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Photochemistry of 9-[2-(*N*-Substituted Aminomethyl)-1-naphthyl]phenanthrenes. Intramolecular Addition of Amines to Excited State of Phenanthrene in Conformationally Rigid System

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Irradiation of benzene solutions of 9-[2-(*N*-substituted aminomethyl)-1-naphthyl]phenanthrenes (**3a**—**d**) gave pyrroline derivatives by the attack of the NH group on the C-9 carbon atom of the phenanthrene ring. The reactions were highly selective in regio- and stereochemical senses, and occurred through exciplexes formed by intramolecular interaction between the amino group and the excited phenanthrene moiety in **3a**—**d**. Mechanistic features of these photoreactions are discussed on the basis of chemical and photochemical properties of substrates and products.

The photochemical reactions of aromatic hydrocarbons with amines have been studied extensively in recent years. For example, primary and secondary amines undergo the photoaddition to aromatics such as benzene[1] and anthracene[2] mainly at their nitrogen atoms, and tertiary amines generally at their carbon atoms α to the amino groups. Similar photoaddition was observed for naphthalene[3] and stilbene.[4] Substituted aromatics sometimes undergo the photosubstitution by amines.[5] It has been reported that these reactions occur through exciplexes or solvated radical anion-radical cation pairs produced by an intermolecular interaction between the excited aromatics and the ground state of amines. However, since these reactions usually afford several products at the same time, the mechanistic interpretation of the reactions often becomes equivocal.

Intramolecular interactions between excited aromatic hydrocarbons and ground state of amines have also been studied in bichromophoric molecules containing both an aromatic moiety and a tertiary amino group.[6] These studies have mainly manifested photophysical processes such as intramolecular electron-transfer and exciplex formation, but the photochemical properties of these systems have not been much elucidated.

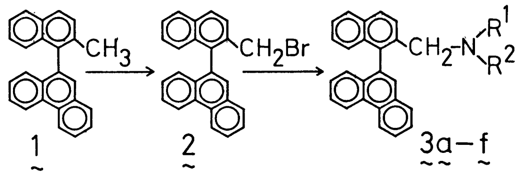
In this study, we synthesized 9-[2-(*N*-substituted aminomethyl)-1-naphthyl]phenanthrenes (**3a**—**f**) from 9-(2-methyl-1-naphthyl)phenanthrene (**1**), and studied their photochemical behavior. In these compounds (Scheme 1), phenanthrene ring (electron acceptor) and amino group (electron donor) are connected by naphthylmethyl group, whereby the spatial relationship between both groups is rendered relatively rigid for a steric reason: a molecular model shows that in these compounds, the two chromophoric groups can be situated in a neighboring position in their favorable conformations. Consequently, these compounds may serve as a good candidate for the elucidation of photochemical properties in a bichromophoric system.

In this paper we demonstrate that the RN group and hydrogen atom of the amino functions in **3a**—**d** add respectively to the C-9 and C-10 atoms of the phenanthrene ring in a *cis* mode to form a pyrroline ring system. This reaction is highly selective in regio- and stereochemical senses and occurs through exciplexes formed by intramolecular interaction between the amino groups and the excited phenanthrene moiety.

Results and Discussion

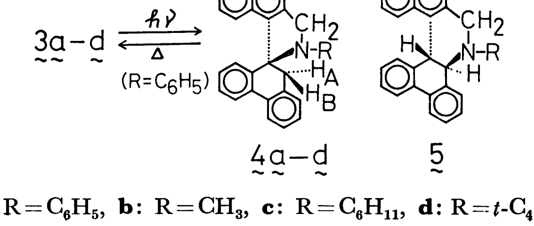
Preparations of the Compounds. The compounds **3a**—**f** were prepared by the route shown in Scheme 1. The structures of these compounds were secured from their elemental analyses and spectral data (see Experimental).

Preparative Photochemistry and Properties of Products. Irradiation of a degassed benzene solution of **3a** in Pyrex tube with a high-pressure mercury arc gave **4a** as a sole isolable product in high yield. Similar irradiation of **3b**—**d** gave the corresponding cyclized compounds, **4b**—**d**, also in high yields (Scheme 2). However, **3e** and **3f** were essentially unreactive under similar conditions, although prolonged irradiation of **3e** afforded a mixture containing at least four compounds. The results are summarized in Table 1. The structures of **4a**—**d** were established from their elemental analyses, spectral data, and chemical properties. The relevant ^{1}H NMR spectral data are listed in Table 2.



a: $R^1=C_6H_5$, $R^2=H$; **b**: $R^1=CH_3$, $R^2=H$; **c**: $R^1=C_6H_{11}$, $R^2=H$; **d**: $R^1=t\text{-}C_4H_9$, $R^2=H$; **e**: $R^1=C_6H_5$, $R^2=CH_3$; **f**: $R^1=R^2=CH_3$

Scheme 1.



a: $R=C_6H_5$, **b**: $R=CH_3$, **c**: $R=C_6H_{11}$, **d**: $R=t\text{-}C_4H_9$

Scheme 2.

Table 1. Photoreaction of **3a**—**d**

Solvent	Compd	Concn / mol l^{-1}	Irradiation time/h	Product	Yield/%
Benzene	**3a**	0.016	1	**4a**	93
	3b	0.016	5	**4b**	30
	3c	0.016	3	**4c**	86
	3d	0.016	3	**4d**	84
Acetonitrile	**3a**	0.006	1	**4a**	82
	3b	0.018	5	**4b**	<2
	3c	0.016	3	**4c**	<2
	3d	0.016	3	**4d**	75
Methanol	**3a**	—	1	—	—
	3b	0.018	5	**4b**	<2
	3c	0.016	3	**4c**	10[a]
	3d	0.016	3	**4d**	45

a) Ethanol was used as solvent.

Table 2. ^{1}H NMR characteristic signals of **3a**—**f** and **4a**—**d**[a]

Compd	Aromatic-H[b]	CH$_2$	H$_A$	H$_B$	J_{AB}/Hz
3a	8.6—8.8	4.10	—	—	—
3b	8.4—8.8	3.50	—	—	—
3c	8.4—8.8	3.50	—	—	—
3d	8.5—8.8	3.50	—	—	—
3e	8.5—8.8	4.10, 4.30 (AB-q, J=17 Hz)	—	—	—
3f	8.4—8.7	3.15	—	—	—
4a	—	5.00	3.45	3.97	19
4b	—	4.20	3.14	3.58	17
4c	—	4.38	3.04	3.68	17
4d	—	4.50	3.37	3.61	18

a) δ Values. Solvent for **3c** and **3f** was CCl$_4$ and that for others was CDCl$_3$. b) Signals in the region of δ 8.4—8.9 ppm were shown.

The ^{1}H NMR spectrum of **3a** (Fig. 1a) remarkably changed after irradiation. A characteristic multiplet around δ 8.6—8.8 (2H, H-4 and H-5 of phenanthrene ring) shifted to higher field region (δ 6—8, usual aromatic region). A broad singlet at δ 3.80 (1H, NH) and a singlet at δ 4.10 (2H, CH$_2$NH) of **3a** disappeared and shifted, respectively. Instead, a singlet at δ 5.00 (2H) and an AB quartet (J_{AB}=19 Hz) centered at δ 3.45 (1H) and 3.97 (1H) appeared (Fig. 1b). The singlet at δ 5.00 was assigned to the methylene protons in the pyrroline ring of **4a**. The higher field signals in the AB quartet were assigned to the H$_A$ proton in the cyclohexadiene ring in **4a** and the lower field ones to the H$_B$ proton in the same ring. A downfield shift of H$_B$ proton compared to the H$_A$ proton may be due to a deshielding effect of lone-pair electrons on the adjacent nitrogen atom. Further support for the structure of **4a** was derived from the following observations.

Irradiation of **3a** in D$_2$O-saturated benzene led to the formation of a monodeuterated compound of **4a** (**4a**-D$_B$): it must be noticed here that the NH hydrogen in **3a** is replaced by deuterium through a rapid H-D exchange to form **3a**-ND before irradiation. The ^{1}H NMR spectrum of **4a**-D$_B$ (Fig. 1c) showed a singlet at δ 3.45 (1H), which indicates that the H$_B$ atom of **4a** is displaced by deuterium atom in the photoreaction of **3a**-ND (see Scheme 3).

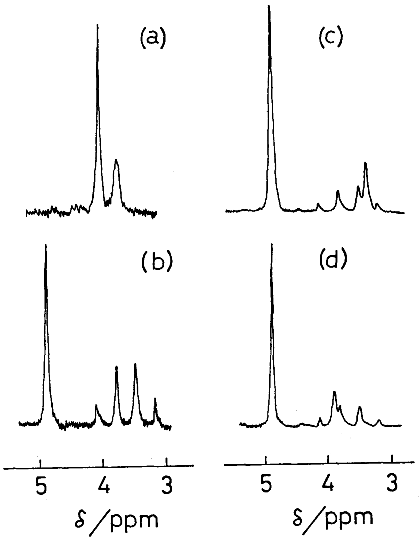
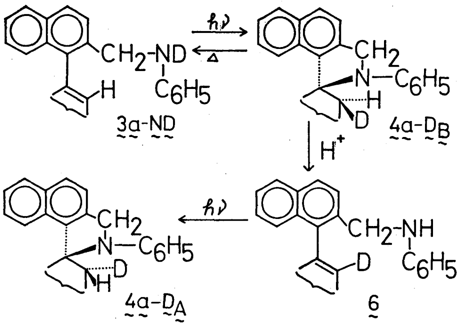


Fig. 1. ^{1}H NMR spectra of **3a** and **4a** in the region of 3—5 ppm.
(a): **3a**, (b): **4a**, (c): **4a**-D$_B$ contaminated by **4a**, (d): **4a**-D$_A$ contaminated by **4a**.



Scheme 3.

Compound **4a** was quantitatively converted back into **3a** by heating at its melting point or by treating with sulfuric acid. Compound **3a** thus obtained gave again **4a** in high yield upon irradiation in benzene. However, the compound obtained by heating **4a**-D$_B$, followed by irradiation in benzene showed the different ^{1}H NMR spectrum from that of the other compound which was obtained by treating **4a**-D$_B$ with sulfuric acid, followed by irradiation in benzene. The ^{1}H NMR spectral examination revealed that the former compound is **4a**-D$_B$ (Fig. 1c) contaminated by a small amount of **4a**. However, the ^{1}H NMR spectrum of the latter compound displayed a singlet at δ 3.93 (1H) (Fig. 1d), indicating that at this time the H$_A$ atom of **4a** is replaced with deuterium atom to give **4a**-D$_A$.

All of the above observations can be explained in terms of the pathway illustrated in Scheme 3. Irradiation of **3a**-ND causes the addition of the ND function to the C-9 and C-10 carbons of the phenanthrene ring in a *cis*-mode to give **4a**-D$_B$. Thermolysis of

4a-D_B gives **3a**-ND by *cis*-elimination of the ND function. On the other hand, treatment of **4a**-D_B with acid affords the deuterium-incorporated compound **6** by *trans*-elimination of the N–H bond. Irradiation of **6** results in the formation of **4a**-D_A.

The ^{1}H NMR spectral data of **4b**—**d** shown in Table 2 strongly support that they also have the structures given in Scheme 2. The possibility of the structure of **5** for these compound can be neglected.

Spectral Studies. Fluorescence of aromatic hydrocarbons is often quenched by amines. It has been demonstrated that such quenching occurs through exciplexes produced by interaction between the excited aromatics and the ground state of amines, and that the exciplexes thus formed have a high polarity due to electron-transfer from the latter to the former.[7]

Compound **1**, which has no amino group in the molecule, emitted strongly fluorescence upon irradiation in benzene. Its spectral pattern was similar to that of phenanthrene. The fluorescence was efficiently quenched by adding triethylamine into the solution. It is therefore supposed that there exists intermolecular electron-transfer interaction between the amine and the excited phenanthrene moiety in **1**.

Figure 2 shows the fluorescence spectra of **3b**, **e**, **f** in benzene; the fluorescence of **3a** was too weak to be detected. The spectral pattern of these compounds was similar to that of phenanthrene and also of **1**. However, the intensities of the fluorescent lights were appreciably weaker than the intensity of fluorescent light of **1**, and decreased with decreasing ionization potentials of the amino moieties of these compounds.[8] In addition, the intensity of fluorescence of **3b** in benzene decreased by adding acetonitrile into the solution (Fig. 3), whereas that of **1** remained substantially unchanged by the addition of acetonitrile. Furthermore, new broad emissions were observed in benzene in 440 nm region for photochemically unreactive compounds, **3e** and **3f**. The maxima of these new emissions shifted to longer wavelength side by the addition of acetonitrile. Therefore, these emissions are attributable to the formation of exciplexes.

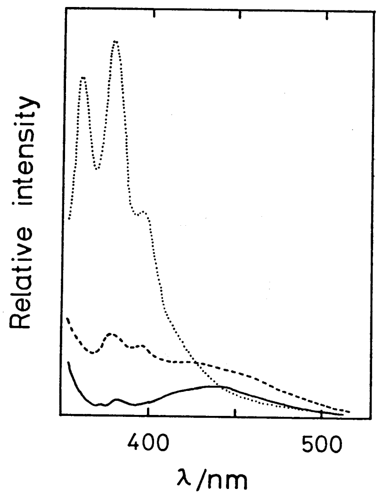


Fig. 2. Fluorescence spectra of **3b**, **3e**, and **3f** in benzene.
·········: **3b**, ——: **3e**, - - - -: **3f**.

These results suggest that intramolecular interaction between the amino groups and the excited phenanthrene ring occurs upon irradiation of **3a**—**d** and also **3e**—**f**, and that the interaction has a character of electron-transfer.

Mechanism and Solvent Effect on the Photochemical Reactivity. We now propose a mechanistic pathway shown in Scheme 4 for the photoreaction of **3a**—**d**.

In an initial stage, intramolecular exciplexes **7** are formed by interaction between the amino groups and the excited phenanthrene moiety. The exciplexes may dissociate to the cation radical-anion radical pairs **8** in polar solvents. The addition of the NH group to the C-9, C-10 bond of phenanthrene ring occurs from **7** or **8** only if the pairs exist in a solvent cage. This reaction takes place almost in a concerted fashion and selectively in a mode of *cis*-addition to form **4a**—**d**. When **7** have no hydrogen on the nitrogen as in the cases of **3e** and **3f**, the addition reaction does not occur. In these cases, the emissions from exciplexes can be observed.

This mechanistic pathway is consistent with the solvent effect on the photochemical reactivity. The results of Table 1 and Fig. 4 indicate that the yields of **4a**—**d** decrease with increasing solvent polarity, and the yield depression of **4b** in polar solvent is particularly remarkable.

If **7** and **8** are in a nonpolar solvent, their amino and phenanthryl groups exist in a neighboring position. In such a case, the addition of the amino groups to

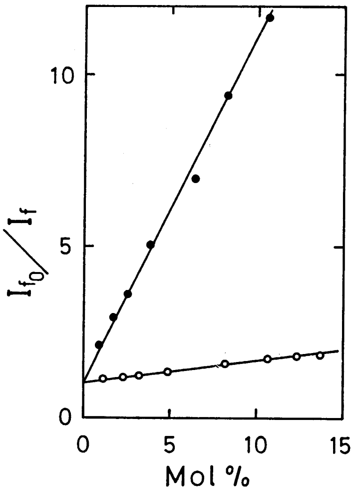
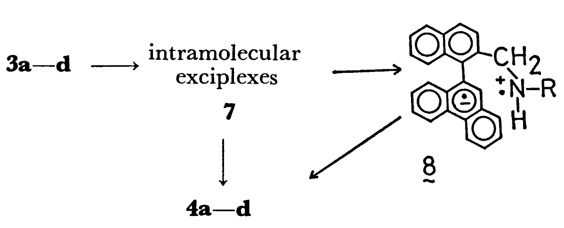


Fig. 3. Effect of addition of polar solvents on the intensity of fluorescent light of **3b** in benzene (ordinate: relative fluorescence intensities; abscissa: mol% of polar solvents in benzene).
—●—: Acetonitrile, —○—: methanol.



Scheme 4.

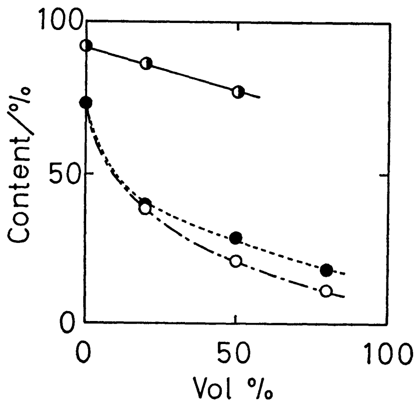


Fig. 4. Contents of the photoproducts **4a** or **4b** in the reaction mixtures obtained by the photoreactions of **3a** or **3b** in mixed solvents (abscissa: vol% of polar solvents in benzene).

—◑—: R=C_6H_5, C_6H_6–CH_3OH, irradiated for 1 h,

—●—: R=CH_3, C_6H_6–CH_3OH, irradiated for 4 h,

—○—: R=CH_3, C_6H_6–CH_3CN, irradiated for 4 h.

the phenanthrene moiety occurs efficiently. On the other hand, they may dissociate in polar solvents to form solvent separated ion pairs which will go back to the component neutral species by back electron-transfer. This assumption accounts for both the stereochemical course of the reaction and the solvent effect on the reactivity. A molecular model shows that in **3a**—**d**, particularly in **3a**, the amino and phenanthryl groups lie in close proximity in their prefered conformation. The preponderance of the conformation will be multiplied by the attachment of a bulky group on the amino nitrogen. As a result, **3a** reacts smoothly to give **4a** in any solvent.

Experimental

All melting points are uncorrected. IR spectra were obtained on a Hitachi 215 infrared spectrophotometer. ^1H NMR spectra were recorded on a Hitachi R-24A spectrometer (60 MHz) with tetramethylsilane as an internal standard. Ultraviolet and visiblelight absorption spectra were obtained on a Hitachi EPS-3T spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-501 fluorophotometer.

Materials. *9-(2-Methyl-1-naphthyl)phenanthrene (**1**)*: Grignard reagent, prepared from 1-bromo-2-methylnaphthalene (6.8 g, 30 mmol), magnesium (0.75 g, 30 mmol), and a small amount of iodine in ether–benzene (1:1, v/v), was added over 30 min to a solution of 9-bromophenanthrene (5.5 g, 20 mmol) and dichlorobis(triphenylphosphine)nickel(II) (0.15 g) in anhydrous ether (50 ml). The mixture was refluxed for 5 h and acidified with dil hydrochloric acid. The organic layer was separated, dried ($MgSO_4$), and evaporated. The gummy residue was triturated with a small amount of hexane to give a white solid. The solid was filtered off and recrystallized from ethanol–benzene (2:1, v/v), giving **1** (4.8 g, 70% based on 9-bromophenanthrene): mp 148—150 °C; NMR (CCl_4) δ=2.12 (3H, s, CH_3) and 6.5—8.8 (15H, m, aromatic). Found: C, 94.32; H, 5.58%. Calcd for $C_{25}H_{18}$: C, 94.30; H, 5.70%.

*9-(2-Bromomethyl-1-naphthyl)phenanthrene (**2**)*: A mixture of **1** (3 g, 9.4 mmol), *N*-bromosuccinimide (1.7 g, 9.5 mmol) and benzoyl peroxide (3 mg) in CCl_4 (50 ml) was refluxed for 8 h. After cooling, the deposited solid was filtered off. Evaporation of the filtrate left a gummy substance which solidified upon treatment with a small amount of petroleum ether. The NMR spectrum showed that this solid contains **2** in 90—97% purity. Chromatography of the crude material on silica gel with hexane gave pure compound: mp 123—125 °C; NMR (CCl_4) δ=4.14 and 4.32 (2H, AB-type q, J=10 Hz, CH_2) and 6.8—8.8 (15H, m, aromatic). Found: C, 75.91; H, 4.14%. Calcd for $C_{25}H_{17}Br$: C, 75.57; H, 4.31%.

*9-(2-Anilinomethyl-1-naphthyl)phenanthrene (**3a**)*: A mixture of **2** (3.4 g, 8.5 mmol) and aniline (3.2 g, 34 mmol) in 1,2-dimethoxyethane (60 ml) was stirred for 24 h at room temperature, and the deposited solid was removed by filtration. The filtrate was concentrated under reduced pressure, and the oily residue crystallized immediately upon adding a small amount of methanol. The solid was recrystallized from benzene–hexane (1:1, v/v) to give **3a** (2.41 g, 64%): mp 169—170 °C; IR (KBr) 3400 (NH) and 1320 cm^{-1} (CN); NMR ($CDCl_3$) δ=3.80 (1H, broad s, NH), 4.10 (2H, s, CH_2), 6.2—8.0 (18H, m, aromatic) and 8.6—8.8 (2H, m, aromatic). Found: C, 90.84; H, 5.56; N, 3.47%. Calcd for $C_{31}H_{23}N$: C, 90.92; H, 5.66; N, 3.42%.

*9-(2-Methylaminomethyl-1-naphthyl)phenanthrene (**3b**)*: A solution of **2** (2.5 g, 6.3 mmol) in 1,2-dimethoxyethane (15 ml) was added to a mixture of methylamine hydrochloride (17 g, 0.25 mol) in methanol (80 ml). Solid potassium hydroxide (14 g, 0.25 mol) was then added in 3 g portions with stirring. After stirring for 12 h, the deposited solid was filtered off, and the filtrate was concentrated *in vacuo*. The residue was poured into water and extracted with ether. The extract was concentrated and chromatographed on silica gel with benzene–ether (1:1, v/v) to give **3b** (0.83 g, 38%): mp 65—67 °C; NMR ($CDCl_3$) δ=1.4 (1H, s, NH), 2.12 (3H, s, CH_3), 3.50 (2H, s, CH_2), 7.0—8.0 (13H, m, aromatic), and 8.4—8.8 (2H, m, aromatic). Found: C, 89.63; H, 6.11; N, 3.87%. Calcd for $C_{26}H_{21}N$: C, 89.88; H, 6.09; N, 4.03%.

*9-(2-Cyclohexylaminomethyl-1-naphthyl)phenanthrene (**3c**)*: A mixture of **2** (2.0 g, 5 mmol) and cyclohexylamine (5 ml) in 1,2-dimethoxyethane (20 ml) was stirred for 12 h at room temperature, and the deposited solid was removed by filtration. The filtrate was poured into 100 ml of water, and extracted with benzene. Evaporation of the solvent gave a white solid which was purified by chromatography on silica gel with benzene–ether (1:1, v/v), yielding **3c** (1.43 g, 73%): mp 160.5—161.5 °C; NMR (CCl_4) δ=0.3—2.4 (12H, m, cyclohexyl and NH), 3.50 (2H, s, CH_2), 6.7—8.3 (13H, m, aromatic), and 8.4—8.8 (2H, m, aromatic). Found: C, 89.44; H, 7.25; N, 3.44%. Calcd for $C_{31}H_{29}N$: C, 89.59; H, 7.03; N, 3.37%.

*9-(2-*t*-Butylaminomethyl-1-naphthyl)phenanthrene (**3d**)*: This compound was prepared by the method similar to that for **3c**. The product was purified by chromatography on silica gel with benzene. The yield of **3d** was 85%: mp 64—70 °C; NMR ($CDCl_3$) δ=0.65 (9H, s, CH_3), 1.0—1.2 (1H, broad s, NH), 3.50 (2H, s, CH_2), 7.0—8.0 (13H, m, aromatic) and 8.5—8.8 (2H, m, aromatic). Found: C, 89.39; H, 6.98; N, 3.55%. Calcd for $C_{29}H_{27}N$: C, 89.42; H, 6.99; N, 3.60%.

*9-[2-(*N*-Methylanilinomethyl)-1-naphthyl]phenanthrene (**3e**)*: This compound was prepared from **2** and *N*-methylaniline in 1,2-dimethoxyethane by the method applied for the preparation of **3a**: mp 167.5—168.5 °C; NMR ($CDCl_3$) δ=2.80 (3H, s, CH_3), 4.10 and 4.30 (2H, AB-type q, J=17 Hz, CH_2) and 6.4—8.8 (20H, m, aromatic). Found: C, 90.53; H, 5.90; N, 3.38%. Calcd for $C_{32}H_{25}N$: C, 90.74;

H, 5.95; N, 3.30%.

*9-(2-Dimethylaminomethyl-1-naphthyl)phenanthrene (**3f**)*: This compound was prepared from dimethylamine hydrochloride and **2** by the method applied for the preparation of **3b**: mp 115—117 °C; NMR (CCl_4) $\delta=1.97$ (6H, s, CH_3), 3.15 (2H, broad s, CH_2), 6.8—7.9 (13H, m, aromatic), and 8.4—8.7 (2H, m, aromatic). Found: C, 89.97; H, 6.36; N, 3.89%. Calcd for $C_{27}H_{23}N$: C, 89.71; H, 6.41; N, 3.88%.

Photoreactions. A general procedure is shown in an example of the photoreaction of **3a**: a solution of **3a** (100 mg, 0.25 mmol) in benzene (10 ml) in a Pyrex tube was degassed by three freeze-pump-thaw cycles under argon and the tube was sealded under reduced pressure. Irradiation was carried out by using a merry-go-round apparatus (Eikosha PIH-300) with a 300 W high-pressure mercury lamp cooled with water. After irradiation, benzene was evaporated under reduced pressure. The residue was dissolved in $CDCl_3$ and its ^1H NMR spectrum was recorded. The yield of the photoproduct **4a** was estimated from the intensities of methylene signals.

Benzene-d_6 solutions of **3a**—**d** (8×10^{-2} M) sealded in NMR measureing tubes were irradiated in a manner similar to that employed for preparative photoreactions. The rates of the photoreactions were measured by following the changes in intensities of signals in the NMR spectra at appropriate time intervals. Yields were estimated on the basis of the relative intensities of methylene signals of each cyclic compound to that of tetramethylsilane used as an internal standard.

Photoproducts. The photoproducts were purified by chromatography on silica gel (**4a** and **4b**) or recrystallization from methanol (**4c** and **4d**). **4a**: mp 105—120 °C (dec); NMR ($CDCl_3$) $\delta=3.97$ and 3.45 (2H, AB-type q, $J=19$ Hz, CH_2), 5.00 (2H, s, CH_2), and 6.2—8.1 (19H, m, aromatic). Found: C, 90.84; H, 5.65; N, 3.53%. Calcd for $C_{31}H_{23}N$: C, 90.92; H, 5.66; N, 3.42%. **4b**: mp 65—75 °C (dec); NMR ($CDCl_3$) $\delta=2.05$ (3H, s, CH_3), 3.58 and 3.14 (2H, AB-type q, $J=17$ Hz, CH_2), 4.20 (2H, s, CH_2) and 6.8—8.0 (14H, m, aromatic). Found: C, 90.03; H, 6.40; N, 4.00%. Calcd for $C_{26}H_{21}N$: C, 89.88; H, 6.09; N, 4.03%. **4c**: mp 125—130 °C (dec); NMR ($CDCl_3$) $\delta=0.5$—1.7 (m, cyclohexyl), 3.04 and 3.68 (AB-type q, $J=17$ Hz, CH_2), 4.38 (s, CH_2) and 6.8—8.0 (m, aromatic). Found: C, 88.97; H, 7.52; N, 3.49%. Calcd for $C_{31}H_{29}N$: C, 89.59; H, 7.03; N, 3.37%. **4d**: mp 100—110 °C (dec); NMR ($CDCl_3$) $\delta=0.92$ (s, CH_3), 3.37 and 3.61 (AB-type q, $J=18$ Hz, CH_2), 4.50 (s, CH_2), and 6.9—8.0 (m, aromatic). Found: C, 90.06; H, 7.33; N, 3.58%. Calcd for $C_{29}H_{27}N$: C, 89.42; H, 6.99; N, 3.60%.

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8) This conclusion was derived from the assumption that the ionization potentials of the amino moieties in these compounds can be estimated from those of the corresponding *N*-substituted methylamines: for example, 8.36 eV for $(CH_3)_2NH$, 8.12 eV for $(CH_3)_3N$, and 7.36 eV for $(CH_3)_2NC_6H_5$ were used as the ionization potentials of the amino moieties in **3b**, **3f**, and **3e**, respectively.