	**1**–H$^+$ g$^-$g$^+$ [b)] PM3
C2–C1–C15–N	−71.4	−84.6	−91.0	−90.9	−70.0
C1–C15–N–C16	−75.2	−79.3	179.3	−179.5	−81.1
C15–N–C16–C17	173.9	173.7	81.0	176.2	85.1
N–C16–C17–C18	−7.5	−84.0	−89.9	−82.2	−100.9
C1–C17 distance		4.51	4.40	4.89	3.45
Inter-ring distance[c)]		6.62	6.41	7.09	4.27
ΔH_f/kcal mol^{-1} [d)]	—	1.0	1.0	0.0	7.0

a) The atomic numbering scheme was shown in Fig. 2. b) g$^-$g$^+$ denotes a conformation with a negative (counter-clockwise) angle of C1–C15–N–C16 and a positive (clockwise) one of C15–N–C16–C17. c) The distance between the center of the anthracene and the center of the ring containing C17 in the naphthalene. d) Relative heat of formation to the most stable (tt) conformer.

Cycloreversion of 4 and 6. When **4** was irradiated at 285 nm in MCH under a vacuum, an absorption band assigned to **1** appeared at 310—390 nm, and its intensity increased along with the irradiation time, indicating the occurrence of photochemical cycloreversion. The ^{1}H NMR spectrum of the photolysate indicated that **1** was formed as the sole product. Cyclomer **6** also underwent the same type of reaction to give **2**, although the reaction proceeded more slowly.

The excitation of **4** in MCH at 285 nm showed dual fluores-

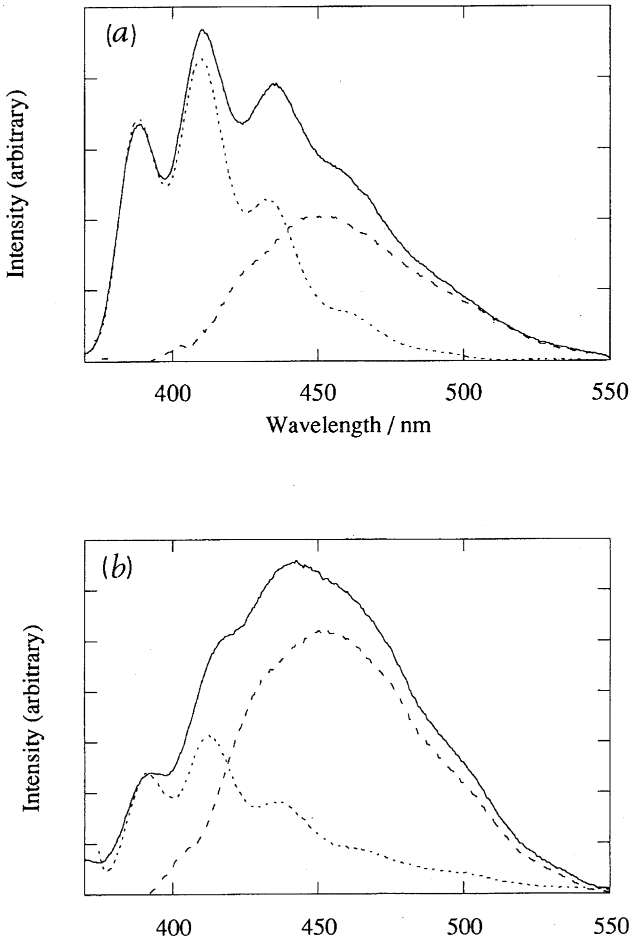
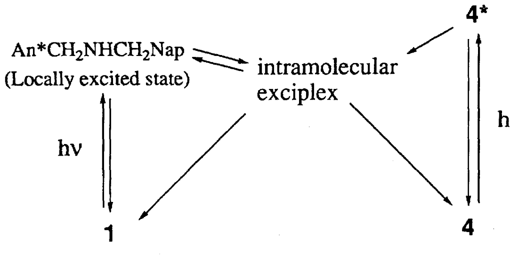


Fig. 3. Fluorescence spectra of **3** and **4** (a) in MCH and (b) in THF at 295 K. —: **4** (excitation at 285 nm), ····: **3** (excitation at 365 nm), - - -: exciplex emission derived from the subtraction of the spectrum of **3** from that of **4** normalized at 390 nm.

cence, as shown in Fig. 3(a). The shorter-wavelength structured emission was assigned to fluorescence from the LE state of the anthracene. By subtracting the fluorescence spectrum of the model compound **3**, a broad emission maximizing at ca. 450 nm was clearly observed, which was assigned to EX emission. As mentioned above, EX emission was also observed upon the excitation of **1** in MCH, though the intensity was much lower (Fig. 1). The excitation spectra detected at 390 and 450 nm were identical, and showed good agreement with the absorption spectrum of **4** (λ_{max} 284 and 274 nm). These results indicate that the cycloreversion took place adiabatically to give the excited state of the product, as was reported for some anthracene–naphthalene cycloadducts.[16) The quantum yields of the LE and the EX emissions were 0.10 and 0.059, respectively. Considering the fluorescence quantum yield of **1** in MCH (0.17), the cycloreversion of **4** proceeded mainly through an adiabatic pathway (Scheme 2). Figure 3(b) shows the fluorescence spectrum of **4** in THF for excitation at 285 nm. Although the total intensity was lower than that in MCH, the ratio of the EX to the LE increased from 0.59 to 1.86 and the EX emission maximum (453 nm) slightly shifted to the red in comparison with that in MCH (450 nm). This solvent dependence suggests that the EX should be stabilized in polar solvent. The difference in the ratio of the EX and the LE emissions between the direct excitation of **1** and the photochemical cycloreversion of **4** indicates that an equilibrium between these two states is not established within the lifetime of the fluorescence. In the cycloreversion of **4**, the radiative decay of the exciplex can compete with a conformational change to give an extended form in which the electronic excitation energy is localized on the anthracene chromophore.

Although the excitation of **6** at 285 nm also showed a structured emission, assigned to the fluorescence of S_1 state of **2**, its intensity was much lower than that of **4**. Albini and Fasani reported that in the cycloreversion of anthracene dimers a nonadiabatic process from the pericyclic minimum in the S_1 surface to the ground state dominated over the adiabatic process.[16) It is likely that the cycloreversion of **6** mainly underwent diabatically to give the ground state of **2**.

In conclusion, the photochemical behavior of **1** and **2** is relatively similar to that of the trimethylene-bridged analog in non-polar solvents, such as MCH. In polar solvents, although the EX state of **1** seems to be stabilized, the effect of intramolecular electron-transfer quenching is more prominent. On the other hand, in acidic aqueous methanol, where the amino nitrogen is protonated, the quantum yield for the cyclomerization of **1** is as high as 0.24.



Scheme 2.

Experimental

Apparatus and Materials. UV-vis spectra were recorded on a Shimadzu UV2200 spectrophotometer. Fluorescence spectra were taken on Shimadzu RF510 fluorophotometer equipped with a quantum counter at 295 K. The excitation and emission bandwidths were 5 and 10 nm, respectively. The fluorescence quantum yields were determined using a solution of quinine sulfate in 0.5 mol dm^{-3} H_2SO_4 as a standard. IR spectra were taken on a Perkin–Elmer Spectrum 2000 FT-IR spectrometer as KBr disk. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL GSX-400 spectrometer with tetramethylsilane or sodium 2,2-dimethyl-2-silapentanesulfonate (DSS) as an internal standard. Mass spectra were obtained by EI (70 eV) or FAB (using *m*-nitrobenzylalcohol as matrix) methods. Mps were obtained on a Yanaco micro-melting point apparatus and are uncorrected. *N*-Methyl-9-aminomethylanthracene (Aldrich) was used as received. The solvents used for spectroscopy and photolysis were of spectroscopic grade.

9-(1-Naphthylmethylaminomethyl)anthracene (1): 9-Anthracenecarboxyaldehyde (360 mg, 1.73 mmol) and 1-aminomethylnaphthalene (270 mg, 1.72 mmol) were stirred in dry toluene (10 cm^3) in the presence of *p*-tolenesulfonic acid monohydrate (14 mg) at 60 °C for 4 h. A hot solution was filtered in order to remove a brown precipitate; the filtrate was then cooled down to room temperature. 9-(1-Naphthylmethyliminomethyl)anthracene was obtained as yellow fine needles (335 mg, 56%). Mp 140—141 °C (from benzene); IR 1635 (C=N), 1620, 1515, 1460, 1445, 880, 800, and 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 5.62$ (2H, s, CH_2), 7.4—7.7 (8H, m), 7.93 (1H, d, $J = 7.5$ Hz), 8.0 (2H, m), 8.32 (1H, d, $J = 8.5$ Hz), 8.43 (2H, m), 8.48 (1H, s), and 9.54 (1H, s, CH=N).

To a solution of the imine (332 mg, 0.96 mmol) in MeOH (12 cm^3) and concd HCl (1.5 cm^3) was added $NaBH_3CN$ (120 mg, 1.9 mmol). The mixture was stirred at room temperature under N_2 for 8 h, and then quenched with 10% H_2SO_4. The amine sulfate was precipitated, which was then filtered, washed with water, and suspended in 10% aq NaOH. The resultant free amine was extracted with ether–benzene. The organic layer was separated, washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The oily residue was triturated with hexane to give **1** as a colorless powder (218 mg, 65%). Pale-yellow plates; mp 85—86 °C (from hexane); IR 3050, 2880, 1620, 1600, 1445, 890, 785, and 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 4.49$ (2H, s, $C\underline{H}_2$Nap), 4.80 (2H, s, $C\underline{H}_2$An), 7.4—7.5 (7H, m), 7.58 (1H, d, $J = 7$ Hz), 7.80 (1H, d, $J = 8$ Hz), 7.88 (1H, m), 8.0 (2H, m), 8.1 (1H, m), 8.2 (2H, m), and 8.39 (1H, s); ^{13}C NMR ($CDCl_3$) $\delta = 45.36$, 52.06, 123.87, 124.18, 124.89, 125.30, 125.64, 125.94, 126.04, 126.51, 127.20, 127.93, 128.66, 129.09, 130.40, 131.55, 131.93, 133.98, and 135.76; MS (EI) *m/z* (rel intensity) 347 (M$^+$; 38), 204 (19), 191 (100), and 179 (78). Found: C, 89.62; H, 6.04; N, 4.05%. Calcd for $C_{26}H_{21}N$: C, 89.88; H, 6.09; N, 4.03%.

Bis(9-anthrylmethyl)amine (2): This compound was prepared from 9-(9-anthrylmethyliminomethyl)anthracene[17) by the same procedures as **1**. Upon recrystallization from benzene, the imine was first precipitated as fine yellow needles. After the filtrate was kept at room temperature in the dark to allow slow evaporation of the solvent, **2** was obtained as large yellow plates. In the ^{1}H NMR spectrum no signal assigned to the imine was detected. Mp 196—197 °C; IR 3050, 2850, 1620, 1445, 880, and 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 4.94$ (4H, s, NCH_2), 7.36 (3H, s, C_6H_6), 7.4—7.5 (8H, m), 8.0 (4H, m), 8.2 (4H, m), and 8.40 (2H, s). ^{13}C NMR (C_6D_6) $\delta = 46.08$, 124.95, 125.05, 125.93, 128.53, 129.28, 131.08, 132.03, and 132.21. Found: C, 90.46; H, 5.94; N, 3.20%. Calcd for $C_{30}H_{23}N\cdot0.5\,(C_6H_6)$: C, 90.79; H, 6.00; N, 3.21%.

***N*-Methyl-9-aminomethylanthracene Hydrochloride (3·HCl):** To an ethereal solution of **3** gaseous hydrogen chloride was introduced. After cooling, the resultant white precipitate was filtered, washed with ether and dried in vacuo. ^{1}H NMR (D_2O) $\delta=2.78$ (3H, s, Me), 4.98 (2H, s, NCH_2), 7.59 (1H, m), 7.67 (1H, m), 8.02 (1H, d, $J=8$ Hz), 8.11 (1H, d, $J=9$ Hz), and 8.45 (1H, s).

Identification of Photoproducts. Photolysis of 1: A solution of **1** (1.6 mg) in C_6D_6 (0.55 cm^3) was irradiated under vacuum with a 400-W high-pressure mercury lamp through an aqueous KNO_3 solution (2 mol dm^{-3}) at 20 °C. The progress of the reaction was monitored by ^{1}H NMR and the irradiation was continued for 4 h, during which **1** was completely consumed. The reaction mixture was concentrated and applied to preparative TLC on neutral alumina (Merck Type E) using benzene as the developing solvent to give dimer **5** as a colorless powder. IR 3060, 2920, 2850, 1480, 1460, 780, and 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=3.65$ (2H, s), 3.77 (4H, s), 4.41 (4H, s), 6.65—6.9 (16H, m), 7.4—7.6 (8H, m), 7.80 (2H, m), 7.88 (2H, m), and 8.18 (2H, m); ^{13}C NMR ($CDCl_3$) $\delta=52.35$, 53.56, 56.26, 61.75, 124.30, 125.18, 125.25, 125.32, 125.61, 125.78, 125.87, 126.54, 127.34, 127.93, 128.54, 131.99, 133.90, 135.46, 142.48, and 143.30; FAB-MS *m*/*z* 695 (M+H$^+$).

A dilute solution of **1** (1.9×10^{-3} mol dm^{-3}) in 0.1 mol dm^{-3} HCl/MeOH–H_2O (9 : 1 v/v) was irradiated under the same conditions for 2.5 h. The mixture was concentrated, neutralized with aq NaOH, and extracted with ether. The organic layer was evaporated up to give 2,3,8,9-tetrahydro-3a, 8[1′,2′]-benzeno-9,13b-etheno-1*H*-2-azadibenzo[*a*,*e*]cyclopenta[*c*]cyclooctene (**4**) as a colorless powder. Mp 169.5—171 °C; UV (MCH) 284 (ε 1500) and 274 (ε 1400) nm; IR 3337 (νNH), 3032, 2924, 2850, 1475, 1453, and 734 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=3.17$ (1H, d, $J=11$ Hz, CH_2), 3.94 (1H, d, CH_2), 3.88—4.02 (2H, ABq, CH_2), 4.00 (1H, ddd, $J_{8,9}=11$ Hz, $J_{9,14}=1$ Hz, $J_{9,15}=7$ Hz, 9-H), 4.38 (1H, d, $J=11$ Hz, 8-H), 5.71 (1H, dd, $J_{14,15}=8$ Hz, $J_{9,14}=1$ Hz, 14-H), 6.09 (1H, dd, $J_{14,15}=8$ Hz, $J_{9,15}=7$ Hz, 15-H), 6.7—6.9 (6H, m), 7.0—7.25 (5H, m), and 7.42 (1H, d); ^{13}C NMR ($CDCl_3$) $\delta=47.96$, 52.87, 54.34, 58.46, 62.34, 65.08, 123.12, 123.32, 123.47, 124.98, 125.24, 125.27, 125.46, 125.77, 126.07, 126.76, 127.24, 127.73, 135.85, 140.78, 144.61, 144.72, 144.79, 144.85, 145.28, and 145.68. The ^{1}H NMR signals were assigned based on ^{1}H–^{1}H COSY experiment. FAB-MS *m*/*z* (rel intensity) 348 (M+H$^+$; 31) and 191 (100). Found: *m*/*z* 348.1728. Calcd for $C_{26}H_{22}N$: (M+H$^+$), 348.1752.

2,3,8,9-Tetrahydro-3a,8[1′,2′],9,13b[1′,2′]-dibenzeno-1*H*-2-azadibenzo[*a*,*e*]cyclopenta[*c*]cyclooctene (6). Amine **2** (1.1 mg) was dissolved in C_6D_6 (0.6 cm^3), degassed and irradiated for 3 h under the same conditions as in the photolysis of **1**. ^{1}H NMR (C_6D_6) $\delta=3.79$ (4H, s), 4.34 (2H, s), and 6.8—6.9 (16H, m); ^{13}C NMR (C_6D_6) $\delta=54.04$, 54.26, 63.26, 124.61, 125.61, 125.77, 128.52, 144.55, and 144.67; FAB-MS *m*/*z* (rel intensity) 398 (M+H$^+$; 34) and 191 (100). Found: *m*/*z* 398.1936 (M+H$^+$). Calcd for $C_{30}H_{24}N$: (M+H$^+$), 398.1909.

Photolysis of 3: A degassed solution of **3**·HCl in D_2O (0.014 mol dm^{-3}; ca. 0.7 cm^3) was irradiated under the same conditions as in the photolysis of **3**. After irradiation for 2 h, all of the starting material was consumed, and only one dimer was detected in the ^{1}H NMR spectrum [$\delta=2.98$ (6H, s), 4.15 (2H, s), 4.57 (4H, s), and 7.0—7.2 (16H, m)]. To the photolysate aq NaOH was added to give a white precipitate, which was filtered, washed with water, and recrystallized from $CHCl_3$–MeOH. The product was identified to be a head-to-tail dimer **7**, based on a comparison of the chemical shift of the bridgehead protons and the thermal stability with the other dimer **8**.

Head-to-Tail Dimer (7): Mp 211—213 °C (decomp); IR 3312 (νNH), 1475, 1452, 1134, 778, 739, and 689 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta=2.59$ (6H, s, Me), 3.70 (2H, s, 10, 10′-H), 3.73 (4H, s, NCH_2), and 6.8—7.1 (16H, m, Ar); ^{13}C NMR ($CDCl_3$) $\delta=36.86$, 56.50, 56.65, 61.87, 125.38, 125.52, 125.57, 127.50, 142.65, and 143.39; FAB-MS *m*/*z* 443 (M+H$^+$).

A degassed C_6D_6 solution (0.7 cm^3) of **3** (0.014 mol dm^{-3}) was irradiated in a Pyrex® NMR tube with a high-pressure mercury lamp (λ >330 nm) at 24 °C, while the progress of the reaction was being monitored by ^{1}H NMR spectroscopy. After irradiation for 2 h, when only 7% of **3** remained and two dimers, **7** and **8**, were formed in 60 and 33% yields, the solvent was removed under reduced pressure to give a white solid. The ^{1}H NMR spectrum of the solid in $CDCl_3$ showed that most of **8** was transformed to monomer **3**.

Head-to-Head Dimer (8): ^{1}H NMR ($CDCl_3$) $\delta=2.45$ (6H, s, Me), 4.15 (2H, s, 10, 10′-H), 4.57 (2H, s, NCH_2), and 7.0—7.2 (16H, m, Ar).

Triplet-Sensitized Photolyses. A degassed solution of **1** or **2** in MCH (1×10^{-3} mol dm^{-3}; 2 cm^3) containing ca. 20 µl of biacetyl was irradiated with a 100-W high-pressure mercury lamp through a Toshiba L-42 glass filter (λ >410 nm) for 20 min. After the solvent and the sensitizer were removed by rotary evaporation, the ^{1}H NMR spectra of the residue were recorded in $CDCl_3$.

Measurements of Cyclomerization Quantum Yield. A

Table 3. Crystal Data and Details of Data Collection and Structure Determination

Compd	**1**	**2**·0.5C_6H_6
Formula	$C_{26}H_{21}N$	$C_{30}H_{23}N\cdot0.5(C_6H_6)$
F.W.	347.46	436.57
Crystal size/mm	$0.4\times0.2\times0.1$	$0.4\times0.3\times0.2$
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	11.945 (11)	11.620 (3)
b/Å	17.302 (9)	12.364 (4)
c/Å	9.731 (10)	9.200 (4)
α/°		101.86 (3)
β/°	111.32 (6)	101.88 (3)
γ/°		109.90 (2)
V/Å^3	1874 (2)	1160.4 (7)
Z	4	2
D_X/g cm^{-3}	1.237	1.249
μ/cm^{-1}	5.42	5.44
F(000)	736	462
Scan width/°	1.4+0.25 tan θ	1.4+0.25 tan θ
Scan speed/° min^{-1}	8 (θ)	8 (θ)
$2\theta_{max}$	120.0	130.0
No. of reflections		
Measured	3843	4142
Unique	2583	3925
Observed	1555	3387
Criteria for obsd	$I_o>3\sigma(I_o)$	$I_o>3\sigma(I_o)$
$(\Delta/\sigma)_{max}$	0.33	0.013
$\Delta\rho_{min}, \Delta\rho_{max}$/eÅ^{-3}	−0.19, 0.12	−0.22, 0.24
No. of parameters	320	412
R	0.084	0.071
wR [a]	0.099	0.082

[a] A weighting scheme of $w=\sigma(F)^{-2}$ was used.

degassed solution (2 cm^3) of **1** or **2** (1.2×10^{-3} mol dm^{-3}) was irradiated by a 100-W high-pressure mercury lamp through Toshiba UV-D1B and UV-35 filters with stirring at ca. 20 °C. After photolysis the solvent was removed under reduced pressure, and the ^{1}H NMR spectrum of the residue was recorded in $CDCl_3$. In the cases of MeOH–HCl solutions the mixture was concentrated, neutralized with aq NaOH, and extracted with $CHCl_3$. The organic layer was separated and evaporated. The yield of the cyclomer was determined based on the integration ratio of the NMR signals to the starting material. The photon flux was measured using $K_3[Fe(ox)_3]$ as an actinometer.

Solid-State Photolysis. A solid sample was irradiated in KBr disks (2% w/w) with a 100-W high-pressure mercury lamp through a Toshiba UV-35 filter ($\lambda > 340$ nm) for 2 h. The IR spectra were recorded before and after irradiation; no difference was observed. After the irradiated disks were ground, the mixture was extracted with $CDCl_3$, and the ^{1}H NMR spectrum was recorded.

Cycloreversion of 4 and 6. A solution of **4** in MCH (ca. 1×10^{-3} mol dm^{-3}, 4 cm^3) was irradiated with 285 nm light in a 1-cm quartz cuvette under a vacuum at 20 °C, and the variation of the UV spectrum was recorded. After photolysis for 7 h the solvent was removed with a rotary evaporator at 30 °C. The ^{1}H NMR spectrum of the residue recorded in $CDCl_3$ indicated that the ratio of **4** : **1** was 72 : 28. Cycloreversion of **6** was carried out under the same conditions. After irradiation for 9 h, **6** was quantitatively transformed to **2**, although the conversion was as low as 10%.

X-Ray Structure Analysis. Data collection was performed on a Rigaku AFC-7R four-circle diffractometer with monochromated Cu $K\alpha$ radiation using the $2\theta-\omega$ scan technique at 25 °C. Three standard reflections were monitored every 150 reflections; there were no significant variations in intensities. The absorption was corrected by a Ψ-scan. The structures were solved by direct methods with SHELXS86.[18] A full-matrix least-squares refinement was carried out on F using the TEXSAN system[19] with anisotropic thermal parameters for non-H atoms. Some of the H-atoms of **1** were located on difference maps and refined isotropically; others were included at the geometrically calculated position but not refined.[20] As for **2**, all of the H-atoms were located on difference maps and refined. The crystal data and details for the data collection and refinements are listed in Table 3.[21]

Calculations. Semiempirical MO calculations were carried out with the program MOPAC Ver. 6.01.[22] A structure optimization was performed using the structure obtained by an X-ray study as the initial model.

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