

## New Photochemical Cyclisation of 9-(6-Anilinohexyl)phenanthrene

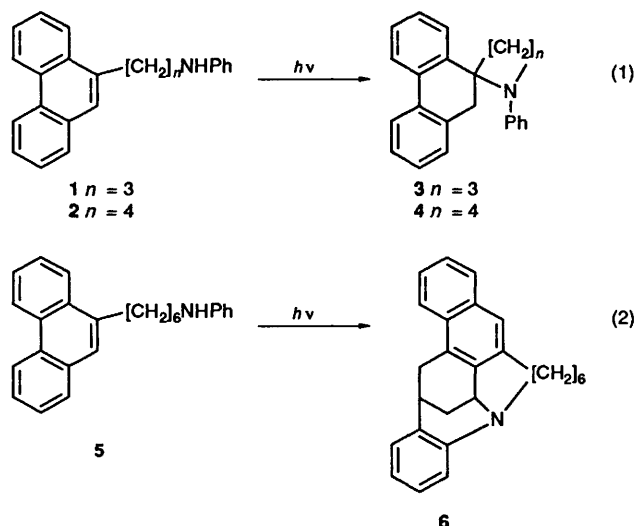
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Irradiation of 9-(6-anilinohexyl)phenanthrene in benzene afforded a new polycyclic compound **6**, the structure of which was determined by an X-ray crystal structure analysis.

Photochemical reactions of aromatic hydrocarbons with amines, studied extensively in relation to the photoinduced electron transfer and exciplex mechanisms,<sup>1</sup> in most cases, are known to proceed *via* a transition state of the sandwich-type overlap of two chromophores, *i.e.* an exciplex intermediate. In the intramolecular cyclisations which are of interest for the preparation of nitrogen-containing heterocycles,<sup>2</sup> the geometry of two chromophores at an excited state is of especial importance.<sup>3</sup> We have already shown that irradiation of 9-(3-anilinopropyl)-**1** and 9-(4-anilinobutyl)-phenanthrene **2** in benzene gives spiro cyclic compounds **3** and **4**, respectively, probably through the formation of an exciplex intermediate<sup>4</sup> [reaction (1)]. We now report that irradiation of 9-(6-anilinohexyl)phenanthrene, **5** in benzene yields a polycyclic compound **6** without the formation of the corresponding spirocyclic compound [reaction (2)].



A solution of the amine **5**† in dry benzene ( $1.6 \times 10^{-2}$  mol  $\text{dm}^{-3}$ ) was placed in a Pyrex tube, degassed under argon by three freeze-pump-thaw cycles, and the tube was sealed under reduced pressure. The solution was irradiated at a distance of 5 cm from a 300 W high-pressure mercury lamp using a merry-go-round apparatus (Eikosha PIH-300) for 5 h.<sup>4</sup> After irradiation, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel with benzene-hexane (1:1, v/v) to give compound **6** as a colourless solid (m.p. 179.5–181 °C; from hexane) in 21% yield with 55%

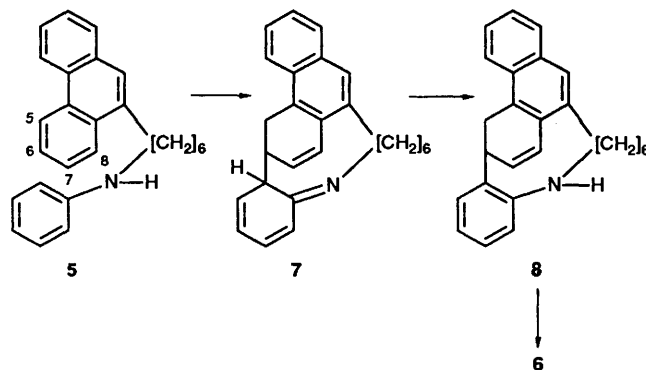
† Starting amine **5** (m.p. 74.5–76.5 °C) was prepared from aniline and 9-phenanthrylhexyl bromide which was obtained from 9-phenanthryllithium and 1,6-dibromohexane. The structure of **5** was established on the basis of the NMR, IR and UV spectra and elemental analysis.

recovery of **5**. When acetonitrile was used as the solvent, the yield of **6** was 2% (69% recovery).

The structure of **6** was determined by the X-ray crystal structure analysis.† Fig. 1 represents the molecular structure of compound **6** which has chiral positions. The crystal belongs to an acentric space group. Furthermore, crystallographic disorder on the methylene chain of the ten-membered ring was observed. Compound **6** has a bent structure in which the dihedral angle between the planes of benzene and naphthalene rings is 106.67°. The spectral data§ and elemental analysis also supported the structure of **6** shown in Fig. 1.

Irradiation of the amine **5** in  $\text{D}_2\text{O}$ -saturated benzene gave the deuterated compound **6**, the <sup>1</sup>H NMR spectrum of which exhibited a lowering of the intensities of the signals at  $\delta$  1.88–2.19 and 3.34–3.54. On the basis of the intensities, it was estimated that two deuterium atoms were incorporated. This fact indicates that the double photoaddition of the anilino group to the phenanthrene ring occurs.

A possible reaction pathway for the formation of **6** is proposed in Scheme 1. The reaction is explained as proceeding



Scheme 1

† Crystal data for **6**.  $\text{C}_{26}\text{H}_{27}\text{N}$ ; orthorhombic; space group  $P2_12_12_1$ ,  $a = 11.625(3)$ ,  $b = 16.666(3)$ ,  $c = 9.780(2)$  Å,  $U = 1895(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.24$  g  $\text{cm}^{-3}$ ,  $\mu$  (Mo-K $\alpha$ ) = 0.66  $\text{cm}^{-1}$ . 2516 Unique reflections ( $6 \leq 2\theta \leq 55^\circ$ ) were collected Rigaku AFC-5R diffractometer using graphite monochromated Mo-K $\alpha$  radiation; 1289 reflections with  $I \geq 3\sigma(I)$  were used in the structure determination. The structure was solved by direct methods and refined by the full-matrix least-square technique with anisotropic thermal parameters for non-hydrogen atoms and with fixed thermal and positional parameters for H atoms to converge to  $R(R_w) = 0.051$  (0.040),  $S = 2.31$ .

§ Spectral and analytical data.  $\delta_{\text{H}}(\text{CDCl}_3)$  1.37–1.47 (2 H, m), 1.61–1.68 (1 H, m), 1.88–2.19 (6 H, m), 2.28–2.43 (1 H, m), 2.71–2.81 (1 H, m), 3.34–3.54 (6 H, m), 4.65–4.67 (1 H, t), 6.70–6.76 (1 H, m), 6.83–6.86 (1 H, d), 6.97–7.04 (1 H, m), 7.12–7.15 (1 H, m), 7.30–7.40 (2 H, m), 7.49 (1 H, s), 7.62–7.67 (1 H, m) and 7.86–7.92 (1 H, m);  $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$  3025, 2910, 2860, 1600, 1490, 1440, 1130, 1110, 875 and 750;  $\lambda_{\text{max}}(\text{hexane})/\text{nm}$  (log  $\epsilon$ ) 234 (4.93), 256.8 (4.04) and 287.6 (3.87) [Found: C, 88.4; H, 7.6; N, 4.0%; M (mass spectrum), 353.  $\text{C}_{26}\text{H}_{27}\text{N}$  requires C, 88.3; H, 7.7; N, 4.0%;  $M$ , 353].

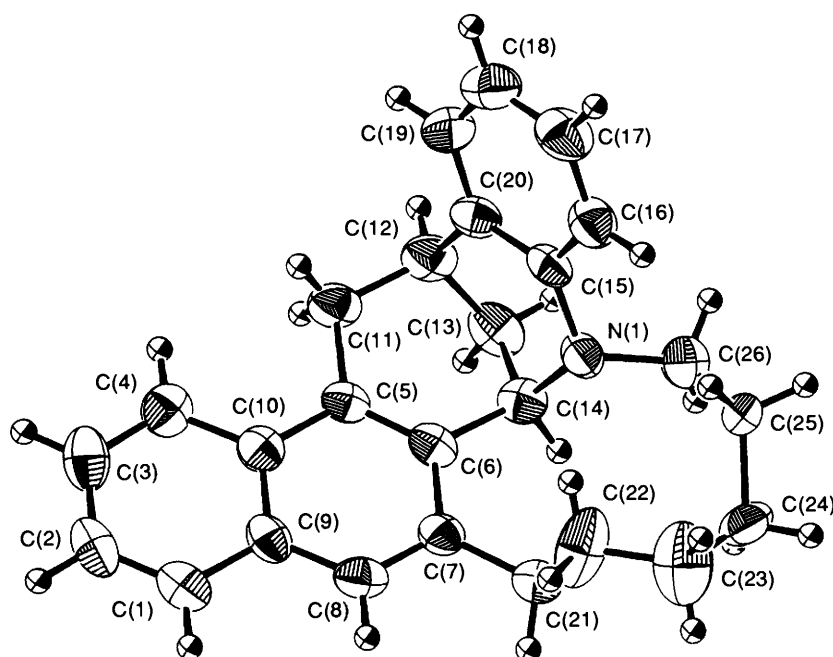


Fig. 1 ORTEP drawing of compound 6

by photoinduced intramolecular cyclisation of the anilino group to the 6-position of the phenanthrene ring to form **7**, which is converted into **8** by hydrogen migration. The consecutive photoaddition of the NH group of **8** to the C(7)–C(8) double bond leads to the formation of **6**. The cyclisation seems to be caused probably by the photoinduced electron transfer from the anilino moiety to the phenanthrene or dihydrophenanthrene ring.

The above results provide evidence for the formation of a polycyclic compound **6**, which has a benzomorphan skeleton, in the photochemical reaction of compound **5** having the hexamethylene bridge.

## References

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