Photocleavage of the C–O bond of 9-phenanthrylmethyl ω-anilinoalkyl ethers via photo-induced intramolecular electron transfer

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Photoreactions of the title compounds {ArCH₂O[CH₂]ₙNHPh: Ar = 9-phenanthryl} **1** and **2** (n = 4 and 5) gave ω-[o-(9-phenanthrylmethyl)anilino]alkan-1-ols **7** and **8** and ω-[spiro-(9′,10′-dihydrophenanthrene-9′,2-indolin)-1-yl]alkan-1-ols **9** and **10**, respectively, by the cleavage of the C–O bond, while that of another title compound **3** (n = 6) gave spiro-compounds **17** and **18** with 12- and 14-membered-rings, respectively, as main products. The photoreaction is proposed to proceed via photo-induced intramolecular electron transfer from comparison of the reaction products with those in the photoreaction of ArCH₂O[CH₂]₃Ph **5** in the presence of N-methylaniline and acetic acid. The structures of spiro-compounds **17**, **18**, and the acetate of **9** were confirmed by X-ray crystal structure analysis.

Introduction

In a series of photochemical reactions of 9-(ω-anilinoalkyl)phenanthrenes {general formula: Ar[CH₂]ₘNHPh; Ar = 9-phenanthryl, m = 2–6}, we have observed recently that the compound with m = 2 undergoes cleavage of the CH₂–CH₂ bond[1] and that those with m = 3–6 undergo a cyclization.[2] These reactions have been reasonably interpreted in terms of an intramolecular electron transfer via exciplex followed by a proton transfer.[2] In relation to these reactions, we investigated the photoreaction of 9-phenanthrylmethyl ω-anilinoalkyl ethers 1–3 {ArCH₂O[CH₂]ₙNHPh; Ar = 9-phenanthryl, 1: n = 4, 2: n = 5, 3: n = 6} and observed the cleavage of the ArCH₂–O bond for substrates **1** and **2**. Although the photochemical reactions of compounds with the benzylic carbon–heteroatom bond have been widely investigated,[3] the cleavage of the C–O bond of the ethers, especially the aryl CH₂O alkyl ethers, on irradiation with Pyrex-filtered light (λ > 290 nm) has been rarely observed to date.[4] We now report the photochemical reactions of the ethers 1–3 and the related compounds **4–6** [9-phenanthrylmethyl phenyl ether **4**, 9-phenanthrylmethyl 3-phenylpropyl ether **5**, and 4-(N-methyl-anilino)butyl 9-phenanthrylmethyl ether **6**].

Results and discussion

Synthesis of ethers

The ethers 1–3 and **6** were prepared by reaction of the sodium salt of 9-phenanthrylmethanol with the corresponding alkanediyl α,ω-dihalides followed by reaction with aniline or N-methylaniline. The ethers **4** and **5** were prepared by the reaction of 9-phenanthrylmethyl bromide with sodium salts of the

corresponding alcohols. Details are given in the Experimental section.

Photoreactions

The photoreactions were carried out by irradiation of the sample solution, degassed either by argon-bubbling in a Pyrex vessel or by three freeze–pump–thaw cycles in a Pyrex tube, with a high-pressure mercury lamp. No difference in the yields of the products obtained by the two procedures was observed. The photoproducts, shown in Schemes 1–4, were separated by chromatography and identified by both spectral methods and elemental analysis.†

The isolated yields of the main photoproducts are shown in Table 1. Irradiation of ethers **1** and **2** in benzene gave ω-[o-(9-phenanthrylmethyl)anilino]alkan-1-ols **7** and **8**, ω-[spiro-(9,10-dihydrophenanthrene-9,2′-indolin)-1′-yl]alkan-1-ols **9** and **10**, ω-[p-(9-phenanthrylmethyl)anilino]alkan-1-ols **11** and **12** and ω-(anilino)alkan-1-ols **13** and **14**, respectively, together with 1,2-di(9-phenanthryl)ethane **15** and 9-methylphenanthrene **16** with recovery of substrates **1** and **2**, thus indicating that the ArCH₂–O bond of compounds **1** and **2** is cleaved (Scheme 1). Furthermore, formation of compound **15** indicates that the phenanthrylmethyl radical is produced as an intermediate. Even if acetonitrile instead of benzene was used as a solvent, the yields of the products were similar to each other except for the increases in those of compounds **9** and **10**. These results are reasonably explained in terms of a rapid proton transfer from radical cation to radical anion, followed by radical coupling. Owing to the intramolecular reaction, the reaction sites are near

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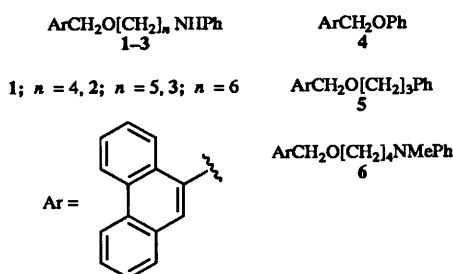
† Among the photoproducts isolated (23 compounds), 9-phenanthrylmethyl acetate and compounds **13, 14, 15, 16, 20** and **26** were identified by direct comparison (spectral data, etc.) with authentic compounds (prepared by the standard methods). Phenol and 3-phenylpropanol (commercially available) were identified by conversion into their respective 3,5-dinitrobenzoates. The structures of the other products were determined by spectral methods as shown in Experimental section. ¹H NMR spectra of spiro-compounds **9, 10, 17, 18** and **23** contain two characteristic sets of AB quartet signals, which are assignable to protons at the 10-position of the 9,10-dihydrophenanthrene ring and those at CH₂O or CH₂C₆H₄N. The structures of spiro-compounds **17, 18**, acetate of **9** and **23** were confirmed by X-ray crystal-structure analysis. As to p-(9-phenanthrylmethyl)-substituted anilines **11, 12, 22** and **25**, their purification was difficult and their respective ¹H NMR spectra were compared with those of the corresponding o-substituted isomers.

ArCH₂O[CH₂]ₙNHPh
1–3

1; n = 4, 2; n = 5, 3; n = 6

ArCH₂OPh
4

ArCH₂O[CH₂]₃Ph
5

ArCH₂O[CH₂]₄NMePh
6

Ar =

Table 1 Yields of the isolated photoproducts and recoveries of substrates[a]

| Substrate	Solvent	Product (yield/%)			15	16	Recovery (%)
1	C$_6$H$_6$	7 (9)	9 (17)	11 (11)	(17)	(4)	6
1	MeCN	7 (0)	9 (23)	11 (12)	(14)	(9)	2
1	C$_6$H$_6$–AcOH	7 (10)	9 (9)	11 (0)	(20)	(13)	7
2	C$_6$H$_6$	8 (8)	10 (17)	12 (5)	(16)	(5)	30
2	MeCN	8 (7)	10 (23)	12 (9)	(19)	(3)	39
3	C$_6$H$_6$	19 (3)	17 (8)	18 (16)	(0)	(4)	49
6	C$_6$H$_6$	25 (0)			(3)	(2)	78
6	C$_6$H$_6$–AcOH	25 (3)			(10)	(29)	32

[a] Other products are 13 from 1, 14 from 2, and 9-phenanthrylmethyl acetate and 26 from 6 in C$_6$H$_6$–AcOH.
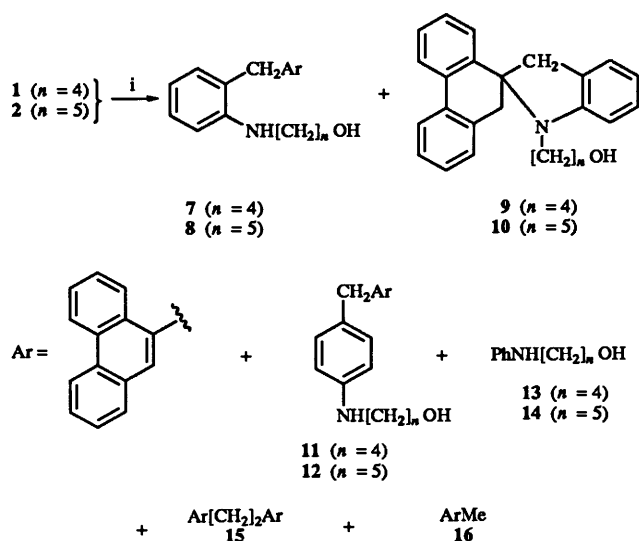
Scheme 1 *Conditions:* i, *hv*

at hand (contact-ion-pair state). Compounds **9** and **10** were confirmed to be formed from alcohols **7** and **8**, respectively, upon irradiation. The reason for the difference in reactivity of open-chain compounds **7** and **8** with that of spiro-compounds in acetonitrile remains equivocal, but it may be caused by the conformation of the ω-hydroxypolymethylene chain. Irradiation of compound **3** in benzene afforded two spiro-cyclic compounds, **17** and **18**, in addition to small amounts of compounds **16** and **19**, thus indicating that cleavage of the ArCH$_2$–O bond is not a main reaction in the case of substrate 3 (Scheme 2).
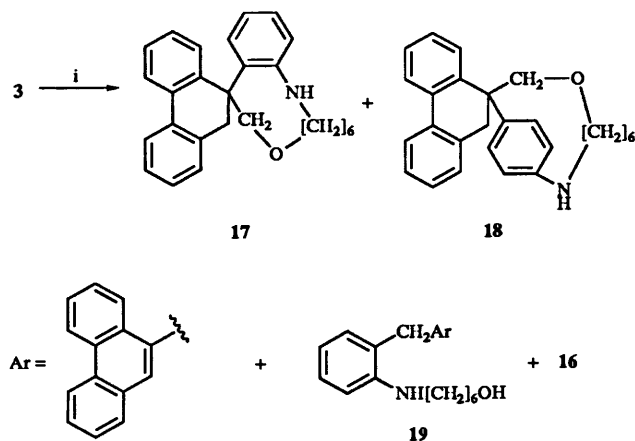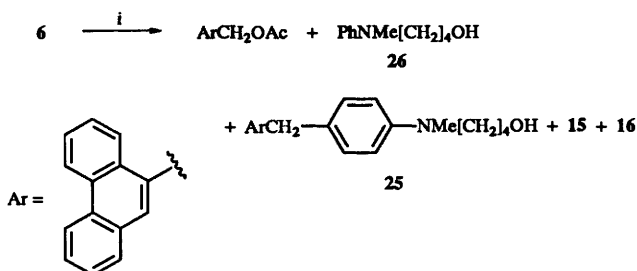

Scheme 2 *Conditions:* i, *hv*

To obtain further information about the role of the anilino group, irradiation of the ethers **4** and **5** in the presence of *N*-methylaniline (NMA) was carried out under similar conditions. In the absence of NMA, irradiation of compound **4** in benzene gave a small amount of compound **15** with recovery of substrate **4**, thus indicating that cleavage of the ArCH$_2$–O bond of compound **4** is much more difficult as compared with that of the simpler ethers **1** and **2**. In the presence of NMA (5-fold equivalent), however, the photoreaction of compound **4** gave the NMA derivatives, *N*-, *o*- and *p*-(9-phenanthrylmethyl)-*N*-methylaniline (**20**, **21** and **22**, in 4, 8 and 12% yield, respectively) and spiro[9,10-dihydrophenanthrene-9,2′-(1′-methylindoline)] **23** (5%) together with products **15** (13%), **16** (3%), *p*-(9-phenanthrylmethyl)phenol **24** (3%), and phenol (49%) (Scheme 3). Thus, NMA was found to promote
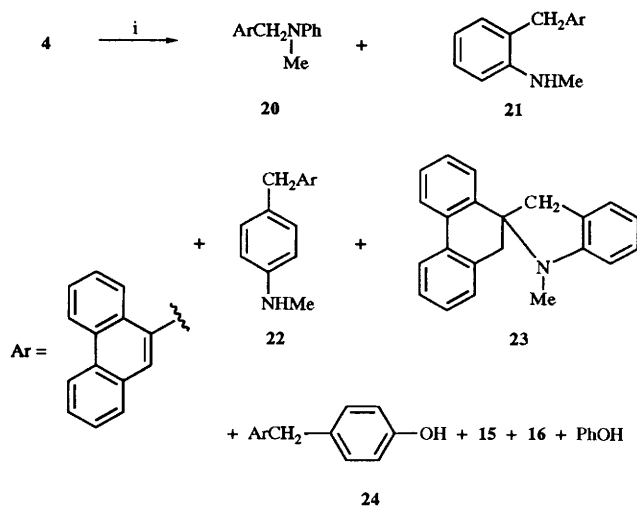
Scheme 3 *Reagents and conditions:* i, PhNHMe, *hv*

significantly the photochemical cleavage of the ArCH$_2$–O bond of **4**. On the other hand, irradiation of the ether **5** resulted in the complete recovery of starting material. In the presence of 5 mol equiv. of NMA, irradiation of compound **5** gave small amounts of products **15** and **16** with recovery of substrate **5**. Phenanthrylmethyl-substituted aniline derivatives, formed in the case of compound **4**, were not detected. These results suggest that the ArCH$_2$–O bond is cleaved by the photo-induced electron transfer from NMA to the excited phenanthrene moiety to give the phenanthrylmethyl radical. The difference in reactivity between ethers **4** and **5** is regarded as being due to the leaving ability of the PhO group. This also suggests that the cleavage of the ArCH$_2$–O bond of compounds **1** and **2** is caused by intramolecular protonation, by the –NH– group, on the ethereal oxygen.

To investigate the effect of protonation on the cleavage, the photoreaction of compounds 5 and 6 was carried out in the presence of both NMA and acetic acid. Irradiation of 5 in the presence of only acetic acid in benzene did not give the products in any appreciable amount. However, cleavage of the ArCH$_2$–O bond was observed in the presence of both acetic acid and NMA: products 15, 16, 20 and 23 were obtained in trace, 7, 5 and 6% yield, respectively, together with 3-phenylpropanol (trace amount) with recovery of substrate 5. On the other hand, irradiation of compound 6 in benzene, in the absence of acetic acid, afforded small amounts of products 15 and 16 with recovery of starting material 6, but, in the presence of acetic acid (10% v/v) this reaction led to the formation of compounds 15, 16, 4-[N-methyl-p-(9-phenanthrylmethyl)-anilino]butan-1-ol 25, 4-(N-methylanilino)butan-1-ol 26, and 9-phenanthrylmethyl acetate in 10, 29, 3, 31 and 17% yield, respectively, with recovery of unchanged amine 6 (32%) (Scheme 4). These observations indicate that both the electron-

Scheme 4 Reagents and conditions: i, AcOH, hv

donating agent and the protonating agent are necessary for the cleavage of the ArCH$_2$–OR (R = alkyl group) bond. From these results, the –NH– group of substrates 1 and 2 is thought to serve as the protonating agent.

A plausible pathway for the formation of compound 7 in the photoreaction of substrate 1 is shown in Scheme 5. The irradiation of compound 1 leads to the formation of an intramolecular radical cation–radical anion pair 28 by an intramolecular electron transfer via exciplex 27 which has a π–π stacking conformation of the aniline and phenanthrene moieties. On the basis of the mechanism of the thermal cleavage of ethereal bonds by alkali metals,[5] the photo cleavage of the ArCH$_2$–O bond is considered to form the aminyl and
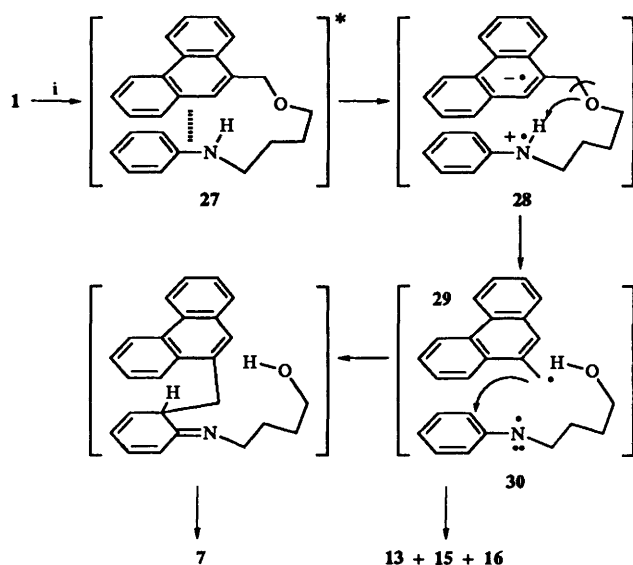
Scheme 5 Conditions: i, hv

phenanthrylmethyl radicals (29 and 30),[6] and protonation on the ethereal oxygen by the –NH– group is thought to assist the cleavage. The coupling reaction between the radicals 29 and 30, followed by aromatization, produces compound 7 which is converted into spiro-compound 9 on irradiation. Compound 15 is produced from radical 29 by coupling at the solvent-separated region (Scheme 5). The photoreaction of compound 2 is also considered to proceed by a pathway similar to that in the case of compound 1. In the case of the ether 3, the ArCH$_2$–O bond is not cleaved probably owing to the difficulty of protonation due to steric factors, but compounds 17 and 18 are produced by the usual cyclization.

The above results provide a new example of the cleavage of the ArCH$_2$–O bond via photo-induced electron transfer.

Experimental

Mps were determined with a Yanaco micromelting point apparatus (MP-500) and are uncorrected. UV spectra were recorded on a Shimadzu UV-160A spectrophotometer. IR spectra were obtained on an FT-IR spectrophotometer (Perkin-Elmer 1600-Type). NMR spectra were recorded on a JNM-GX270 (270 MHz) spectrometer using tetramethylsilane as internal standard; J-values are in Hz. Mass spectra were obtained on a JEOL-DX302 spectrometer (Nippon Denshi). Elemental analyses were performed on a Yanagimoto MT3 CHNcorder

Chromatography was carried out on silica gel (C-300; Wako Pure Chemical Ind.) and isolated yields are shown unless otherwise noted.

Materials

4-Bromobutyl 9-phenanthrylmethyl ether. To a mixture of sodium hydride (300 mg of oil containing 60% of NaH; 7.5 mmol) in dimethylformamide (DMF) (10 cm^3) was added dropwise a solution of 9-phenanthrylmethanol (1.1 g, 5.3 mmol) in DMF (5 cm^3) and the mixture was stirred for 30 min. To this mixture was added 1,4-dibromobutane (3 cm^3, 25 mmol) all at once. After being stirred for 1 h at 60 °C, the mixture was treated with water-saturated diethyl ether. The mixture was shaken with diethyl ether–water and the ether layer was separated and dried (Na$_2$SO$_4$). After evaporation of the solvent, the mixture was chromatographed with benzene–hexane (1:1, v/v) to give the title bromide as a solid (435 mg, 24%), mp 51–52 °C (Found: C, 66.7; H, 5.6. C$_{19}$H$_{19}$BrO requires C, 66.5; H, 5.6%); ν_{max}(KBr)/cm^{-1} 1110 and 1040 (C–O–C); δ_H(CDCl$_3$) 1.73–1.83 (2 H, m, CH$_2$), 1.90–2.01 (2 H, m, CH$_2$), 3.39 (2 H, t, J 6.7, CH$_2$), 3.59 (2 H, t, J 6.1, CH$_2$), 4.97 (2 H, s, CH$_2$), 7.55–7.70 (4 H, m, ArH), 7.74 (1 H, s, ArH), 7.85–7.88 (1 H, m, ArH), 8.13–8.16 (1 H, m, ArH) and 8.64–8.72 (2 H, m, ArH).

4-Anilinobutyl 9-phenanthrylmethyl ether 1. A mixture of aniline (1.5 cm^3, 16.5 mmol), potassium carbonate (1.0 g, 7.2 mmol) and 4-bromobutyl 9-phenanthrylmethyl ether (170 mg, 0.5 mmol) was stirred for 20 h. The usual work-up of the reaction mixture gave compound 1 (98 mg, 56%), mp 61–62 °C (from hexane) (Found: C, 84.4, H, 7.1; N, 3.9. C$_{25}$H$_{25}$NO requires C, 84.5; H, 7.1; N, 3.9%); λ_{max}(cyclohexane)/nm 253 (log ε 4.83), 276 (4.19), 284 (4.11) and 296 (4.18); ν_{max}(KBr)/cm^{-1} 3390 (NH); δ_H(CDCl$_3$) 1.71–1.79 (4 H, m, CH$_2$), 3.07–3.12 (2 H, t, CH$_2$), 3.61–3.66 (2 H, t, CH$_2$), 5.01 (2 H, s, CH$_2$), 6.52–6.55 (2 H, m, ArH), 6.63–6.69 (1 H, m, ArH), 7.10–7.16 (2 H, m, ArH), 7.56–7.71 (4 H, m, ArH), 7.76 (1 H, s, ArH), 7.86–7.89 (1 H, m, ArH), 8.16–8.20 (1 H, m, ArH) and 8.66–8.75 (2 H, m, ArH).

5-Bromopentyl 9-phenanthrylmethyl ether. This bromide was obtained similarly to the case of the butyl derivative, in 38% yield, mp 56–57 °C (from hexane) (Found: C, 66.95; H, 5.9.

$C_{20}H_{21}BrO$ requires C, 67.2; H, 5.9%); $\nu_{max}(KBr)/cm^{-1}$ 1126 (C–O–C); $\delta_H(CDCl_3)$ 1.46–1.57 (2 H, m, CH_2), 1.62–1.73 (2 H, m, CH_2), 1.79–1.89 (2 H, m, CH_2), 3.33–3.38 (2 H, m, CH_2), 3.56–3.61 (2 H, m, CH_2), 4.99 (2 H, s, $ArCH_2O$), 7.55–7.70 (4 H, m, ArH), 7.75 (1 H, s, ArH), 7.86–7.89 (1 H, m, ArH), 8.17–8.19 (1 H, m, ArH) and 8.65–8.74 (2 H, m, ArH).

5-Anilinopentyl 9-phenanthrylmethyl ether 2. Similar procedure for the preparation of compound 1 gave *title product* 2 in 56% yield, mp 46–47 °C (from pentane) (Found: C, 84.65, H, 7.55; N, 3.8. $C_{26}H_{27}NO$ requires C, 84.5, H, 7.4; N, 3.8%); $\lambda_{max}(MeOH)/nm$ 252 (log ε 4.86), 275 (4.17), 283 (4.09) and 295 (4.16); $\nu_{max}(KBr)/cm^{-1}$ 3408 (NH); $\delta_H(CDCl_3)$ 1.43–1.74 (6 H, m, CH_2), 2.35 (1 H, s, NH), 3.02–3.07 (2 H, m, CH_2), 3.56–3.61 (2 H, m, CH_2), 4.98 (2 H, s, CH_2), 6.53–6.56 (2 H, m, ArH), 6.64–6.70 (1 H, m, ArH), 7.11–7.18 (2 H, m, ArH), 7.55–7.69 (4 H, m, ArH), 7.75 (1 H, s, ArH), 7.85–7.88 (1 H, m, ArH), 8.18–8.19 (1 H, m, ArH) and 8.64–8.73 (2 H, m, ArH).

6-Bromohexyl 9-phenanthrylmethyl ether. This *bromide* was obtained by a similar method to that in the case of the butyl derivative, in 63% yield, mp 49.5–50.5 °C (from hexane) (Found: C, 67.7; H, 6.0. $C_{21}H_{23}BrO$ requires C, 67.9; H, 6.2%); $\lambda_{max}(MeOH)/nm$ 212 (log ε 4.49), 252 (4.78), 275 (4.12), 283 (4.03) and 295 (4.09); $\nu_{max}(KBr)/cm^{-1}$ 1133 (C–O–C); $\delta_H(CDCl_3)$ 1.37–1.42 (4 H, m, CH_2), 1.60–1.68 (2 H, m, CH_2), 1.78–1.86 (2 H, m, CH_2), 3.32–3.37 (2 H, m, CH_2), 3.55–3.60 (2 H, m, CH_2), 4.99 (2 H, s, $ArCH_2O$), 7.56–7.68 (4 H, m, ArH), 7.75 (1 H, s, ArH), 7.86–7.89 (1 H, m, ArH), 8.16–8.19 (1 H, m, ArH) and 8.65–8.74 (2 H, m, ArH).

6-Anilinohexyl 9-phenanthrylmethyl ether 3. Through a similar procedure to that used for the preparation of the parent 1, this *compound* was obtained in 35% yield, mp 56.5–58 °C (Found: 84.8; H, 7.8; N, 3.3. $C_{27}H_{29}NO$ requires C, 84.6, H, 7.6; N, 3.65%); $\lambda_{max}(MeOH)/nm$ 252 (log ε 4.85), 275 (4.17), 283 (4.06) and 295 (4.13); $\nu_{max}(KBr)/cm^{-1}$ 3409 (NH); $\delta_H(CDCl_3)$ 1.36–1.43 (4 H, m, CH_2), 1.52–1.70 (4 H, m, CH_2), 3.02–3.07 (2 H, m, CH_2), 3.56–3.61 (3 H, m, CH_2, NH), 5.00 (2 H, s, CH_2), 6.55–6.58 (2 H, m, ArH), 6.68–6.70 (1 H, m, ArH), 7.12–7.16 (2 H, m, ArH), 7.56–7.67 (4 H, m, ArH), 7.76 (1 H, s, ArH), 7.86–7.89 (1 H, m, ArH), 8.19–8.21 (1 H, m, ArH) and 8.65–8.73 (2 H, m, ArH).

9-Phenanthrylmethyl phenyl ether 4. Mp 138–139 °C (Found: C, 88.8; H, 5.4. $C_{21}H_{16}O$ requires C, 88.7; H, 5.7%); $\lambda_{max}(MeOH)/nm$ 223 (log ε 4.52), 275 (4.14), 283 (4.01) and 295 (4.08); $\nu_{max}(KBr)/cm^{-1}$ 1243 and 1085 (C–O–C); $\delta_H(CDCl_3)$ 5.53 (2 H, m, CH_2), 6.97–6.98 (1 H, m, ArH), 7.01–7.11 (2 H, m, ArH), 7.31–7.38 (2 H, m, ArH), 7.56–7.72 (4 H, m, ArH), 7.87–7.90 (2 H, m, ArH), 8.10–8.11 (1 H, m, ArH) and 8.67–8.77 (2 H, m, ArH).

9-Phenanthrylmethyl 3-phenylpropyl ether 5. By a similar method to that for the preparation of bromobutyl 9-phenanthrylmethyl ether, this *ether* was prepared in 27% yield, mp 44.5–46.5 °C (Found: C, 88.4; H, 6.8. $C_{24}H_{22}O$ requires C, 88.3; H, 6.8%); $\lambda_{max}(MeOH)/nm$ 212 (log ε 4.54), 252 (4.78), 275 (4.10), 283 (4.00) and 295 (4.08); $\nu_{max}(KBr)/cm^{-1}$ 1110 and 1040 (C–O–C); $\delta_H(CDCl_3)$ 1.90–2.01 (2 H, m, CH_2), 2.66–2.72 (2 H, t, CH_2), 3.55–3.60 (2 H, t, CH_2), 4.96 (2 H, s, CH_2), 7.10–7.24 (6 H, m, ArH), 7.54–7.68 (4 H, m, ArH), 7.73 (1 H, s, ArH), 7.83–7.86 (1 H, m, ArH), 8.16–8.20 (1 H, m, ArH) and 8.63–8.72 (2 H, m, ArH).

4-(N-Methylanilino)butyl 9-phenanthrylmethyl ether 6. Reaction of 4-bromobutyl 9-phenanthrylmethyl ether (605 mg, 1.8 mmol) with NMA (2 cm³, 18 mmol) in the presence of potassium carbonate (1 g, 7.2 mmol) gave *title compound* 6 in 71% yield (Found: C, 84.7; H, 7.5; N, 3.5. $C_{26}H_{27}NO$ requires C, 84.5, H, 7.4; N, 3.8%); $\lambda_{max}(MeOH)/nm$ 252 (log ε 4.80), 274 (4.05), 284 (3.95) and 295 (4.04); $\delta_H(CDCl_3)$ 1.66–1.69 (4 H, m, CH_2), 2.86 (3 H, s, Me), 3.27–3.32 (2 H, t, CH_2), 3.58–3.62 (2 H,

t, CH_2), 4.98 (2 H, s, CH_2), 6.63–6.68 (3 H, m, ArH), 7.15–7.22 (2 H, m, ArH), 7.55–7.67 (4 H, m, ArH), 7.74 (1 H, s, ArH), 7.85–7.88 (1 H, m, ArH), 8.17–8.18 (1 H, m, ArH) and 8.65–8.73 (2 H, m, ArH).

Authentic compounds. 1,2-Di(9-phenanthryl)ethane 15 mp 251.5–253.5 °C (lit.,[7] 252.5–254.5 °C), and 9-methylphenanthrene 16, mp 91–91.51 °C (lit.,[8] 90–91 °C), were prepared by the method reported previously.[9]

9-*Phenanthrylmethyl acetate* was prepared by the reaction of 9-phenanthrylmethanol with acetic anhydride in the presence of triethylamine (88% yield), mp 80.5–81.5 °C (from hexane) (Found: C, 81.9; H, 5.6. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%); $\lambda_{max}(MeOH)/nm$ 212 (log ε 4.40), 223 (4.32), 252 (4.71), 275 (4.02), 283 (3.94) and 295 (3.99); $\nu_{max}(KBr)/cm^{-1}$ 1725 (CO); $\delta_H(CDCl_3)$ 2.15 (3 H, s, Me), 5.62 (2 H, s, CH_2), 7.61–7.71 (4 H, m, ArH), 7.83 (1 H, s, ArH), 7.88–7.92 (1 H, m, ArH), 8.04–8.05 (1 H, m, ArH) and 8.63–8.77 (2 H, m, ArH).

N-Methyl-N-(9-phenanthrylmethyl)aniline 20. This *compound* was prepared by the reaction of 9-phenanthrylmethyl bromide with NMA, mp 131.5–133 °C (Found: C, 89.0; H, 6.4; N, 4.9. $C_{22}H_{19}N$ requires C, 88.85; H, 6.4; N, 4.7%); $\lambda_{max}(cyclohexane)/nm$ 254 (log ε 4.88) and 296 (4.11); $\delta_H(CDCl_3)$ 3.14 (3 H, s, Me), 4.99 (2 H, s, CH_2), 6.72–6.84 (3 H, m, ArH), 7.21–7.27 (2 H, m, ArH), 7.52–7.81 (6 H, m, ArH), 8.01–8.05 (1 H, m, ArH) and 8.66–8.79 (2 H, m, ArH).

4-Anilinobutan-1-ol 13. This was prepared by the reaction of aniline with ethyl succinyl chloride followed by reduction with lithium aluminium hydride, bp 165–170 °C/6 mmHg (lit.,[10] 125–135 °C/1 mmHg) (Found: C, 72.4; H, 9.2; N, 8.4. Calc. for $C_{10}H_{15}NO$: C, 72.7; H, 9.15; N, 8.5%); $\delta_H(CDCl_3)$ 1.62–1.78 (4 H, m, CH_2), 2.57 (1 H, br s, NH or OH), 3.12–3.19 (2 H, m, CH_2), 3.66–3.71 (2 H, m, CH_2), 6.59–6.73 (3 H, m, ArH) and 7.14–7.21 (2 H, m, ArH). Complex with 1,3,5-trinitrobenzene; dark red needles from hexane, mp 75.5–76.5 °C (lit.,[10] 73–74 °C).

5-Anilinopentan-1-ol 14. This was prepared by the reaction of aniline with ethyl 5-bromopentanoate followed by reduction with $LiAlH_4$, bp 160 °C/1 mmHg (lit.,[11] 164 °C/1.4 mmHg) (Found: C, 73.75; H, 9.6; N, 7.7. Calc. for $C_{11}H_{17}NO$: C, 73.7; H, 9.6; N, 7.8%); $\delta_H(CDCl_3)$ 1.40–1.70 (6 H, m, CH_2), 2.4 (br s, NH and OH), 3.09–3.14 (2 H, t, CH_2), 3.61–3.66 (2 H, t, CH_2), 6.58–6.72 (3 H, m, ArH) and 7.13–7.20 (2 H, m, ArH).

4-(N-Methylanilino)butanol 26. Bp 150–155 °C/6 mmHg (Found: C, 73.9; H, 9.8; N, 8.0. $C_{11}H_{17}NO$ requires C, 73.7; H, 9.6; N, 7.8%); $\nu_{max}(neat)/cm^{-1}$ 3342 (OH); $\delta_H(CDCl_3)$ 1.53–1.77 (5 H, m, CH_2 and OH), 2.91 (3 H, s, Me), 3.32 (2 H, t, CH_2), 3.64 (2 H, t, CH_2), 6.66–6.73 (3 H, m, ArH) and 7.18–7.26 (2 H, m, ArH).

Photoreactions

(i) 1 (Scheme 1). A typical example of irradiation in a Pyrex vessel. A solution of amine 1 (626 mg, 1.76 mmol) in benzene (110 cm³), placed in a Pyrex vessel, was degassed by argon bubbling for 30 min. The solution was irradiated with a 300 W high-pressure mercury lamp under argon bubbling (Eikosha PIH-300) for 5 h. After removal of the solvent under reduced pressure, the residue was separated to two components by chromatography with benzene. The first component contained 1,2-di(9-phenanthryl)ethane 15 (32 mg) and 9-methylphenanthrene 16 (26 mg), which were separated by chromatography with hexane–benzene (3:1, v/v). Chromatography of the second component with benzene–diethyl ether (15:1, v/v) gave unchanged ether (30 mg) from the first eluent, 4-[spiro-(9,10-dihydrophenanthrene-9,2′-indolin)-1′-yl]butan-1-ol 9 (98 mg) from the second, and 4-[o-(9-phenanthrylmethyl)anilino]butan-1-ol 7 (54 mg) from the third, and a mixture of 4-[p-(9-phenanthrylmethyl)anilino]butan-1-ol 11 and 4-anilinobutanol 13 [151 mg, 11 (20% from 1) and 13 (10%

from 1) based on the intensity of ^{1}H NMR signals] from the fourth. The last mixture showed two mass spectra, one of which (low temperature) demonstrated the presence of the alcohol 13 {m/z 165 (M$^+$, 18%), 106 (M − [CH$_2$]$_3$OH, 100), 77 (18)} and another one (high temperature) showed signals at m/z 355 (M$^+$, 65%), 296 (100), 191 (23), and 148 (25), indicating the presence of compound 11.

Spectral data for the products.—Compound 7, mp 106–108.5 °C (Found: C, 84.6; H, 7.15; N, 3.9. C$_{25}$H$_{25}$NO requires C, 84.5; H, 7.1; N, 3.9%); λ_{max}(MeOH)/nm 207 (log ε 4.69), 253 (4.79), 277 (4.15), 285 (4.07) and 297 (4.10); ν_{max}(KBr)/cm^{-1} 3382 and 3380 (OH and NH); δ_H(CDCl$_3$) 1.41–1.44 (2 H, m, CH$_2$), 1.54–1.60 (2 H, m, CH$_2$), 3.12–3.17 (2 H, t, CH$_2$), 3.47–3.49 (2 H, t, CH$_2$), 4.32 (2 H, s, CH$_2$), 6.68–6.76 (2 H, m, ArH), 7.01–7.04 (1 H, m, ArH), 7.24–7.30 (1 H, m, ArH), 7.39 (1 H, s, ArH), 7.52–7.77 (5 H, m, ArH), 8.11–8.15 (1 H, m, ArH) and 8.67–8.78 (2 H, m, ArH).

Compound 9, mp 120–123.5 °C (Found: C, 84.3; H, 7.4; N, 3.6. C$_{25}$H$_{25}$NO requires C, 84.5; H, 7.1; N, 3.9%); λ_{max}(MeOH)/nm 213 (log ε 4.67), 254 (4.44) and 296 (3.77); ν_{max}(KBr)/cm^{-1} 3450 (OH); δ_H(CDCl$_3$) 1.54–1.64 (2 H, m, CH$_2$), 1.73–1.85 (2 H, m, CH$_2$), 2.78 and 3.19 (2 H, AB q, J 15.87, CH$_2$), 2.87 and 3.36 (2 H, AB q, J 14.65, CH$_2$), 3.04–3.13 (1 H, m, CH$_2$), 3.22–3.33 (1 H, m, CH$_2$), 3.62–3.67 (2 H, m, CH$_2$), 6.48–6.51 (1 H, m, ArH), 6.57–6.62 (1 H, m, ArH), 6.88–6.89 (1 H, m, ArH), 7.08–7.34 (7 H, m, ArH) and 7.73–7.81 (2 H, m, ArH). The structure of product 9 was confirmed by conversion into its acetate ester, the X-ray molecular-structure analysis of which demonstrated the polycyclic structure with spiro-type rings. Acetate of 9: mp 94.5–95 °C (from hexane); ν_{max}(KBr)/cm^{-1} 1732 (CO); δ_H(CDCl$_3$) 1.49–1.55 (2 H, m, CH$_2$), 1.74–1.85 (2 H, m, CH$_2$), 2.04 (3 H, s, Me), 2.80 and 3.16 (2 H, AB q, J 15.87, CH$_2$), 2.88 and 3.36 (2 H, AB q, J 14.65, CH$_2$), 3.04–3.15 (1 H, m, CH$_2$), 3.24–3.34 (1 H, m, CH$_2$), 4.07–4.12 (2 H, m, CH$_2$), 6.47–6.50 (1 H, m, ArH), 6.59–6.64 (1 H, m, ArH), 6.89–6.91 (1 H, m, ArH), 7.10–7.13 (1 H, m, ArH), 7.15–7.27 (4 H, m, ArH), 7.30–7.37 (2 H, m, ArH) and 7.75–7.83 (2 H, m, ArH).

Crystal data for acetate of compound 9.—C$_{27}$H$_{27}$NO$_2$. Orthorhombic, a = 9.22(1), b = 38.30(1), c = 12.38(1) Å, V = 4370 Å^3, space group Pna2$_1$ (No. 33), Z = 8, D_c = 1.208 g cm^{-3}, μ(Mo-Kα) = 0.70 cm^{-1}. 4713 Reflections (6 ⩽ 2θ ⩽ 55°) were collected and 1459 reflections with I > 2.5σ(I) were used in the determination. The structure was solved and refined isothermally except for O and N which were refined with anisotropic thermal parameters. Final refinements converged to R (R_w) = 0.068 (0.042), S = 1.78. An ORTEP drawing of the acetate of compound 9 is shown in Fig. 1.‡

Compound 11, ν_{max}(KBr)/cm^{-1} 3360 (NH and OH); δ_H(CDCl$_3$) 1.66–1.77 (4 H, m, CH$_2$), 2.4 (2 H, br s, NH and OH), 3.11–3.16 (2 H, m, CH$_2$), 3.66–3.70 (2 H, m, CH$_2$), 4.39 (2 H, s, CH$_2$), 6.53–6.63 (2 H, m, ArH), 7.04–7.07 (2 H, m, ArH), 7.52–7.65 (5 H, m, ArH), 7.79–7.82 (1 H, m, ArH), 8.05–8.09 (1 H, m, ArH) and 8.64–8.73 (2 H, m, ArH); m/z 355 (M$^+$, 39%), 296 (37), 118 (100) and 91 (29).

Compound 15, mp 256–258 °C;[7] λ_{max}(MeOH)/nm 212, 253 and 298; δ_H(CDCl$_3$) 3.64 (4 H, s, CH$_2$), 7.61–7.73 (10 H, m, ArH), 7.83–7.87 (2 H, m, ArH), 8.22–8.26 (2 H, m, ArH) and 8.69–8.82 (4 H, m, ArH).

Compound 16, mp 87.5–88.5 °C;[8] λ_{max}(MeOH)/nm 212, 252 and 296; δ_H(CDCl$_3$) 2.74 (3 H, s, Me), 7.53–7.68 (5 H, m, ArH), 7.79–7.83 (1 H, m, ArH), 8.04–8.08 (1 H, m, ArH) and 8.64–8.75 (2 H, m, ArH).

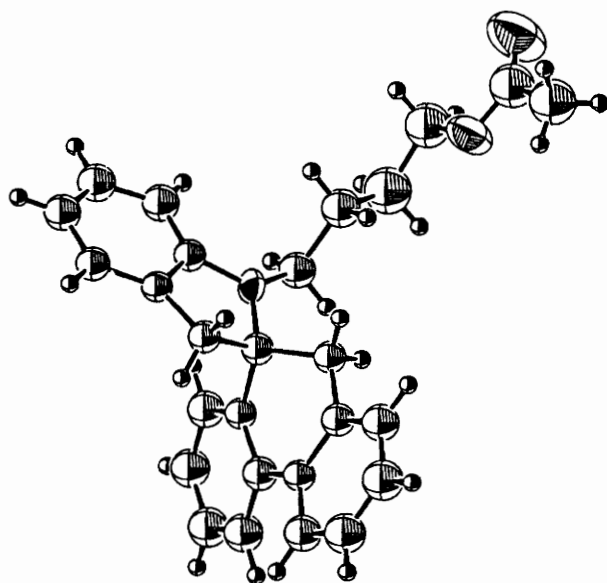‡ *Supplementary data (Instructions for Authors, January issue):* Tables of atomic coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

Fig. 1 ORTEP drawing of the acetate of compound 9

Compound 13, oil, δ_H(CDCl$_3$) 1.66–1.76 (4 H, m, CH$_2$), 2.50 (2 H, br s, OH and NH), 3.11–3.16 (2 H, m, CH$_2$), 3.66–3.70 (2 H, m, CH$_2$), 6.53–6.63 (2 H, m, ArH), 6.67–6.73 (1 H, m, ArH) and 7.13–7.21 (2 H, m, ArH).

(ii) **1 in acetonitrile.** A typical example of irradiation in a Pyrex tube. A solution of ether 1 (114 mg, 0.32 mmol) in acetonitrile (20 cm^3), placed in a Pyrex tube, was degassed under argon by three freeze–pump–thaw cycles and the tube was then sealed under reduced pressure. The solution was irradiated on a merry-go-round apparatus for 5 h. The photoproducts were separated by chromatography as described above (Scheme 1). The yields of the products are shown in Table 1.

(iii) **2 (Scheme 1).** A solution of compound 2 (118 mg, 0.32 mmol) in benzene (20 cm^3), placed in a Pyrex tube, was irradiated. The photoproducts, separated by chromatography with benzene–diethyl ether (10:1, v/v), were eluted in the following order: 16 (5%), 15 (16%), unchanged ether 2 (30% recovery), 5-[spiro-(9,10-dihydrophenanthrene-9,2'-indolin)-1'-yl]pentan-1-ol 10 (17%), 5-[o-(9-phenanthrylmethyl)-anilino]pentan-1-ol 8 (8%), 5-anilinopentan-1-ol 14, and a mixture of 5-[p-(9-phenanthrylmethyl)anilino]pentan-1-ol 12 (5%) and compound 14 (total 14%) (estimated on the intensities of ^{1}H NMR signals). The last mixture showed two mass spectra, the patterns of which were similar to those of compounds 11 and 13. The spectrum of the compound observed at low temperature demonstrated the presence of compound 14 {m/z 179 (M$^+$, 18%), 106 (100, M − [CH$_2$]$_4$OH), 77 (13)} and another one (high temperature) showed signals at m/z 369 (M$^+$, 63%), 296 (100), 191 (24), 148 (26), indicating the presence of compound 12.

Spectral data for the products.—Compound 8, mp 92–93 °C (Found: C, 84.6; H, 7.7; N, 3.3. C$_{26}$H$_{27}$NO requires C, 84.5; H, 7.4; N, 3.8%); ν_{max}(KBr)/cm^{-1} 3367 (NH) and 3267 (OH); δ_H(CDCl$_3$) 1.14–1.56 (6 H, m, CH$_2$), 3.09–3.14 (2 H, m, CH$_2$), 3.36–3.41 (2 H, m, CH$_2$), 4.34 (2 H, s, CH$_2$), 6.69–6.75 (2 H, m, ArH), 7.03–7.08 (1 H, m, ArH), 7.20–7.25 (2 H, m, ArH), 7.49–7.74 (5 H, m, ArH), 8.12–8.15 (1 H, m, ArH) and 8.66–8.78 (2 H, m, ArH).

Compound 10, mp 70–73 °C (Found: C, 84.3; H, 7.3; N, 3.5. C$_{26}$H$_{27}$NO requires C, 84.5; H, 7.4; N, 3.8%); ν_{max}(KBr)/cm^{-1} 3380 (OH); δ_H(CDCl$_3$) 1.26–1.65 (6 H, m, CH$_2$), 2.77 and 3.13 (2 H, AB q, J 15.25, CH$_2$), 2.85 and 3.33 (2 H, AB q, J 14.65,

CH$_2$), 2.98–3.10 (1 H, m, CH$_2$), 3.15–3.31 (1 H, m, CH$_2$), 3.63–3.68 (2 H, m, CH$_2$), 6.47–6.50 (1 H, m, ArH), 6.57–6.63 (1 H, m, ArH), 6.88–6.91 (1 H, m, ArH), 7.09–7.36 (7 H, m, ArH) and 7.74–7.83 (2 H, m, ArH).

Compound **12**, oil; v_{max}(KBr)/cm^{-1} 3334 (NH and OH); δ_H(CDCl$_3$) 1.40–1.69 (6 H, m, CH$_2$), 2.3 (2 H, br s, NH and OH), 3.05–3.13 (2 H, m, CH$_2$), 3.59–3.66 (2 H, m, CH$_2$), 4.36 (2 H, s, CH$_2$), 6.68–6.71 (2 H, m, ArH), 7.03–7.06 (2 H, m, ArH), 7.52–7.62 (5 H, m, ArH), 7.78–7.81 (1 H, m, ArH), 8.05–8.09 (1 H, m, ArH) and 8.63–8.72 (2 H, m, ArH); m/z 369 (M$^+$, 63%), 296 (100), 191 (24) and 148 (26).

Compound **14**, oil; δ_H(CDCl$_3$) 1.42–1.71 (6 H, m, CH$_2$), 3.05–3.15 (2 H, m, CH$_2$), 3.63–3.69 (2 H, m, CH$_2$), 6.57–6.72 (3 H, m, ArH) and 7.13–7.19 (2 H, m, ArH); m/z 179 (M$^+$, 18%), 106 (100) and 77 (13).

(iv) **3** (Scheme 2). Chromatography of the irradiation mixture [compound **3** (1.17 g) in benzene (190 cm^3) was irradiated in a Pyrex vessel] with benzene–diethyl ether (10:1, v/v) gave a mixture of compound **16** (22 mg, 4%) and spiro{9,10-dihydrophenanthrene-9,14′-6′,7′,8′,9′,10′,11′,13′,14′-octa-hydro-5′H-12′-oxa- 5′-azabenzo[12] annulene} **17** (91 mg, 8%) from the first eluent, unchanged starting ether (571 mg, 49% recovery) from the second, spiro{9,10-dihydrophenanthrene-9,10′-2′,3′,4′,5′,6′,7′,9′,10′-octahydro-1′H-8′-oxa-1′-aza-[10]-paracyclophane} **18** (190 mg, 16%) from the third, and 6-[o-(9-phenanthrylmethyl)anilino]hexan-1-ol **19** (39 mg, 3%) from the fourth. Compounds **17** and **18** were purified by the recrystallization from hexane.

Spectral data for the products.—Compound **17**, mp 192.5–193 °C (Found: C, 84.5; H, 7.7; N, 3.4. C$_{27}$H$_{29}$NO requires C, 84.6; H, 7.6; N, 3.65%); λ_{max}(MeOH)/nm 209 (log ε 4.33) and 256 (3.88); v_{max}(KBr)/cm^{-1} 3335 (NH) and 1098 (C–O–C); δ_H(CDCl$_3$) 1.5–1.8 (8 H, m, CH$_2$), 2.92 and 4.15 (2 H, AB q, J 15.26, CH$_2$), 2.9–3.05 (1 H, m, CH$_2$), 3.2–3.3 (1 H, m, CH$_2$), 3.4–3.5 (1 H, m, CH$_2$), 3.65–3.75 (1 H, m, CH$_2$), 4.08 and 4.31 (2 H, AB q, J 8.54, CH$_2$), 6.16–6.22 (1 H, m, ArH), 6.27–6.30 (1 H, m, ArH), 6.47–6.50 (1 H, m, ArH), 6.66 (1 H, br s, NH), 6.87–6.94 (1 H, m, ArH), 7.06–7.42 (6 H, m, ArH), 7.59–7.62 (1 H, m, ArH) and 7.81–7.85 (1 H, m, ArH).

Crystal data for compound **17**.—C$_{27}$H$_{29}$NO. Triclinic, a = 10.555(2), b = 11.512(2), c = 9.524(2) Å, α = 99.58(1), β = 95.05(1), γ = 65.25(1)°, V = 1036.1(3) Å^3, space group $P\bar{1}$ (No. 2), D_c = 1.229 g cm^{-3}, Z = 2, μ(Mo-Kα) = 0.69 cm^{-1}. 5058 Reflections (6 ⩽ 2θ ⩽ 55°) were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and 3593 reflections with I > 3.0σ(I) were used in the structure determination. The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic thermal parameters for non-hydrogen atoms; hydrogen atoms were found in the final difference Fourier maps or in calculated positions and were refined isothermally. All computations for the structure determination were carried out on a VAX station 3100 using the crystallographic program package TEXSAN.[13] Final refinements converged to R (R_w) = 0.041 (0.038), S = 2.66. An ORTEP drawing of compound **17** is shown in Fig. 2.§

Compound **18**, mp 163–164 °C (Found: C, 84.5; H, 7.8; N, 3.4%); λ_{max}(MeOH)/nm 209 (log ε 4.77) and 262 (4.40); v_{max}(KBr)/cm^{-1} 3400 (NH) and 1096 (C–O–C); δ_H(CDCl$_3$) 0.72–0.95 (4 H, m, CH$_2$), 1.15–1.25 (2 H, m, CH$_2$), 1.47–1.57 (2 H, m, CH$_2$), 2.66–2.74 (1 H, m, CH$_2$), 2.95–3.05 (1 H, m, CH$_2$), 3.18–3.24 (2 H, m, CH$_2$), 2.98 and 3.42 (2 H, AB q, J 14.65,
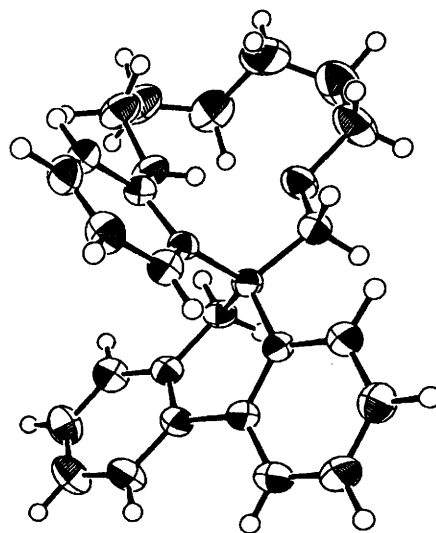

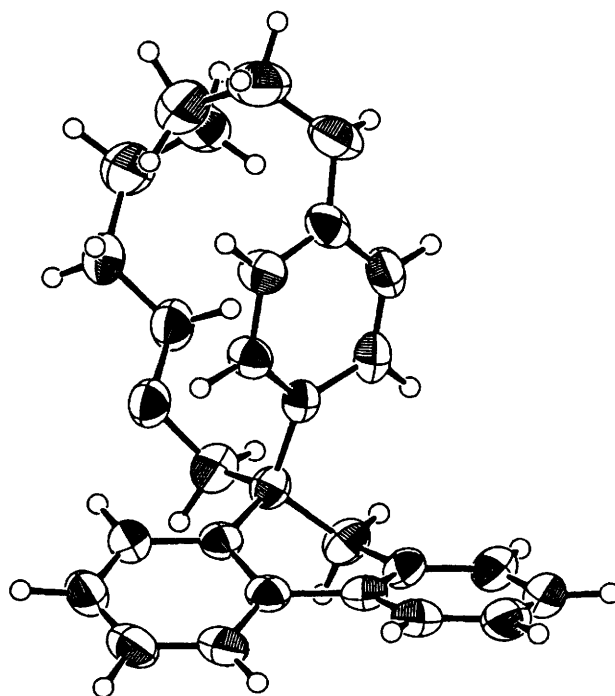Fig. 2 ORTEP drawing of compound **17**

Fig. 3 ORTEP drawing of compound **18**

CH$_2$), 3.42 and 4.11 (2 H, AB q, J 9.76, CH$_2$), 6.51–6.68 (3 H, m, ArH), 7.16–7.22 (2 H, m, ArH), 7.28–7.35 (1 H, m, ArH), 7.36–7.42 (3 H, m, ArH), 7.63–7.66 (1 H, m, ArH), 7.76–7.79 (1 H, m, ArH) and 7.85–7.88 (1 H, m, ArH).

Crystal data for compound **18**.—C$_{27}$H$_{29}$NO. Monoclinic, a = 6.172(1), b = 13.074(1), c = 13.194(1) Å, β = 90.72(1)°, V = 1064.6(2) Å^3, space group $P2_1$ (No. 4), Z = 2, D_c = 1.196 g cm^{-3}, μ(Mo-Kα) = 0.67 cm^{-1}. 2799 Reflections (6 ⩽ 2θ ⩽ 55°) were collected and 2407 reflections with I > 3.0σ(I) were used. The structure was solved and refined similarly to that of isomer **17**. Final refinements converged to R (R_w) = 0.035 (0.031), S = 2.87. An ORTEP drawing of compound **18** is given in Fig. 3.§

Compound **19**, v_{max}(liq. film)/cm^{-1} 3410br (NH and OH); δ_H(CDCl$_3$) 1.15–1.60 (10 H, br m, CH$_2$, NH, and OH), 3.07–3.12 (2 H, t, CH$_2$), 3.44–3.49 (2 H, t, CH$_2$), 4.30 (2 H, s, CH$_2$), 6.66–6.75 (2 H, m, ArH), 6.99–7.02 (1 H, m, ArH), 7.20–7.26 (1
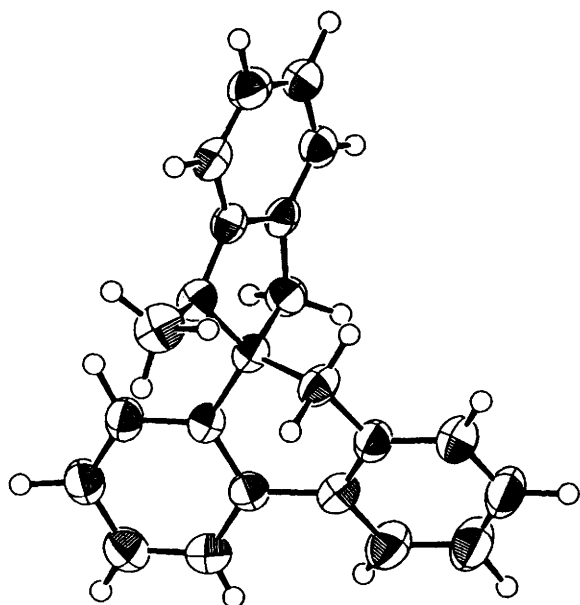
Fig. 4 ORTEP drawing of compound 23

H, m, ArH), 7.36–7.37 (1 H, m, ArH), 7.51–7.74 (5 H, m, ArH), 8.11–8.14 (1 H, m, ArH) and 8.66–8.78 (2 H, m, ArH).

(v) **4 with no additives.** Compound **4** (91 mg) in benzene (20 cm³) in a sealed tube was irradiated to obtain compound **15** (4 mg, 7%) and the unchanged ether **4** (71 mg, 78% recovery).

(vi) **4 in the presence of NMA (Scheme 3).** Argon was bubbled through a solution of compound **4** (864 mg, 3.04 mmol) and NMA (1.65 cm³, 15 mmol) in benzene (190 cm³) in a Pyrex vessel for 30 min and then the solution was irradiated for 5 h with passage of argon. After irradiation, the solution was extracted with aq. sodium hydroxide. Usual treatment of this alkaline extract gave phenol (141 mg, 49%), which was identified by conversion into its 3,5-dinitrobenzoate (mp 142.5–143.5 °C; lit.,[13] 145.8 °C). The benzene layer was distilled under reduced pressure and the residue was chromatographed with toluene. The first eluent contained compounds **15** (76 mg, 13%), **16** (19 mg, 3%), spiro[9,10-dihydrophenanthrene-9,2′-(1′-methylindoline)] **23** (45 mg, 5%), unchanged starting ether **4** (112 mg, 14% recovery) and N-methyl-N-(9-phenanthrylmethyl)aniline **20** (39 mg, 4%) which were separated by chromatography with benzene–hexane (1 : 3, v/v); the second fraction afforded N-methyl-o-(9-phenanthrylmethyl)aniline **21** (69 mg, 8%); and the third contained N-methyl-p-(9-phenanthrylmethyl)aniline **22** (112 mg, 12%) and p-(9-phenanthrylmethyl)-phenol **24** (26 mg, 3%) which were separated by chromatography with toluene–dichloromethane (3 : 1, v/v).

Spectral data for the products.—Compound **21**, mp 144–145.5 °C (Found: C, 88.5; H, 6.4; N, 4.9. $C_{22}H_{19}N$ requires C, 88.85; H, 6.4; N, 4.7%); δ_H(CDCl₃) 2.83 (3 H, s, Me), 4.30 (2 H, s, CH₂), 6.68–6.77 (2 H, m, ArH), 6.96–6.99 (1 H, m, ArH), 7.24–7.30 (1 H, m, ArH), 7.35 (1 H, s, ArH), 7.51–7.75 (5 H, m, ArH), 8.08–8.12 (1 H, m, ArH) and 8.66–8.78 (2 H, m, ArH); λ_{max}(MeOH)/nm 207 (log ε 4.68), 252 (4.81), 276 (4.17), 285 (4.09) and 297 (4.14); ν_{max}(KBr)/cm⁻¹ 3423 (NH).

Compound **22**, mp 111–116 °C; δ_H(CDCl₃) 2.80 (3 H, s, Me), 4.38 (2 H, s, CH₂), 6.54–6.57 (2 H, m, ArH), 7.06–7.09 (2 H, m, ArH), 7.53–7.65 (5 H, m, ArH), 7.79–7.82 (1 H, m, ArH), 8.06–8.07 (1 H, m, ArH) and 8.63–8.73 (2 H, m, ArH).

Compound **24**, mp 152–155 °C (Found: C, 88.4; H, 5.8. $C_{21}H_{16}O$ requires C, 88.7; H, 5.7%); λ_{max}(MeOH)/nm 207 (log ε 4.60), 253 (4.66), 276 (4.10), 284 (4.00) and 297 (3.97); ν_{max}(KBr)/cm⁻¹ 3370 (OH); δ_H(CDCl₃) 4.41 (2 H, s, CH₂), 4.65 (1 H, br s, OH), 6.73–6.76 (2 H, m, ArH), 7.10–7.13 (2 H, m,

ArH), 7.53–7.66 (5 H, m, ArH), 7.79–7.83 (1 H, m, ArH), 8.01–8.04 (1 H, m, ArH) and 8.65–8.74 (2 H, m, ArH).

Compound **23**, mp 135.5–136.5 °C (Found: 88.6; H, 6.4; N, 4.4. $C_{22}H_{19}N$ requires C, 88.85; H, 6.4; N, 4.7%); λ_{max}(MeOH)/nm 252 (log ε 4.49) and 296 (3.80); δ_H(CDCl₃) 2.74 and 3.16 (2 H, AB q, CH₂), 2.80 and 3.29 (2 H, AB q, CH₂), 2.82 (3 H, s, Me), 6.51–6.54 (1 H, m, ArH), 6.62–6.68 (1 H, m, ArH), 6.93–6.96 (1 H, m, ArH), 7.13–7.40 (6 H, m, ArH), 7.54–7.59 (1 H, m, ArH) and 7.76–7.84 (2 H, m, ArH).

Crystal data for compound **23**.—$C_{22}H_{19}N$. Monoclinic, a = 9.752(3), b = 6.471(2), c = 12.898(2) Å, β = 91.58(2)°, V = 813.6(4) Å³, space group $P2_1$ (No. 4), Z = 2, D_c = 1.214 g cm⁻³, μ(Mo-Kα) = 0.65 cm⁻¹. 2169 Reflections (6 ⩽ 2θ ⩽ 55°) were collected and 1334 reflections with I > 2.5σ(I) were used in the structure determination. The structure was solved and refined as for compounds **17** and **18**. Final refinements converged to R (R_w) = 0.049 (0.040), S = 2.31. An ORTEP drawing of compound **23** is shown in Fig. 4.§

(vii) **5 in the presence of NMA.** A solution of compound **5** (105 mg, 0.32 mmol) and NMA (0.18 cm³, 1.6 mmol) in benzene (20 cm³) in a Pyrex tube was prepared. Two tubes of the solution were irradiated and the irradiated mixture was chromatographed to afford compounds **15** (2 mg, 2%), **16** (2 mg, 2%), and unchanged ether **5** (160 mg, 76% recovery).

(viii) **5 in the presence of acetic acid.** Compound **5** (105 mg) in benzene (18 cm³)–acetic acid (2 cm³) in a sealed tube was irradiated, to give the unchanged ether **5** (90 mg, 86% recovery); no other product was detected by ¹H NMR spectroscopy.

(ix) **5 in the presence of NMA and acetic acid.** A mixture of compound **5** (105 mg), NMA (0.18 cm³), acetic acid (2 cm³) and benzene (18 cm³) in a Pyrex tube was irradiated. The products were separated by chromatography with benzene–diethyl ether (10 : 1, v/v) to give a mixture of compounds **15** (trace), **16** (4 mg, 7%), **23** (6 mg, 6%), **20** (5 mg, 5%), and unchanged ether **5** (63 mg, 60% recovery), which were separated by chromatography with benzene–hexane (1 : 3, v v), together with NMA and 3-phenylpropan-1-ol (16 mg, 36%), which was identified as its 3,5-dinitrobenzoate, mp 88–90 °C (lit.,[14] 88–90 °C).

(x) **6 with no additives.** A solution of compound **6** (119 mg, 0.32 mmol) in benzene (20 cm³) in a Pyrex tube was prepared. Two tubes of the solution were irradiated and the irradiated mixture was chromatographed to afford compounds **15** (2 mg, 3%), **16** (1 mg, 2%), and unchanged ether **6** (183 mg, 78% recovery).

(xi) **6 in the presence of acetic acid (Scheme 4).** A solution of compound **6** (119 mg, 0.32 mmol) in benzene (18 cm³)–acetic acid (2 cm³) in a Pyrex tube was irradiated. Chromatography of the irradiation mixture with benzene–diethyl ether (10 : 1, v/v) gave a mixture of compounds **16** (18 mg, 29%), **15** (6 mg, 10%), and 9-phenanthrylmethyl acetate (14 mg, 17%), which were separated by further chromatography, with benzene–hexane (1 : 1, v/v); unchanged ether **6** (38 mg, 32% recovery); and a mixture of 4-[N-methyl-p-(9-phenanthrylmethyl)anilino]-butan-1-ol **25** (3 mg, 3%) and 4-(N-methylanilino)butan-1-ol **26** (18 mg, 31%), which were separated by chromatography with benzene–diethyl ether (5 : 1, v/v).

Spectral data for the products.—9-Phenanthrylmethyl acetate. Mp 77–78.5 °C; ν_{max}(KBr)/cm⁻¹ 1727 (C=O) and 1250 (C–O–C); δ_H(CDCl₃) 2.14 (3 H, s, Me), 5.62 (2 H, s, CH₂), 7.57–7.70 (4 H, m, ArH), 7.83 (1 H, s, ArH), 7.88–7.91 (1 H, m, ArH), 8.03–8.07 (1 H, m, ArH) and 8.66–8.76 (2 H, m, ArH).

Compound **25**, δ_H(CDCl₃) 1.58–1.68 (4 H, m, CH₂), 2.92 (3 H, s, Me), 3.28–3.33 (2 H, m, CH₂), 3.64–3.69 (2 H, m, CH₂), 4.34 (2 H, s, CH₂), 6.69–6.71 (2 H, m, ArH), 7.09–7.12 (2 H, m,

§ See footnote on p. 1464.

ArH), 7.51–7.71 (5 H, m, ArH), 7.80–7.83 (1 H, s, ArH), 8.08–8.10 (1 H, m, ArH) and 8.65–8.74 (2 H, m, ArH).

Compound **26**, oil; v_{max}(neat)/cm^{-1} 3340 (OH); δ_H(CDCl$_3$) 1.54–1.72 (4 H, m, CH$_2$), 2.91 (3 H, s, Me), 3.29–3.34 (2 H, m, CH$_2$), 3.65–3.70 (2 H, t, CH$_2$), 6.64–6.73 (3 H, m, ArH) and 7.18–7.26 (2 H, m, ArH).

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