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Photoinduced Intramolecular Cyclization of 9-(ω-Anilinoalkyl)phenanthrenes

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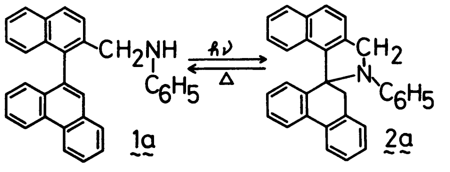
Photoreactions of a series of compounds of the type 9-phenanthryl–A–$CH_2NHC_6H_5$ [–A–=*o*-phenylene (**1b**), $-(CH_2)_2-$ (**1c**), $-(CH_2)_3-$ (**1d**), $-(CH_2)_4-$ (**1e**), $-CH_2-$ (**1f**)] in benzene were studied. From **1b**—**d**, the spiro compounds are obtained by an intramolecular *cis*-addition of the N–H function to the C_9, C_{10}-double bond of the phenanthrene ring. These photoproducts can be converted to the starting materials by treating with trifluoroacetic acid or heating above their melting temperatures. The mechanistic features of these reactions are described.

Photoreactions between excited aromatic hydrocarbons and amines in their ground states have been extensively studied in recent years.[1] For example, primary and secondary amines undergo the photoaddition to aromatic hydrocarbons such as benzene,[2] naphthalene,[3] and anthracene[4] *via* an exciplex or an electron-transfer from the amines to the excited aromatics.[5]

In a previous paper, we reported that irradiation of 9-(2-anilinomethyl-1-naphthyl)phenanthrene (**1a**) in benzene affords pyrroline derivative **2a** in high yield by an intramolecular addition of the anilino function to the phenanthrene ring (Scheme 1).[6] The high efficiency of this photoreaction was attributed to a structural feature that the anilino function lies close to the phenanthrene ring in **1a** by a steric reason. We now report the photoinduced intramolecular cyclization of 9-(ω-anilinoalkyl)phenanthrenes **1b**—**f** which have a much greater flexibility in conformation compared with **1a**.

Results and Discussion

The phenanthrene derivatives, **1b**—**f**, were prepared by the routes shown in Scheme 2 and characterized from their ¹H NMR and IR spectral data and elemental analyses.

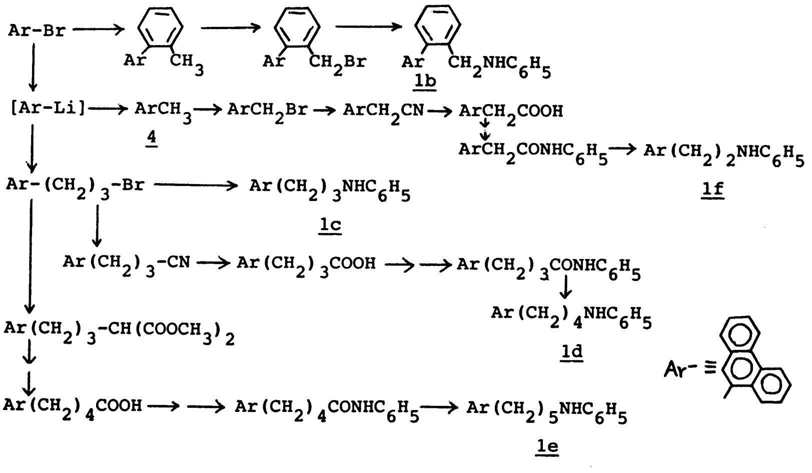


Scheme 1.

Photoproducts. Irradiation of a degassed benzene solution of **1b** (1.6×10^{-2} mol/dm³) through a Pyrex filter with a 300 W Hg lamp for 90 min gave spiro compound **2b** in 73% yield. The irradiation for 3 h gave **2b** in quantitative yield. Similar irradiation of **1c** and **1d** afforded the corresponding spiro compounds **2c** and **2d**, respectively. The yields are shown in Table 1, together with the UV and fluorescence spectral data of the starting materials.

The spiro compounds produced by the photoreaction could be converted to the starting materials in quantitative yields by treating with trifluoroacetic acid or by heating above their melting temperatures. Structures of the photoproducts were established from their spectral data and chemical behaviors. The pertinent ¹H NMR and IR spectral data are listed in Table 2, together with those of the starting materials.

The IR spectrum of **2b** showed no NH stretching band. The ¹H NMR spectrum of **1b** changed markedly upon UV irradiation. A characteristic multiplet around δ 8.5 (2H, the H-4 and H-5 protons on the phenanthrene ring) shifted to up-field and became overlapped with signals due to other aromatic protons. A broad singlet at δ 3.54 (1H, NH) disappeared. A singlet at δ 3.91 (2H, $-CH_2-N=$) shifted to δ 4.81. A new AB quartet (J=16 Hz) centered at δ 2.60 (1H) and δ 4.30 (1H) appeared, and these signals were assigned to the H_A



Scheme 2.

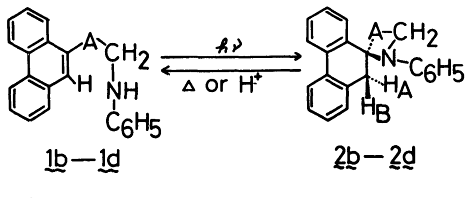
Table 1. PHOTOREACTION AND SPECTRAL DATA OF PHENANTHRENE DERIVATIVES[a)]

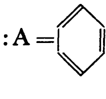
Compd	UV absorption maximum λ/nm (log ε)	Relative intensity of fluorescence at 366 nm[b)]	Product	Yield (Recovery)[c)]/% In C_6H_6		In CH_3CN	
1b	299 (4.11)	1	**2b**	73[d)]	(27)[d)]	69[d)]	(31)[d)]
1c	298 (4.11)	11	**2c**	76	(12)	68	(16)
1d	298 (4.11)	20	**2d**	31	(61)	40	(52)
1e	298 (4.11)	61	—		(83)		(82)
1f	298 (4.00)	69	**3**	56	(26)	38	(41)
4	297 (4.06)	780	—		(100)	—	

a) All the photoreactions were carried out by irradiating 1.6×10^{-2} mol/dm^3 solutions with a 300 W Hg lamp for 90 min under the same conditions. b) Excited by a 300 nm light in hexane. c) Isolated yields. d) Estimated from the intensity of ^{1}H NMR signals.

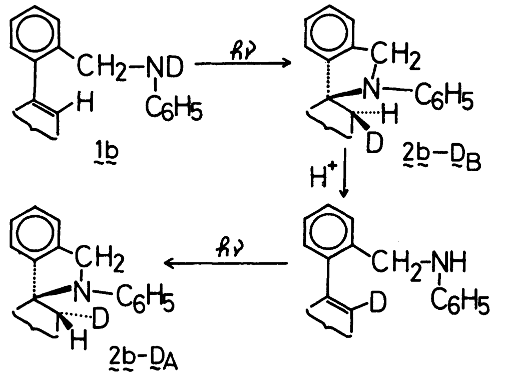
Table 2. ^{1}H NMR AND IR DATA OF STARTING MATERIALS AND PHOTOPRODUCTS

Compd	δ -A-CH_2-N=	H_A	H_B	J_{AB}/Hz	ν_{NH}/cm^{-1}
1b	3.91	—	—	—	3430
1c	2.8—3.2	—	—	—	3420
1d	2.8—3.7	—	—	—	3380
1e	2.8—3.2	—	—	—	3400
1f	3.1—3.8	—	—	—	3400
2b	4.81	2.60	4.30	16	—
2c	3.5—3.75	2.30	4.03	16	—
2d	3.5—4.0	2.94	3.84	16	—
1a[6)]	4.10	—	—	—	3400
2a[6)]	5.00	3.45	3.97	19	—

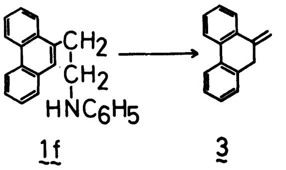


b:A= , **c**:A = -CH_2CH_2-, **d**:A = -$CH_2CH_2CH_2$-

Scheme 3.



Scheme 4.



Scheme 5.

and H_B protons on the pyrroline ring of **2b** (Scheme 3), respectively. A down-field shift of the H_B proton compared with the H_A proton may be due to a deshielding effect of lone-pair electrons on the nitrogen atom of the pyrroline ring. A similar spectral pattern was also observed in **2a**.[6)] A further support for the structure of **2b** was obtained from the following observations.

Irradiation of **1b** in a D_2O-saturated benzene gave a monodeuterated compound of **2b** (**2b**-D_B) which showed a singlet at δ 2.60 (1H) but no signal at δ 4.30 in its ^{1}H NMR spectrum. Other ^{1}H NMR pattern of this compound was identical to that of **2b**. Treatment of **2b**-D_B with trifluoroacetic acid, followed by irradiation in benzene, afforded as a major product the other monodeuterated compound of **2b** (**2b**-D_A), whose ^{1}H NMR spectrum showed a singlet at δ 4.30 but no signal at δ 2.60, along with a small amount of **1b**. These results can be explained in terms of the reaction pathway shown in Scheme 4 and support the assigned structure for **2b**. A remarkable feature of the photocyclization of **1b** to the spiro compound **2b** is that the N–H function adds stereospecifically to the C_9, C_{10} double bond of the phenanthrene ring in a *cis*-mode. The acid-catalyzed conversion of **2b** to **1b** occurs preferentially *via* the *trans*-elimination of the N–H function.

Compounds **1c** and **1d** behaved similarly when the compounds were irradiated in a D_2O-saturated benzene, supporting the assigned structures for **2c** and **2d**. In the case of **1e**, no photoreaction occurred. However, irradiation of **1f** in benzene gave 9-methylene-9,10-dihydrophenanthrene (**3**) (Scheme 5) which was characterized by ^{1}H NMR and IR spectra (see Experimental) and chemical evidence.[7)]

Mechanistic Features. UV spectra of **1b**—**f** in hexane were similar to each other in shape and resemble that of 9-methylphenanthrene (**4**) (Table 1). All these compounds also displayed fluorescence spectra similar to the fluorescence spectrum of **4** in the region of 340—450 nm in hexane (Fig. 1). Their intensities of the emission at 370 nm decreased in the order; **4**>**1f**>**1e**>**1d**>**1c**>**1b** (Table 1). The fluorescence of **4** was quenched by *N*-methylaniline. The low intensities of

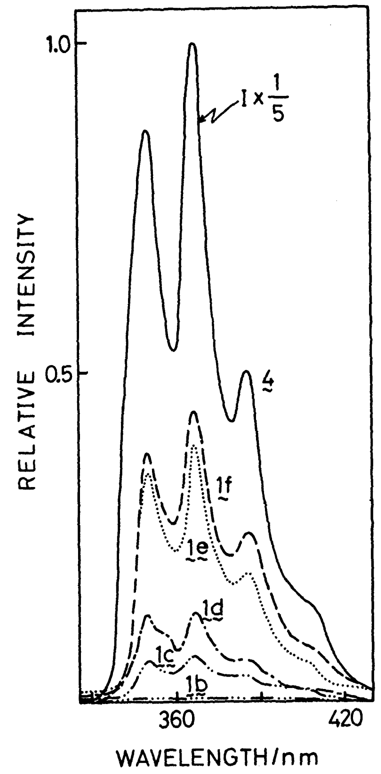
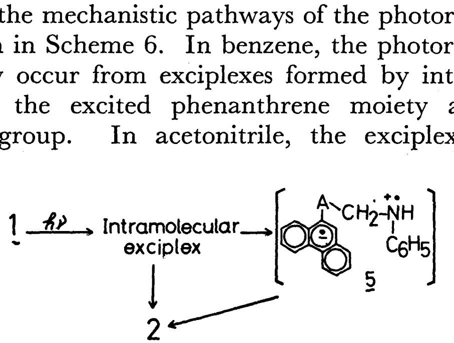


Fig. 1. Fluorescence spectra of the phenanthrene derivatives in hexane: concentration 1.00×10^{-4} mol/dm^3, excited at 300 nm.

1b—**f** compared with **4** suggest that an intramolecular quenching of fluorescence by the anilino group occurs in these compounds. The quenching of fluorescence of an aromatic hydrocarbon by a primary or secondary amine has been attributed to the formation of an exciplex between the excited aromatic hydrocarbon and the amine.[5] Accordingly, the above results strongly suggest that intramolecular exciplexes are formed between the excited phenanthrene moiety and the anilino group in **1b**—**d**, and that the Hirayama rule[8] in intramolecular exciplex formation can also be applicable to these systems.

In the photoreactions of **1b**—**e**, the less emissive compounds afford the photoproducts in the higher yields as shown in Table 1. No appreciable solvent effect on the yields of the photoproducts was observed in these photoreactions (Table 1).

On the basis of all the results presented above, we propose the mechanistic pathways of the photoreactions as shown in Scheme 6. In benzene, the photoreactions probably occur from exciplexes formed by interaction between the excited phenanthrene moiety and the anilino group. In acetonitrile, the exciplexes may dissociate to ion-radical pairs **5**. However, no appreciable solvent effect on these photoreactions suggests that the photoreactions occur in a solvent cage even if the ion-radical pairs are formed. This assumption was supported by the fact that no quenching was observed when the photoreactions were carried out in triethylamine: irradiations of **1b** and **1c** in triethylamine for 90 min gave **2b** in 80% yield and **2c** in 82% yield (compare these yields with those cited in Table 1). The mechanism of the formation of **3** from **1f** remains equivocal.



Scheme 6.

Experimental

All melting points are uncorrected. IR spectra were obtained on a Hitachi 215 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Hitachi R-24A spectrometer (60 MHz) with tetramethylsilane as an internal standard. UV and visible absorption spectra were obtained on a Hitachi EPS-3T spectrometer. Fluorescence spectra were obtained for degassed samples with a Nippon Bunko FP-500S Fluorophotometer by exciting with 300 nm light.

Materials. *9-(o-Anilinomethylphenyl)phenanthrene (1b)*: A Grignard reagent, prepared from *o*-bromotoluene (17.5 g, 0.102 mol) and magnesium (2.5 g, 0.103 mol) in ether (40 cm^3) was added to a solution of 9-bromophenanthrene (15.5 g, 0.06 mol) and dichlorobis(triphenylphosphine)nickel(II) (0.20 g) in benzene–ether (1 : 1, v/v) (100 cm^3) over 1.5 h under gentle refluxing.[9] The mixture was refluxed further for 30 min and acidified with dil hydrochloric acid. The organic layer was separated, dried (Na_2SO_4), and evaporated. The residue solidified upon trituration with petroleum ether to give 11.7 g (69% based on 9-bromophenanthrene) of 9-(*o*-tolyl)phenanthrene. Recrystallization from hexane gave an analytical sample; mp 132—133 °C: ^{1}H NMR (CCl_4) δ 7.0—8.7 (13H, m, aromatic), 2.00 (3H, s, CH_3). Found: C, 93.98; H, 5.83%. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01%.

A mixture of 9-(*o*-tolyl)phenanthrene (2.7 g, 7.8 mmol), *N*-bromosuccinimide (1.9 g, 10.7 mmol) and a small amount of benzoyl peroxide in CCl_4 (50 cm^3) was refluxed for 16 h. After cooling, the mixture was filtered and the filtrate was concentrated to give 9-(*o*-bromomethylphenyl)phenanthrene as a viscous oil which was purified by chromatography on silica gel with hexane.

A mixture of 9-(*o*-bromomethylphenyl)phenanthrene (2.9 g, 8 mmol) and aniline (3 g, 32 mmol) in 1,2-dimethoxyethane (10 cm^3) was stirred for 20 h at room temperature and filtered. The filtrate was concentrated under reduced pressure. The viscous oily residue was washed with dil hydrochloric acid to give a solid which was suspended in benzene and washed with dil aqueous sodium hydroxide. The benzene layer was dried and evaporated. The residue was recrystallized from hexane to give **1b** as a colorless needles in 57% yield; mp 141—141.5 °C: ^{1}H NMR (CCl_4) δ 6.0—8.7 (18H, m, aromatic), 3.91 (2H, s, CH_2), 3.55 (1H, s, NH); IR (KBr) 3430 cm^{-1} (NH). Found: C, 90.50; H, 5.61; N, 3.86%. Calcd for $C_{27}H_{21}N$: C, 90.21; H, 5.89; N, 3.90%.

9-(3-Anilinopropyl)phenanthrene (1c). To a stirred solution of 7.8 g (30 mmol) of 9-bromophenanthrene in 40 cm^3 of anhydrous ether was added butyllithium (60 mmol) in hexane and then 13 g (64 mmol) of 1,3-dibromopropane. After refluxing for 4 h, the mixture was poured into water and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. The oily residue was chromatographed on silica gel with hexane to give 1.96 g (22%) of 1-bromo-3-(9-phenanthryl)propane as colorless solid; mp 55—57 °C: ^{1}H NMR

($CDCl_3$) δ 7.3—8.7 (9H, m, aromatic), 3.0—3.5 (4H, m, $-CH_2-C-CH_2$), and 2.1—2.5 (2H, m, $C-CH_2-C$).

A mixture of 1-bromo-3-(9-phenanthryl)propane (670 mg, 2.2 mmol), aniline (5 cm^3, 54 mmol), and Na_2CO_3 (5 g) in DMF (30 cm^3) was stirred for 42 h at room temperature. The deposited solid was filtered off and washed with a small amount of benzene. The filtrate and the benzene washing were combined and evaporated. The residue was washed with 100 cm^3 of hydrochloric acid to give a solid which was dissolved in benzene and washed with an aqueous Na_2CO_3 solution. The benzene layer was dried (Na_2SO_4) and evaporated. TLC of the residue gave 450 mg (65%) of **1c**; mp 77—79 °C: ^{1}H NMR ($CDCl_3$) δ 6.3—8.7 (14H, m, aromatic), 3.4 (1H, br s, NH), 2.8—3.2 (4H, m, CH_2-C-CH_2), and 1.6—2.2 (2H, m, $C-CH_2-C$). IR (KBr) 3420 cm^{-1} (NH). Found: C, 88.98; H, 6.69; N, 4.57%. Calcd for $C_{23}H_{21}N$: C, 88.71; H, 6.80; N, 4.50%.

9-(4-Anilinobutyl)phenanthrene (1d). A mixture of 1-bromo-3-(9-phenanthryl)propane (1.49 g, 5 mmol) and KCN (0.4 g, 6.1 mmol) in ethanol (40 cm^3) was refluxed for 42 h. The solvent was evaporated under reduced pressure and the residue was washed with water and extracted with ether. The extract was dried (Na_2SO_4) and evaporated to give 1.17 g (96%) of 4-(9-phenanthryl)butanenitrile as colorless needles which was recrystallized from hexane–benzene (9 : 1); mp 90—91 °C: IR (KBr) 2250 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 7.4—8.8 (9H, m, aromatic), 3.22 (2H, t, J=7 Hz, $Ar-CH_2-$), 1.9—2.5 (4H, m, $-CH_2CH_2CN$). Found: C, 87.99; H, 5.78; N, 5.48%. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71%.

The hydrolysis of 4-(9-phenanthryl)butanenitrile with KOH in ethanol by refluxing for 20 h gave 4-(9-phenanthryl)-butanoic acid in 90% yield; mp 169—170 °C (lit,[10] 172.8—174 °C); IR (KBr) 1710 cm^{-1} (CO).

4-(9-Phenanthryl)butanoic acid (1.1 g, 4.1 mmol) was added in small portions to thionyl chloride (13 cm^3) and the mixture was refluxed for 10 min. Excess thionyl chloride was removed by evaporation under reduced pressure. The residue was dissolved in ether (140 cm^3) and added to a solution of aniline (3 cm^3, 32 mmol) in ether (15 cm^3). The mixture was stirred for 4.5 h at room temperature, washed with 3 M hydrochloric acid, and the ether layer was separated. The aqueous layer was extracted with dichloromethane. Both the organic solutions were combined and evaporated to give 1.35 g (98%) of *N*-phenyl-4-(9-phenanthryl)butanamide; mp 152.5—155.5 °C: IR (KBr) 3300 (NH) and 1660 cm^{-1} (CO).

To a stirred solution of *N*-phenyl-4-(9-phenanthryl)butanamide (1.27 g, 3.7 mmol) in THF–ether (40 cm^3) was added $LiAlH_4$ (1.0 g) in small portions over 10 min. After refluxing for 3.5 h, the mixture was washed with a saturated aqueous solution of ammonium chloride and extracted with ether. Evaporation of the solvent from the ether extract under reduced pressure gave the amine **1d** (1.1 g, 90%) which was chromatographed on silica gel with benzene and then recrystallized from hexane; mp 101—102 °C: IR (KBr) 3380 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 9.0—6.5 (14H, m, aromatic), 2.8—3.7 (5H, m, NH and CH_2), and 1.5—2.2 (4H, m, CH_2). Found: C, 88.53; H, 7.08; N, 4.25%. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30%.

9-(5-Anilinopentyl)phenanthrene (1e). A solution of 1-bromo-3-(9-phenanthryl)propane (0.86 g, 2.85 mmol) in benzene (10 cm^3) was added at 50 °C to a stirred mixture of sodium methoxide (prepared from 0.1 g of sodium) and dimethyl malonate (0.7 cm^3, 6.1 mmol) in methanol (10 cm^3). The mixture was refluxed for 3 d and diluted with a large amount of water, and then extracted with ether. The extract was dried (Na_2SO_4) and the solvent was evaporated completely. The residue was added to a solution of KOH (3 g) in methanol (20 cm^3) and water (3 cm^3), and the mixture was refluxed for 40 h. After removal of the solvent, the residue was shaken with a mixture of water and ether. The aqueous layer was separated, acidified with hydrochloric acid and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. The colorless solid obtained (0.69 g) was heated up to its melting temperature under argon atmosphere to give 5-(9-phenanthryl)pentanoic acid (0.45 g); mp 145—150 °C: IR (KBr) 1710 cm^{-1} (CO).

5-(9-Phenanthryl)pentanoic acid was converted to the amine **1e** in 60% yield by the method similar to that used for the preparation of **1d**. Colorless solid; mp 101.5—103 °C: IR (KBr) 3400 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 6.3—8.7 (14H, m, aromatic), 3.4 (1H, br s, NH), 2.8—3.2 (4H, m, CH_2), and 1.3—2.1 (6H, m, CH_2). Found: C, 88.38; H, 7.53; N, 4.11%. Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.13%.

9-(2-Anilinoethyl)phenanthrene (1f). 9-Phenanthreneacetic acid[11] (2.4 g, 10.2 mmol) was converted to the corresponding anilide by a standard method *via* the acid chloride, mp 225—226 °C; IR (KBr) 3300 (NH), 1670 cm^{-1} (CO). Found: C, 84.85; H, 5.33; N, 4.63%. Calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50%. To a solution of this anilide (1.56 g) in THF–ether (2 : 1, v/v, 140 cm^3) was added $LiAlH_4$ (1.0 g) in small portions at room temperature. The mixture was refluxed for 5 h and washed with an aqueous ammonium chloride solution, and then extracted with ether. The extract was dried (Na_2SO_4) and evaporated. The residue was recrystallized from hexane to give **1f** as colorless needles (840 mg, 56%); mp 108—108.5 °C: IR (KBr) 3400 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 6.3—8.7 (14H, m, aromatic), 3.1—3.8 (5H, m, CH_2 and NH). Found: C, 89.01; H, 6.50; N, 4.34%. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71%.

Photoreactions. A general procedure is shown with the photoreaction of **1b**. A solution of **1b** in benzene (1.6×10^{-2} mol/dm^3) in a Pyrex tube was degassed by three freeze-pump-thaw cycles under argon, and the tube was sealded under reduced pressure. The solution was irradiated externally with a 300 W high-pressure mercury lamp using a merry-go-round apparatus (Eikosha PIH-300): The distance between the light source and the sample solutions was 5 cm. After irradiation for 90 min, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Elution with benzene–hexane (1 : 1) gave **2b**, mp 96—135 °C: ^{1}H NMR ($CDCl_3$) δ 6.3—8.0 (17H, m, aromatic), 4.81 (2H, s, CH_2), and AB quartet signals centered at 4.30 and 2.60 (2H, J=16 Hz, CH_2). Found: C, 90.25; H, 5.74; N, 3.62%. Calcd for $C_{27}H_{21}N$: C, 90.22; H, 5.89; N, 3.90%. **2c**: mp 100—102 °C; ^{1}H NMR ($CDCl_3$) δ 6.3—7.8 (13H, m, aromatic), AB quartet signals centered at 4.03 and 2.30 (2H, J=16 Hz, CH_2), 3.5—3.75 (2H, m, $=N-CH_2$), and 1.7—2.2 (4H, m, $-CH_2CH_2-$). Found: C, 88.56; H, 6.57; N, 4.67%. Calcd for $C_{23}H_{21}N$: C, 88.70; H, 6.80; N, 4.50%. **2d**: mp 117—120 °C; ^{1}H NMR ($CDCl_3$) δ 6.5—8.0 (13H, m, aromatic), AB quartet signals centered at 3.84 and 2.94 (2H, J=16 Hz, CH_2), 3.5—4.0 (2H, m, $N-CH_2-C$), 2.2—1.3 (6H, m, $CH_2CH_2CH_2$). Found: C, 88.64; H, 7.05; N, 4.46%. Calcd for $C_{24}H_{23}N$: C, 88.57; H, 7.12; N, 4.30%. **3**[7]: IR (liquid film) 3060, 3030, 2945, 1635, 1605, 1490, 1455, 895, 770, and 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.0—7.8 (8H, m, aromatic), 5.26 (1H, d, J=1.5 Hz, $=CH_2$), 5.06 (1H, d, J=1.5 Hz, $=CH_2$), and 3.65 (2H, s, CH_2). Found: C, 93.71; H, 6.02%. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29%.

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