Stereochemical Studies on the Amination of Arenes with Ammonia and Alkylamines *via* Photochemical Electron Transfer

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Photoamination of 9-methoxyphenanthrene (**1**) with ammonia in the presence of *m*-dicyanobenzene (DCNB) gives *cis*- and *trans*-9-amino-10-methoxy-9,10-dihydrophenanthrene (**6a**, **b**) in a ratio of 75:25. The stereochemistry of **6a** has been confirmed by X-ray crystallographic analysis of its acetamide. The photoamination of **1** with isopropylamine and 9-ethoxyphenanthrene (**2**) with *tert*-butylamine gives exclusively *N*-substituted *cis*-9-amino-10-alkoxy-9,10-dihydrophenanthrene. Also, the photoamination of phenanthrene (**4**) and anthracene (**5**) proceeds with *trans* addition of ammonia with high selectivities. The photoamination proceeds by nucleophilic addition of amine to the cation radical of the arene, generated from photochemical electron transfer to DCNB. The resulting aminated cation radicals undergo reduction by an anion radical of DCNB, followed by protonation to give final products. Selective *trans* additions of ammonia and alkylamines to arenes are suggested to arise from the protonation of the aminated anion.

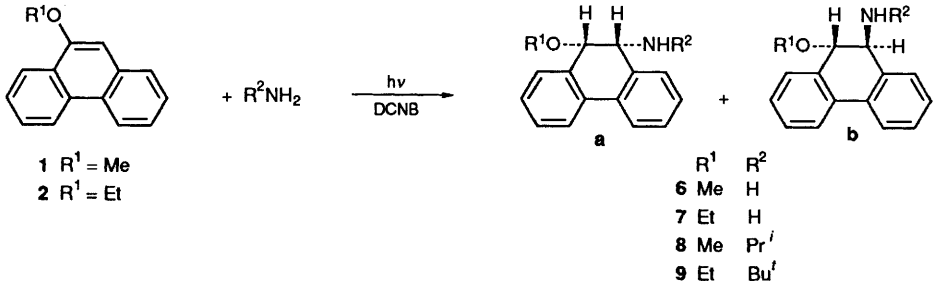
Photoaddition of nucleophiles to a variety of substrates *via* photochemical electron transfer has been widely investigated from synthetic and mechanistic points of view.[1] The photoaddition provides a potentially useful synthetic procedure to achieve the direct introduction of functional groups into electron-rich substrates. However, few stereochemical studies on the photoaddition have been reported.[2–7] Recently, we have discovered an efficient photoamination procedure using ammonia and primary amines as nucleophiles, and have investigated it in order to establish its mechanism[8] and synthetic scope and limitations.[7,9] However, the stereochemistry of the addition of the amine is left undetermined. Herein we wish to report the stereochemistry of photoamination of some phenanthrene derivatives **1**–**4** and anthracene **5**.

Results and Discussion

Stereochemistry.—Irradiation of a 9:1 (v/v) acetonitrile–water solution containing an arene (**1**–**5**), *m*-dicyanobenzene (DCNB), and ammonia or primary alkylamines (*i.e.* propylamine, isopropylamine and *tert*-butylamine) with a high-pressure mercury lamp through a Pyrex filter gave the corresponding 9-amino- or 9-alkylamino-9,10-dihydroarenes **6**–**13**. The photoamination of 9-methoxyphenanthrene (**1**) with ammonia gave *cis*- and *trans*-9-amino-10-methoxy-9,10-dihydrophenanthrene (**6a**, **b**) in a ratio of 75:25 (Scheme 1). The structure of the major product was confirmed by X-ray crystallographic analysis; the acetamide of **6a** has a *cis* configuration between the acetylamino and methoxy groups. Table 1 lists the final atomic parameters for the acetamide of **6a**, and Table 2 lists bond distances and bond angles. The crystal packing diagram and an ORTEP drawing are shown in Fig. 1. Simultaneously the structure of the minor product was found to be *trans* isomer **6b**.

The ^{1}H NMR spectrum [Fig. 2(*a*)] of **6a**, **b** shows that a hydrogen (H^c) attached to the methoxylated carbon of **6b** (4.18 ppm) appeared at higher field than H^a of **6a** (4.26 ppm). This is clearly due to the substantial shielding effect of an amino group towards a hydrogen (H^c) which is located in the *cis* position towards the amino group. In the ^{1}H NMR spectrum [Fig. 2(*b*)] of the acetamide of **6a**, **b**, the peak for H^c of the acetamide of **6b** shows a downfield shift of 0.18 ppm from that of parent **6b** whereas the peak for H^a of the acetamide of **6a** shows only a slight shift from parent **6a**, thus indicating that the deshielding effect of the acetamide group operates effectively for a hydrogen (H^c) which is located in the *cis* configuration toward the acetamide group.

On the basis of these observations from ^{1}H NMR spectra, the configuration of aminated compounds **7**–**9** from 9-alkoxyphenanthrenes **1**–**3** was assigned by their ^{1}H NMR spectra (Figs. 3 and 4). Table 3 lists the isomer ratios determined from peak ratios for methine protons at C-9 or C-10 in the ^{1}H NMR spectra as well as product yields. The photoamination of **2** with ammonia gave *cis*- and *trans*-9-amino-10-ethoxy-9,10-dihydrophenanthrene (**7a**, **b**) in a ratio of 73:27. The photoamination of **1** with isopropylamine and of **2** with *tert*-butylamine



Scheme 1

Table 1 Final atomic coordinates ($\times 10^3$) with their estimated standard deviations

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
O(1)	−47(0)	−70(1)	805(0)	C(8)	−104(1)	260(1)	705(3)
O(2)	223(1)	47(1)	1271(1)	C(9)	−21(1)	306(1)	668(3)
N(1)	145(1)	5(1)	1017(2)	C(10)	82(1)	270(1)	731(2)
C(1)	−161(1)	33(1)	908(2)	C(11)	103(1)	188(2)	833(2)
C(2)	−243(1)	−20(1)	946(2)	C(12)	18(1)	141(1)	871(2)
C(3)	−338(1)	32(2)	921(3)	C(13)	41(1)	53(1)	990(2)
C(4)	−355(1)	126(2)	860(2)	C(14)	−49(1)	−24(1)	942(2)
C(5)	−272(1)	178(1)	824(2)	C(15)	−106(1)	−161(1)	769(2)
C(6)	−175(1)	129(1)	850(2)	C(16)	218(1)	7(1)	1152(2)
C(7)	−85(1)	180(1)	805(2)	C(17)	319(1)	−61(2)	1153(3)

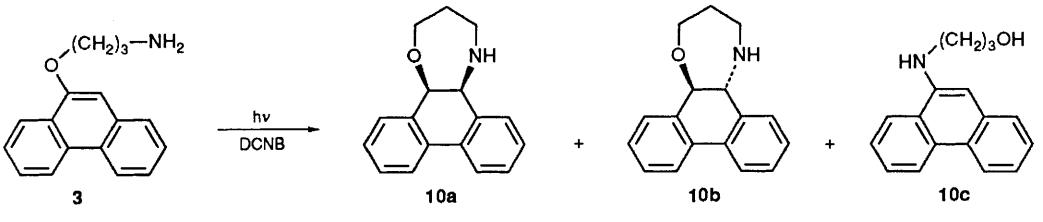
Table 2 Bond distances and bond angles of the acetamide of **6a**

Bond distance/Å				Bond angle/deg			
O(1)–C(14)	1.38(2)	C(8)–C(9)	1.38(2)	C(14)–O(1)–C(15)	114(1)	C(8)–C(9)–C(10)	119(2)
O(1)–C(15)	1.38(2)	C(9)–C(10)	1.35(3)	C(13)–N(1)–C(16)	120(1)	C(9)–C(10)–C(11)	120(2)
O(2)–C(16)	1.19(2)	C(10)–C(11)	1.37(3)	C(2)–C(1)–C(6)	122(1)	C(10)–C(11)–C(12)	120(2)
N(1)–C(13)	1.45(2)	C(11)–C(12)	1.41(2)	C(2)–C(1)–C(14)	117(2)	C(7)–C(12)–C(11)	118(2)
N(1)–C(16)	1.28(2)	C(12)–C(13)	1.53(2)	C(6)–C(1)–C(14)	121(1)	C(7)–C(12)–C(13)	121(2)
C(1)–C(2)	1.41(2)	C(13)–C(14)	1.49(2)	C(1)–C(2)–C(3)	117(2)	C(11)–C(12)–C(13)	121(2)
C(1)–C(6)	1.34(2)	C(16)–C(17)	1.58(3)	C(2)–C(3)–C(4)	122(2)	N(1)–C(13)–C(12)	113(1)
C(1)–C(14)	1.58(2)			C(3)–C(4)–C(5)	121(2)	N(1)–C(13)–C(14)	111(1)
C(2)–C(3)	1.37(3)			C(4)–C(5)–C(6)	119(2)	C(12)–C(13)–C(14)	110(1)
C(3)–C(4)	1.33(3)			C(1)–C(6)–C(5)	120(2)	O(1)–C(14)–C(1)	109(1)
C(4)–C(5)	1.41(3)			C(1)–C(6)–C(7)	119(2)	O(1)–C(14)–C(13)	108(1)
C(5)–C(6)	1.36(2)			C(5)–C(6)–C(7)	121(2)	C(1)–C(14)–C(13)	109(1)
C(6)–C(7)	1.53(2)			C(6)–C(7)–C(8)	122(2)	O(2)–C(16)–N(1)	134(2)
C(7)–C(8)	1.35(2)			C(6)–C(7)–C(12)	117(2)	O(2)–C(16)–C(17)	116(2)
C(7)–C(12)	1.37(2)			C(8)–C(7)–C(12)	121(2)	N(1)–C(16)–C(17)	110(2)
				C(7)–C(8)–C(9)	122(2)		

Table 3 Photoamination of arenes **1**–**5** with amines[a]

Arene	RNH_2	Irradn. time/h	Product (**a**:**b**)[c]	Yield[b] (%)	Conv. of arene (%)	Recov. of DCNB (%)
1	NH_3	2	**6** (75:25)	100	69	95
2	NH_3	5	**7** (73:27)	95	79	81
1	Pr^iNH_2	5	**8** (100:0)	99	92	80
2	*tert*-$BuNH_2$	5	**9** (100:0)	81	76	83
3		1.5	**10** (65:35)	41	100	100
			10c	18		
4	ND_3	4	**11** (84:16)	86	68	80
4-d_{10}	$PrNH_2$	10	**12** (17:83)	88	93	87
5	ND_3	1.5	**13** (95:5)	64	87	100

[a] For an acetonitrile–H_2O (9:1) or acetonitrile–D_2O (9:1) solution (50 cm^3) containing an arene (2.5 mmol), DCNB (2.5 mmol), and RNH_2 (25 mmol). [b] Isolated yield based on consumed arene. [c] Isomer ratio of **a** to **b**.



3 **10a** **10b** **10c**

Scheme 2

gave exclusively *cis*-9-(*N*-isopropylamino)-10-methoxy-9,10-dihydrophenanthrene (**8a**) and *cis*-9-(*N*-*tert*-butylamino)-10-ethoxy-9,10-dihydrophenanthrene (**9a**), respectively (Scheme 1). Intramolecular photoamination of 9-(3-aminopropoxy)-phenanthrene (**3**) gave phenanthro[9,10-*b*]-4-oxazepine derivatives (**10a**, **b**) in a *trans* to *cis* isomer ratio of 65:35, along with 3-[*N*-(9-phenanthryl)amino]propanol (**10c**) (Scheme 2).

The stereochemistry of the photoamination of phenanthrene (**4**) was studied using [$^2H_3$]ammonia in CH_3CN–D_2O; 9-(*N*,*N*-dideuterioamino)-10-deuterio-9,10-dihydrophenanthrene (**11a**, **b**) was formed (Scheme 3). In the ^1H NMR spectrum [Fig. 5(*c*)] of 9-amino-9,10-dihydrophenanthrene (**11c**) formed by photoamination of **4** with ammonia, the methylene protons (H^a and H^b) appear as two AB-type doublets of doublets, of which the peak at higher field can be assigned to the hydrogen (H^a) located in the *cis* position to the amino group. The ^1H NMR spectrum [Fig. 5(*b*)] of **11a**, **b** showed that deuterium was incorporated at C-10 in 90% yield and that a

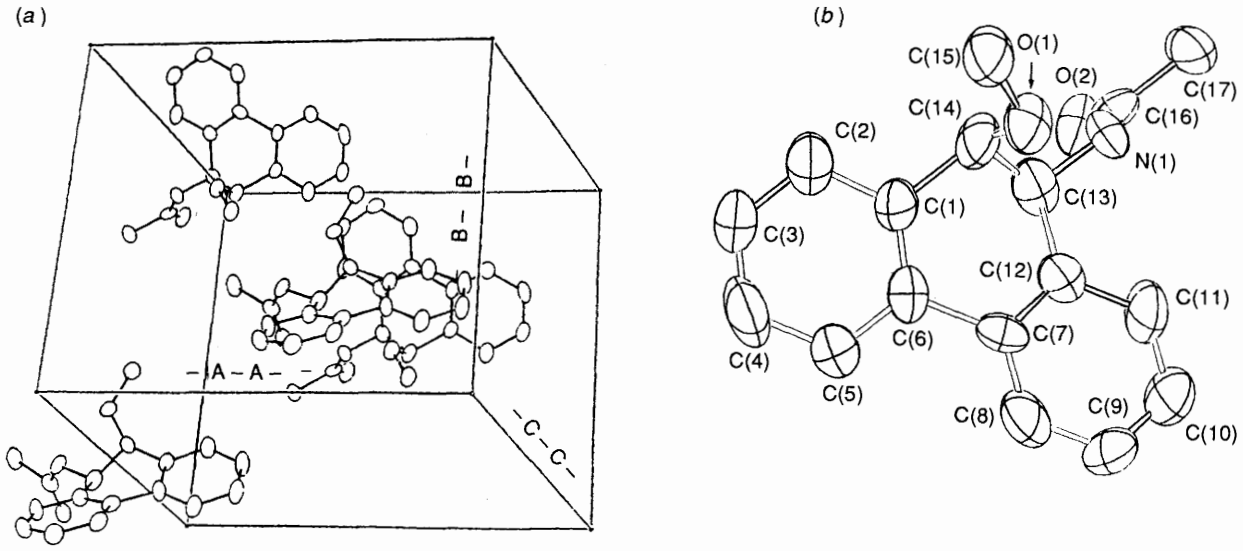
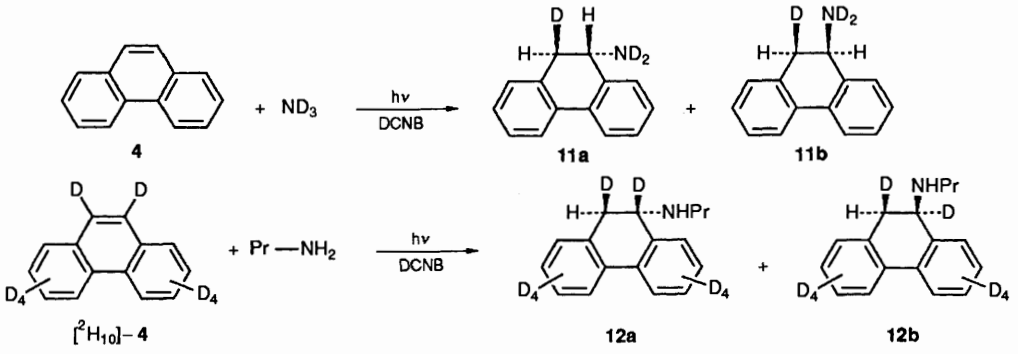
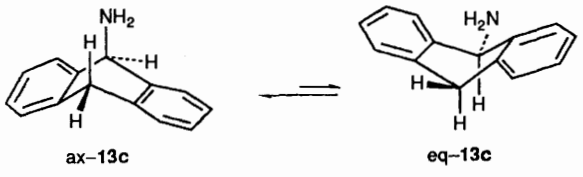


Fig. 1 (*a*) Crystal-packing diagram in unit cell and (*b*) an ORTEP drawing of the acetamide of **6a**. The numbering of carbon atoms is performed independently to the text but corresponds to Tables 1 and 2.



Scheme 3



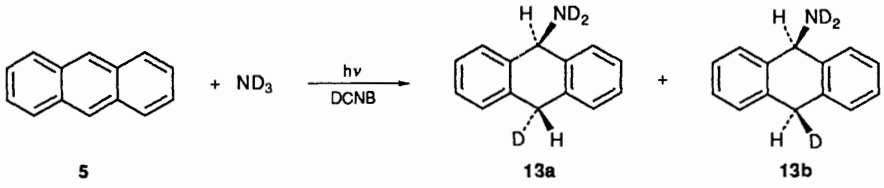
Scheme 4

ratio of the *cis* to *trans* configuration between the amino group and the hydrogen on C-10 was 84:16. The photoamination of [$^2H_{10}$] phenanthrene (**4**-d_{10}) with propylamine gave 9-propylamino-9,10-dihydro[$^2H_{10}$]phenanthrene (**12a, b**), of which the amino group and the hydrogen on C-10 were arranged in *cis* and *trans* configurations in a ratio of 17:83 [Fig. 5(*a*)]. Thus the addition of the amine and ammonia to the phenanthrene moiety occurred predominantly in a *trans* manner.

In the case of anthracene **5**, 1,4-addition of ammonia occurred to give 9-amino-9,10-dihydroanthracene (**13c**). The axial conformer ax-**13c** in which the amino group occupies an axial position is suggested to be more stable than the equatorial one eq-**13c** from ^{1}H NMR studies[10] and molecular mechanics calculation,* as shown in Scheme 4. In the ^{1}H NMR spectrum [Fig. 6(*c*)] of the acetamide of **13c**, doublets at 3.96 ppm and 4.12 ppm can be assigned to be equatorial and axial proton of the methylene group, respectively, since the equatorial proton experiences the strong deshielding effect of the aromatic ring. The ^{1}H NMR spectra [Figs. 6(*a*) and 6(*b*)] for parent and the acetamide of 9-(*N,N*-dideuterioamino)-10-deuterio-9,10-dihydroanthracene (**13a, b**) formed from the photoamination of **5** with [$^2H_3$]ammonia show that a deuterium atom was incorporated mainly at the equatorial position of the C-10 methylene group, demonstrating that 1,4-addition of ammonia to **5** occurs in a prediminantly *trans* manner (Scheme 5).

Mechanism.—As has been discussed previously, for the photoamination of **4**,[8] photochemical electron transfer from **1–3**, **5** to DCNB is responsible for the initiation process of the

* Optimized conformation and total strain energy of **13c** was calculated by Prof. Y. Inoue at Himeji Institute of Technology using MM2 molecular mechanics program by Prof. E. Osawa at Toyohashi University of Technology; the axial conformer ax-**13c** is more stable by *ca.* 12 kJ mol^{-1} than the equatorial one eq-**13c**.



Scheme 5

Table 4 Rate constants and calculated free energy changes for fluorescence quenching of **1–5** with DCNB

Arene	$E_{\frac{1}{2}}^{ox}$ [a]/V	τ_f [b]/ns	E_{0-0} [c]/kJ mol^{-1}	K_{SV} [d]/dm^3 mol^{-1}	k_q [e]/10^{10} dm^3 mol^{-1} s^{-1}	ΔG [f]/k mol^{-1}
1	0.97	25	327	350	1.4	−35.1
2	0.93	25	329	240	0.96	−41.0
3	0.72	26	329	600	2.3	−61.1
4	1.29	53	347	296	0.56	−24.3
5	0.93	5.3	319	75	1.4	−31.4

[a] Oxidation potentials in acetonitrile *vs.* $Ag/AgNO_3$. [b] Lifetime of fluorescence. [c] Excitation energy for the excited singlet of the arene estimated from fluorescence spectra. [d] Stern–Volmer constants for fluorescence quenching of arene. [e] Rate constants for fluorescence quenching of arene. [f] Calculated free energy change by Rehm–Weller equation (ref. 11).

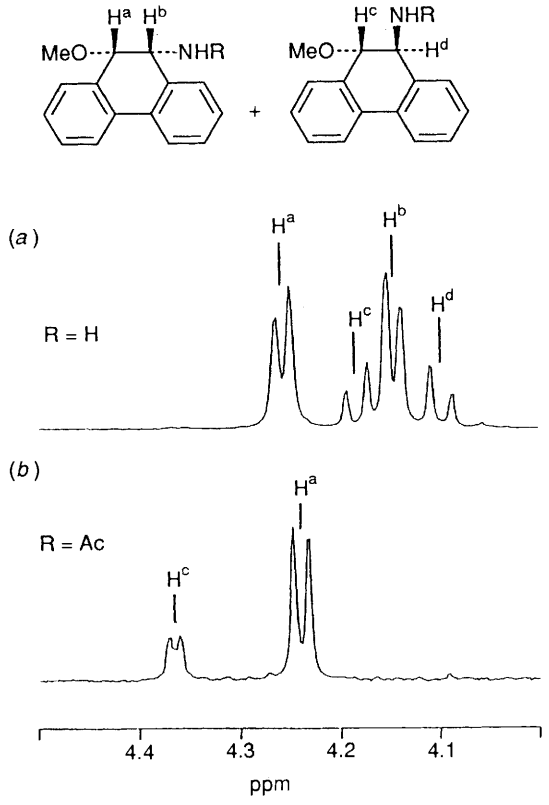


Fig. 2 ^{1}H NMR spectra of (*a*) **6a** and **6b**, and (*b*) the acetamides of **6a** and **6b** in the 4.0–4.5 ppm region

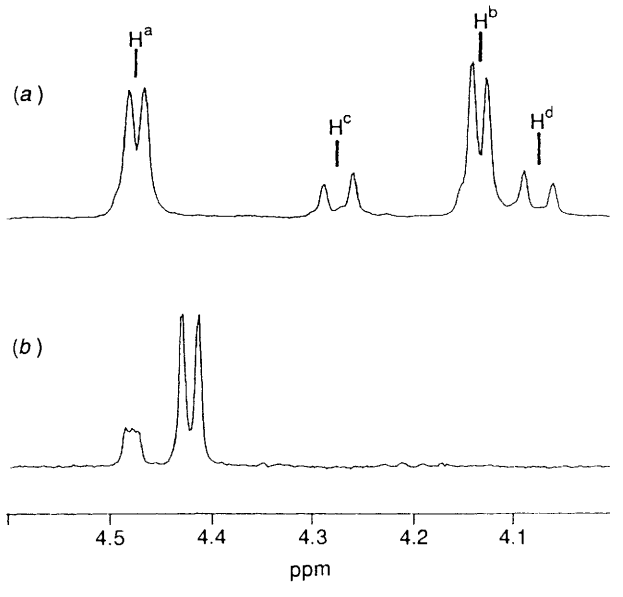


Fig. 3 ^{1}H NMR spectra of (*a*) **7a** and **7b** and (*b*) the acetamides of **7a** and **7b** in the 4.0–4.6 ppm region

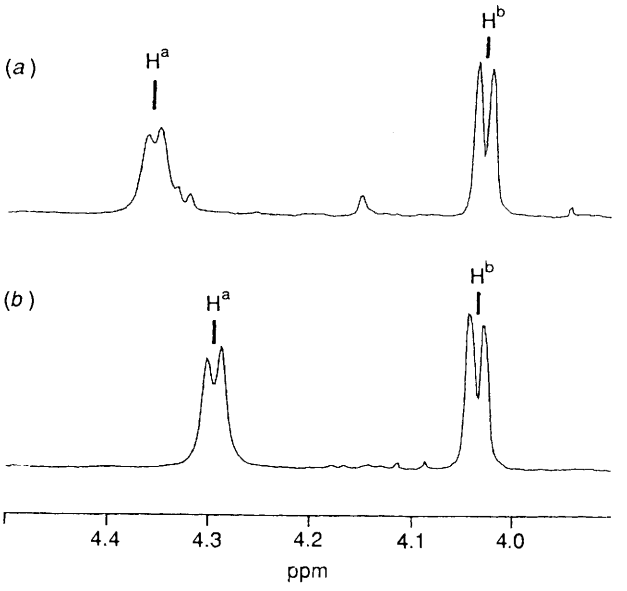


Fig. 4 ^{1}H NMR spectra of (*a*) **8a** and (*b*) **9a** in the 3.9–4.5 ppm region

photoamination, since the fluorescence of these arenes (ArH) was quenched by DCNB at a diffusion-controlled limit, and since the free energy change for electron transfer from the excited singlet state of ArH to DCNB was calculated to be substantially negative by the Rehm–Weller equation[11] as shown in Table 4. Therefore, the photoamination of **1–5** proceeds *via* nucleophilic addition of ammonia or amine to the cation radicals.[8] The aminated cation radicals are deprotonated by amine and undergo reduction by an anion radical of DCNB followed by protonation (Scheme 6).

$$ArH + DCNB \xrightarrow{h\nu} ArH^{\bullet+} + DCNB^{\bullet-}$$

$$ArH^{\bullet+} + R\text{-}NH_2 \longrightarrow {}^{\bullet}ArH\text{-}\overset{+}{N}H_2\text{-}R$$

$${}^{\bullet}ArH\text{-}\overset{+}{N}H_2\text{-}R + DCNB^{\bullet-} \longrightarrow {}^{-}ArH\text{-}NHR + DCNB + H^+$$

$${}^{-}ArH\text{-}NHR + H^+ \longrightarrow H\text{-}ArH\text{-}NHR$$

Scheme 6

In the case of aminated products **6–12** from phenanthrene derivatives **1–4**, the configuration around C-9 and C-10 can be related to the conformation of the aminated anions (**14**). The electron pair of **14** may exist in an axial position which is favourable for maximum orbital overlap of the electron pair with the aromatic ring. The resulting aminated anion **14** may adopt either conformation ax-**14** or eq-**14**, depending on the bulkiness of the amine as shown in Scheme 7. Steric interactions between the amino group on C-9 and the substituent on C-10 may be expected to favour ax-**14**. It has been reported that the 9,10-dialkyl-9,10-dihydrophenanthryl anion adopts predominantly the *cis* arrangement between the two alkyl groups

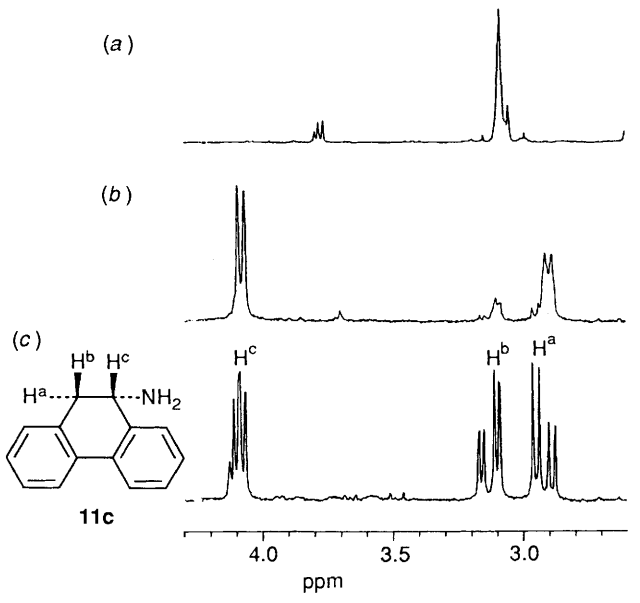


Fig. 5 ^{1}H NMR spectra of (*a*) **12a** and **12b**, (*b*) **11a** and **11b**, and (*c*) **11c** in the 2.6–4.3 ppm region

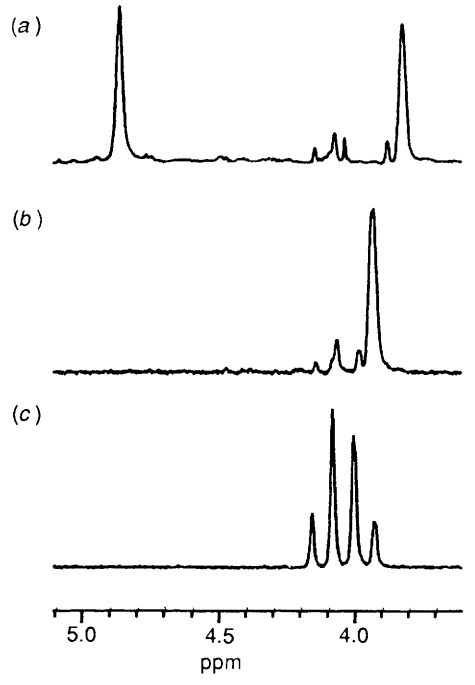
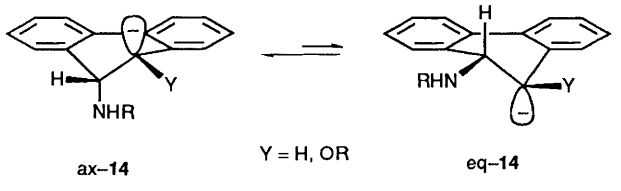


Fig. 6 ^{1}H NMR spectra (*a*) of **13a** and **13b**, (*b*) the acetamides of **13a** and **13b**, and (*c*) the acetamide of **13c** in the 3.6–5.1 ppm region

rather than *trans*.[12] Thus mainly *cis* isomers were formed on protonation of ax-**14**.

In the case of **5**, *trans* 1,4-addition of ammonia occurs selectively. However, it is difficult to explain the *trans* addition of ammonia to **5** in a similar way to the case of phenanthrene derivatives, since it is assumed, from a similar consideration to that applied in the case of the phenanthrene moiety, that both the amino group and the anion orbital occupy axial positions. Probably the amino group lies in the equatorial position because of the occurrence of electrostatic repulsion between the anion and the lone pair of the amino group.



Scheme 7

Experimental

^{1}H and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions using a Bruker AC-250P spectrometer. *J* values are in Hz. Mass spectra were recorded on a JEOL D-300S instrument. Fluorescence spectra were measured on a Hitachi MPF-4 instrument. Fluorescence lifetimes were measured on a Horiba NAES 550 instrument by a single-photon-counting method. GLC analysis was performed in a Shimadzu GC-8A or GC-14A using OV-17 or capillary column. Oxidation potentials were measured in acetonitrile using a Hokuto Denko HA-501G and HB-105 as potentiostat and function generator.

Materials.—Commercially available **4** was used after purification by column chromatography on silica gel. 9-Alkoxyphenanthrenes **1**, **2** were prepared from the 9-bromophenanthrene by the reported method.[13] According to the reported method,[14] **3** was prepared from the reaction of 9-phenanthrol with 1,2-dibromoethane, followed by cyanation with NaCN and the subsequent reduction with $LiAlH_4$. Primary amines were purified by distillation from sodium metal. [$^2H_3$]Ammonia was prepared from the reaction of Mg_2N_3 with D_2O. [$^2H_{10}$]-Phenanthrene was prepared by treatment of phenanthrene with D_2O in the presence of BF_3.[15]

Photoamination of Arenes with Ammonia and Primary Amines.—*General procedure*. In 140 cm^3 of 9:1 (v/v) acetonitrile–water solution was dissolved a mixture of an arene (14 mmol), an electron acceptor (3.5 mmol), and an amine (140–350 mmol), and then the solution was purged with argon for 20 min. In the case of ammonia, ammonia gas was bubbled into argon-bubbled 9:1 acetonitrile–water solutions containing an arene and an electron acceptor. The solutions were irradiated with an Eikosha PIH-300 high-pressure mercury lamp through Pyrex under cooling with water. Details of the follow-up process have been described in the literature.[9]

3: δ_H 1.66 (br s, 2 H), 2.07–2.17 (m, 2 H), 3.05 (t, *J* 6.8, 2 H), 4.33 (t, *J* 6.0, 2 H), 6.99 (s, 1 H), 7.45–7.77 (m, 5 H), 8.36 (dd, *J* 8.0 and 1.9, 1 H), 8.56–8.59 (m, 1 H), 6.60 (d, *J* 7.8, 1 H). δ_C 32.93, 39.44, 65.83, 102.61, 122.48, 122.53, 124.20, 126.36, 126.58, 127.11, 127.27, 131.23, 132.90, 152.70. *m/z* 251 (M^+).

The photoamination of **4** *and* **5** *with* [$^2H_3$]*ammonia*. The ^{1}H NMR spectrum of the aminated products (**11a–c**) obtained from the photoamination of **4** with [$^2H_3$]ammonia shows that the integral ratio of signals at δ 2.90, 3.12 and 4.08 ppm was 0.853:0.241:1, revealing that **11a**, **11b** and **11c** were formed in a ratio of 75.9:14.7:9.5. Moreover, the ^{1}H NMR spectrum in the case of **5** shows that the integral ratio for signals of δ 3.82, 4.15 and 4.86 ppm was 0.964:0.252:1, showing that **13a**, **13b** and **13c** were formed in a ratio of 74.8:3.6:21.6.

cis-9-*Amino*-10-*methoxy*-9,10-*dihydrophenanthrene* **6a**.[9] δ_H 1.92 (br s, 2 H), 3.40 (s, 3 H), 4.14 (d, *J* 3.7, 1 H), 4.26 (d, *J* 3.7, 1 H), 7.28–7.48 (m, 6 H), 7.73–7.78 (m, 2 H); δ_C 52.19, 56.86, 81.55, 123.77, 124.07, 127.17, 127.50, 127.99, 128.15, 128.25, 128.75, 132.80, 133.05, 133.94, 137.51.

trans-9-*Amino*-10-*methoxy*-9,10-*dihydrophenanthrene* **6b**. δ_H 1.92 (br s, 2 H), 3.38 (s, 3 H), 4.10 (d, *J* 5.4, 1 H), 4.18 (d, *J* 5.4, 1 H), 7.28–7.48 (m, 6 H), 7.73–7.78 (m, 2 H); δ_C 54.13, 57.47, 83.27, 123.37, 124.28, 127.58, 127.84, 128.25, 128.43, 129.17, 129.54, 131.94, 133.05, 135.88, 138.25.

cis-9-*Amino*-10-*ethoxy*-9,10-*dihydrophenanthrene* **7a**. δ_H 1.26 (t, *J* 6.9, 3 H), 1.94 (br s, 2 H), 3.62 (q, *J* 6.9, 2 H), 4.13 (d, *J* 3.7, 1 H), 4.47 (d, *J* 3.7, 1 H), 7.26–7.44 (m, 4 H), 7.49–7.76 (m, 2 H),

7.75 (d, *J* 7.1, 2 H); δ_C 15.40, 52.28, 64.77, 79.31, 123.81, 123.89, 127.49, 127.72, 127.97, 128.19, 128.25, 128.34, 132.83, 132.94, 134.64, 137.42. The acetamide: m.p. 169.5–170.5 °C. Calc. for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98 (Found: C, 76.4; H, 6.55; N, 4.8%).

trans-9-*Amino*-10-*ethoxy*-9,10-*dihydrophenanthrene* **7b**. δ_H 1.24 (t, *J* 6.9, 3 H), 1.94 (br s, 2 H), 3.73 (q, *J* 6.9, 2 H), 4.07 (d, *J* 7.2, 1 H), 4.27 (d, *J* 7.2, 1 H), 7.26–7.44 (m, 4 H), 7.49–7.76 (m, 2 H), 7.75 (d, *J* 7.1, 2 H); δ_C 15.40, 54.44, 65.92, 81.92, 124.16, 124.52, 126.92, 127.94, 128.19, 128.71, 128.96, 129.43, 132.34, 133.31, 134.75, 138.24.

cis-9-(N-*Isopropylamino*)-10-*methoxy*-9,10-*dihydrophenanthrene* **8a**. δ_H 1.01 (d, *J* 6.1, 3 H), 1.17 (d, *J* 6.2, 3 H), 1.71 (br s, 1 H), 3.01–3.06 (m, 1 H), 3.35 (s, 3 H), 4.03 (d, *J* 3.5, 1 H), 4.35 (d, *J* 3.5, 1 H), 7.20–7.46 (m, 6 H), 7.73–7.85 (m, 2 H); δ_C 23.05, 23.57, 45.33, 55.58, 56.60, 78.35, 123.78, 124.08, 127.25, 127.41, 127.52, 127.82, 128.59, 128.88, 133.02, 134.11, 137.41.

cis-9-(N-tert-*Butylamino*)-10-*ethoxy*-9,10-*dihydrophenanthrene* **9a**. δ_H 1.07 (t, *J* 6.9, 3 H), 1.19 (s, 9 H), 1.81 (br s, 1 H), 3.42 (q, *J* 6.9, 2 H), 4.03 (d, *J* 3.4, 1 H), 4.29 (d, *J* 3.4, 1 H), 7.22–7.44 (m, 6 H), 7.69–7.73 (m, 1 H), 7.80 (d, *J* 7.7, 1 H), 7.89–8.06 (m, 1 H); δ_C 15.10, 30.36, 50.88, 53.68, 63.72, 79.56, 123.31, 124.13, 126.89, 127.90, 128.04, 129.08, 133.13, 134.29, 134.64, 139.67.

cis-8b,10,11,12,13,13a-*Hexahydrophenanthro*[9,10-b]-4-*oxazepine* **10a**. δ_H 1.86–2.04 (m, 2 H), 2.64 (br s, 1 H), 3.08 (t, *J* 5.4, 2 H), 3.97 (t, *J* 5.5, 2 H), 4.17 (d, *J* 4.2, 1 H), 4.84 (d, *J* 4.2, 1 H), 7.14–7.78 (m, 8 H); δ_C 33.55, 45.58, 60.28, 66.47, 78.46, 123.45, 123.73, 127.57, 128.05, 128.05, 128.14, 128.20, 128.30, 132.48, 132.96, 133.75, 138.00.

trans-8b,10,11,12,13,13a-*Hexahydrophenanthro*[9,10-b]-4-*oxazepine* **10b**. δ_H 1.86–2.04 (m, 2 H), 2.64 (br s, 1 H), 2.91–3.04 (m, 2 H), 3.91 (d, *J* 7.1, 1 H), 4.21–4.31 (m, 2 H), 4.40 (d, *J* 7.1, 1 H), 7.14–7.77 (m, 8 H); δ_C 34.32, 44.90, 63.37, 69.06, 84.66, 123.47, 123.62, 127.45, 127.62, 127.84, 128.20, 128.30, 130.93, 132.86, 133.57, 137.75.

3-[N-(9-*phenanthryl*)*amino*]*propanol* **10c**. δ_C 1.86–2.04 (m, 2 H), 2.64 (br s, 2 H), 3.41 (t, *J* 6.2, 2 H), 3.77 (t, *J* 5.7, 2 H), 6.73 (s, 1 H), 7.14–7.77 (m, 5 H), 7.86 (d, *J* 8.8, 1 H), 8.49 (d, *J* 8.1, 1 H), 8.65 (d, *J* 7.8, 1 H); δ_C 31.22, 42.60, 61.79, 101.61, 122.71, 123.32, 123.75, 124.24, 125.43, 126.20, 126.44, 126.47, 127.67, 127.90, 135.30, 135.59, 141.44.

X-Ray Crystal Diffraction Analysis of the Acetamide of **6a**.—The sample was recrystallized friom methanol.

Crystal data. $C_{17}H_{17}O_2N$, M = 267.33, monoclinic, a = 13.085(5), b = 12.955(6), c = 9.125(5) Å, α = 90.07(4), β = 109.48(4), γ = 89.95(3), V = 1457.4 Å^3, space group C_c, Z = 4, D_m = 1.22 Mg m^{-3}, D_x = 1.218 Mg m^{-3}, F(000) 568, λ = 0.710 69 Å. Approximate crystal dimensions: 0.4 × 0.5 × 0.5 mm.

Data collection and processing. The intensity data were measured on a CAD-4 Enraf-Nonius diffractometer with graphite-monochromated Mo-Kα radiation by ω–2θ scan technique. A total 4086 independent reflections were measured for θ < 30, of which 737 were considered to be observed [$I > 3\sigma(I)$].

Structure analysis and refinement. The structure was solved by direct methods using MULTAN 82 and refined by full-matrix least-squares methods. In the final refinement anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogen atoms were refined with isotropic thermal parameters. Final R and R_w values are 0.0895, 0.0897. There are no significant features in the final difference Fourier map. Anisotropic thermal parameters of non-hydrogen atoms and hydrogen atom-coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC).*

Acknowledgements

This work was supported in part by a Grant-in-Aid for scientific research from the Ministry of Education, Science, and Culture, Japan.

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Paper 1/01822A
Received 18*th April* 1991
Accepted 15*th October* 1991

* For details, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1992, issue 1.