

# Formation of polycyclic compounds in the photoreactions of 9-( $\omega$ -anilinoalkyl)phenanthrenes

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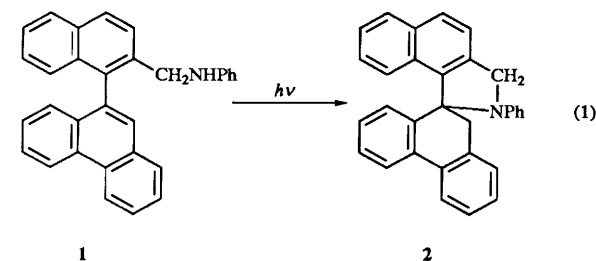
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Photoirradiation of the title compounds, Ar(CH<sub>2</sub>)<sub>n</sub>NHPh (Ar = 9-phenanthryl, *n* = 6–10, and 12), in benzene under anaerobic conditions gave polycyclic compounds with the 2-azabicyclo[3.3.1]nonane skeleton. It is proposed that the photoreaction proceeds by electron transfer *via* an exciplex to give polycyclic compounds as a result of the addition of the NH group to the phenanthrene ring.

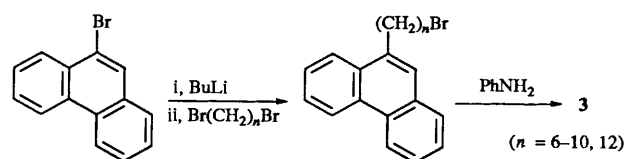
The photochemical reactions of amines with alkenes and arenes have been extensively investigated mainly in connection with electron-transfer reactions.<sup>1</sup> Intramolecular reactions have, in particular, attracted attention as a method for the preparation of nitrogen heterocycles.<sup>2</sup> In our earlier study of the photochemical reaction of 9-(2-anilinomethyl-1-naphthyl)-phenanthrene **1**, the exciplex between the phenanthrene ring and the anilino group was thought to be formed as an intermediate which leads to the formation of the cyclic product **2** [Eqn. (1)].<sup>3</sup>

On the basis of this reaction, we have studied recently the photochemical reactions of 9-( $\omega$ -anilinoalkyl)phenanthrenes **3** (*n* = 3–5), in which the anilino group and the phenanthrene



Scheme 1

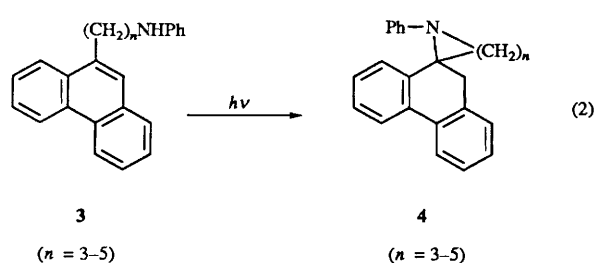
9-(9-anilinonyl)-, 9-(10-anilinodecyl)- and 9-(12-anilinodecyl)-phenanthrenes [**3** (*n* = 6–10 and 12)] were prepared by the method described previously<sup>5</sup> (Scheme 1).



## Photoreaction and identification of products

The photoreaction was carried out by irradiation of the sample solutions, degassed by argon-bubbling in a Pyrex vessel, with a 300 W high-pressure mercury lamp. The photoproducts were separated and purified by column chromatography. The results are summarized in Table 1. As shown in Scheme 2, depending on the length of the methylene chain, the anilino group underwent cyclization to the 6,8-, 1,3- and 9-positions of the phenanthrene ring, to give the cyclic compounds **5–8**. As mentioned later, since compound **6** was converted into compound **5** on irradiation, it was postulated as being an intermediate in the formation of **5**. Since the irradiation of compound **3** (*n* = 6) afforded the cyclic products **5** (*n* = 6) and **6** (*n* = 6) without the formation of **7** and **8**, the cyclization must occur on the 6,8-positions. With a longer methylene chain, however, the cyclization of the anilino group to the 1,3-positions was observed: irradiation of **3** (*n* = 7–10, 12) afforded the corresponding cyclic compounds **5** and **7**, as shown in Table 1.

Spectroscopic and elemental analytical results for the products were consistent with the assigned structures. Representative X-ray crystal-structure analyses were performed for compounds **5** (*n* = 6),<sup>6</sup> **7** (*n* = 9)† and **8** (*n* = 12).‡ Fig. 1



ring are connected by the polymethylene chain at *n* = 3–5, and reported that the spiro compounds **4** (*n* = 3–5) are produced by cyclization of the anilino group with the 9-position of the phenanthrene ring [Eqn. (2)].<sup>4</sup> Here, we describe the photochemical reactions of 9-( $\omega$ -anilinoalkyl)phenanthrenes **3** (*n* = 6–10 and 12), which undergo cyclization of the anilino group with the 1,3- and 6,8-positions of the phenanthrene ring.

## Results and discussion

### Preparation of **3** (*n* = 6–10 and 12)

9-(6-Anilinoethyl)-, 9-(7-anilinoheptyl)-, 9-(8-anilinooctyl)-,

† Crystal data for **7** (*n* = 9). C<sub>29</sub>H<sub>33</sub>N; orthorhombic; space group *Pna*2<sub>1</sub> (No. 33); *a* = 21.673(3), *b* = 8.996(3), *c* = 22.397(4) Å, *U* = 4367(3) Å<sup>3</sup>, *Z* = 8, *D<sub>c</sub>* = 1.203 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.64 cm<sup>-1</sup>. Unique reflections: 5654 (6° < 2 $\theta$  < 55°); used reflections: 2137 [*I* > 2.00 $\sigma$ (*I*)]; *R*(*R<sub>w</sub>*) = 0.062 (0.038); *S* = 1.97.

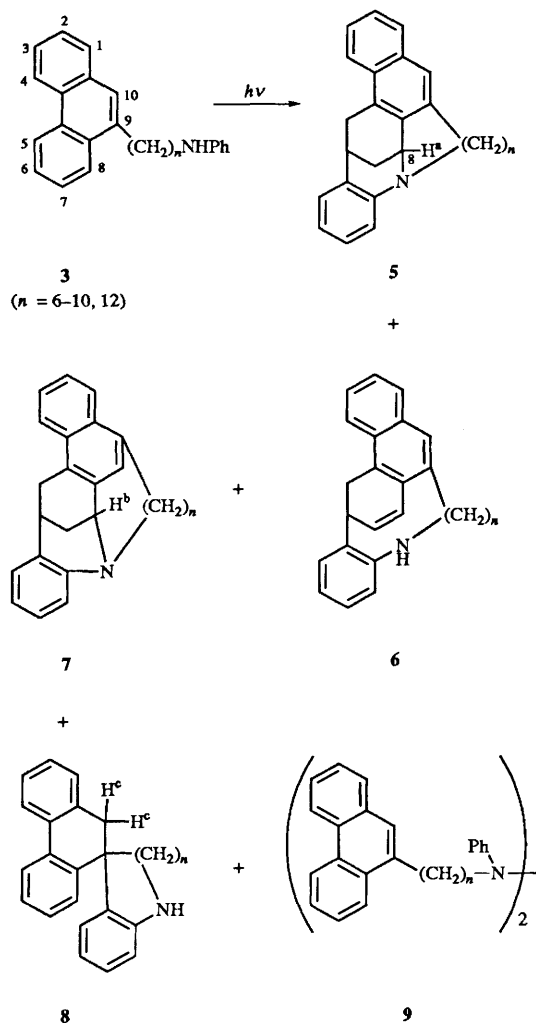
Crystal data for **7** (*n* = 10). C<sub>30</sub>H<sub>35</sub>N; monoclinic; space group *P2<sub>1</sub>/n* (No. 14); *a* = 12.418(7), *b* = 8.710(3), *c* = 21.80(1) Å,  $\beta$  = 103.38(5)°, *U* = 2293(4) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.186 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.63 cm<sup>-1</sup>. Unique reflections: 4277 (6° < 2 $\theta$  < 50°); used reflections: 1313 [*I* > 2.5 $\sigma$ (*I*)]; *R*(*R<sub>w</sub>*) = 0.077 (0.058); *S* = 1.98.

‡ Crystal data for **8** (*n* = 12). C<sub>32</sub>H<sub>39</sub>N; monoclinic; space group *P2<sub>1</sub>/n* (No. 14); *a* = 9.440(3), *b* = 21.646(5), *c* = 12.436(3) Å,  $\beta$  = 101.66(2)°, *U* = 2489(1) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.168 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.62 cm<sup>-1</sup>. Unique reflections: 5741 (6° < 2 $\theta$  < 55°); used reflections: 1815 [*I* > 3.0 $\sigma$ (*I*)]; *R*(*R<sub>w</sub>*) = 0.052 (0.036); *S* = 1.91.

**Table 1** Isolated yields of photoreaction products and recoveries

Compd.	<i>n</i>	Irrad'n time (t/h)	Yield (%)					Recovery (%) 3
			5	6	7	8	9	
3 <sup>a</sup>	6	1.5	17	2	—	0	2	59
3 <sup>a</sup>	7	7.5	5	0	6	0	0	23
3 <sup>b</sup>	7	5	2	—	0	0	1	84
3 <sup>a</sup>	8	8	8	4	11	0	0	35
3 <sup>a</sup>	9	3.6	1	0	1	0	3	58
3 <sup>a</sup>	10	3.5	1	0	4	Trace	0	46
3 <sup>a</sup>	12	3.5	2	0	1	2	Trace	46

<sup>a</sup> An irradiated benzene solution (0.016 mol dm<sup>-3</sup>) in a Pyrex vessel. <sup>b</sup> Degassed by three freeze-pump-thaw cycles and irradiated in a Pyrex sealed tube. Concentration: 0.16 mol dm<sup>-3</sup> in benzene.

**Scheme 2**

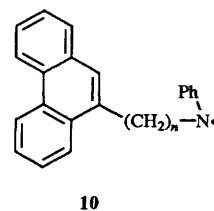
shows the molecular structures of the cyclic products **7** ( $n = 9$ ) and **8** ( $n = 12$ ), thus demonstrating that the anilino group undergoes cyclization to the 1,3- and 9-positions, respectively. The UV spectra for compounds **5**, **7** and **8** were similar to those of 1,2,3-substituted naphthalenes,<sup>7</sup> 1,2,4-substituted naphthalenes,<sup>7</sup> and biphenyl,<sup>8</sup> respectively. The characteristic signals of their <sup>1</sup>H NMR spectra were the singlet signals with fine splitting at  $\delta$  4.6–4.9 and 4.3–4.5 due to C-CH<sup>a</sup>-N-Ph of **5** and C-CH<sup>b</sup>-N-Ph of **7**, respectively, and the AB-type quartet signals at *ca.*  $\delta$  3–4 due to 10-H<sup>c</sup> of the 9,10-dihydrophenanthrene moiety of **8**. In addition, the <sup>1</sup>H NMR signals of **8** at  $\delta$  6.3–7.0 (t, d, d and t

patterns with fine splitting) indicated the presence of the *ortho*-substituted anilino group.

#### Probable intermediates

**Compound 6.** The structures of compounds **6** ( $n = 6, 8$ ) were also established on the basis of spectral results. The <sup>1</sup>H NMR spectrum of **6** exhibited signals similar to those of **5**, due to aromatic hydrogen at  $\delta$  6.6–8.0, the NH group at  $\delta$  4.45 and the olefinic hydrogens at  $\delta$  6.0–6.05 and 7.23–7.25; there was no signal at  $\delta$  4.67 due to the N-CH group of **5**. (Details of the spectral data are shown in the Experimental section.) A solution of compound **6** in C<sub>6</sub>D<sub>6</sub> was irradiated and the spectral changes of its <sup>1</sup>H NMR were followed. Initially, the signals of compound **5** increased as those of **6** decreased; however, prolonged irradiation caused the intensities of the signals of **5** to decrease, thus suggesting further photoreaction (see Fig. 2). In the light of these results, it is reasonable to consider that compound **6** is an intermediate in the formation of **5**.

**Aminyl radical 10.** In addition to the cyclic products, the substituted hydrazines **9** ( $n = 6–10, 12$ ), were obtained in small amounts (see Table 1), the structures of which were established



on the basis of spectral results. Although the UV and <sup>1</sup>H NMR spectra of **9** ( $n = 6–10, 12$ ) resembled very closely those of the starting aniline derivatives **3** ( $n = 6–10, 12$ ) in shape and pattern, there was a remarkable difference in the <sup>1</sup>H NMR spectra for the signals due to NCH<sub>2</sub> and ArCH<sub>2</sub> at  $\delta$  3.0–3.5: **3** ( $n = 6–10, 12$ ) exhibited a multiplet signal centred at  $\delta$  3.1 (4 H) whilst **9** ( $n = 6–10, 12$ ) had two triplets at *ca.*  $\delta$  3.0 (4 H) and 3.4 (4 H). The structure of **9** ( $n = 7$ ) was further confirmed by comparison of its spectral data with those of *N,N'*-bis[7-(9-phenanthryl)heptyl]hydrazobenzene. The formation of **9** indicates that the aminyl radicals **10** are formed as a transient intermediate in the photoreaction process.

#### Yields of cyclic products

As described previously,<sup>4</sup> the yields of the cyclic compounds **4** ( $n = 3–5$ ) decreased in the following order: **4** ( $n = 3$ ) [76% with 12% recovery of **3** ( $n = 3$ )] > **4** ( $n = 4$ ) [31% with 61% recovery of **3** ( $n = 4$ )] > **4** ( $n = 5$ ) [0% with 83% recovery of **3**

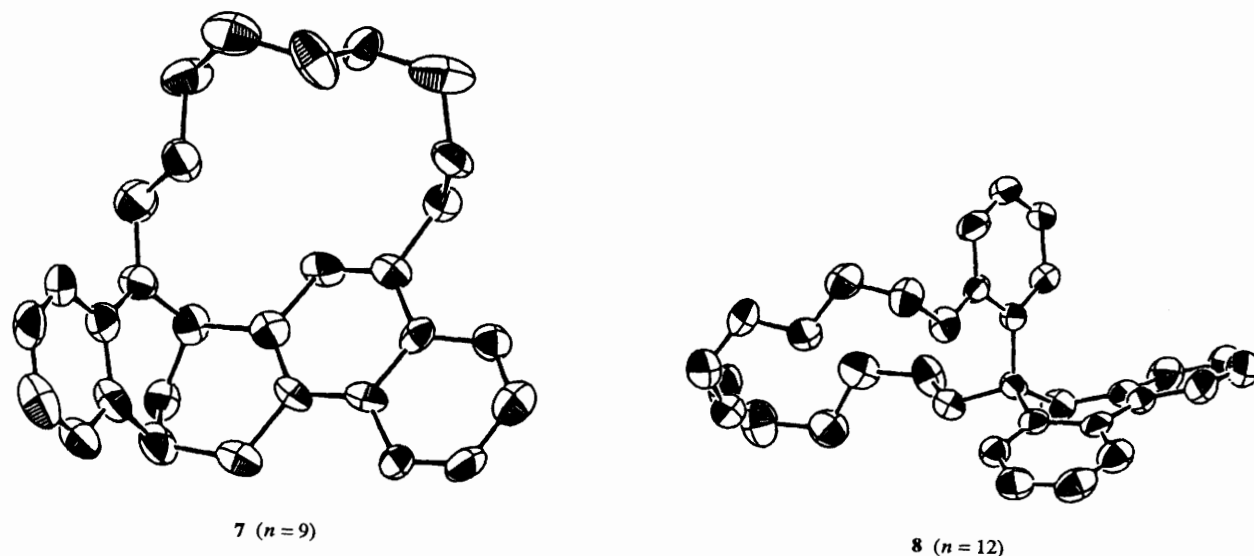


Fig. 1 ORTEP drawings of compounds **7** ( $n = 9$ ) and **8** ( $n = 12$ ). H atoms are excluded for clarity.

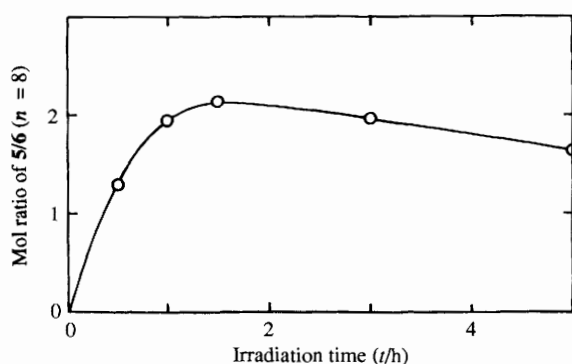


Fig. 2 Change of **6** ( $n = 8$ ) on irradiation

( $n = 5$ )].<sup>§</sup> At  $n \geq 6$ , formation of the cyclic compounds **5–8** was observed, although the yields were much lower (Table 1). As described above, prolonged irradiation failed to increase the yields of compounds **5–8**, because of their further photoreaction (Fig. 2). Furthermore, there was no increase in the products yields for higher concentrations of substrate (10-fold increase over those given in Table 1). The yield of **5** ( $n = 6$ ) was solvent dependent decreasing significantly with a change from benzene (21% yield with 55% recovery) to acetonitrile (2% yield, 69% recovery).<sup>6</sup> This may arise because, as has been suggested by Okada *et al.*,<sup>9</sup> on irradiation, the hydrogen-bonded interaction of the NH group with the  $\pi$ -electrons of the phenanthrene moiety is disturbed by the polar solvent.

#### Proposed reaction pathway for the formation of compounds **5**, **6** and **7**

As in a series of reactions described in our previous paper, it is reasonable to consider that the reaction proceeds by the photoinduced electron transfer *via* an exciplex **11**, having the  $\pi$ - $\pi$  stacking structure with the NH/ $\pi$  interaction, to form the radical anion–radical cation pair **12** (Scheme 3). The reaction pathway for the formation of **5**, **6** and **7** from **12** is proposed in Scheme 3. A proton transfer from the radical cation of **12** to the 5- and 4-positions of the phenanthryl radical anion brings about intermediate formation of **13** and **14**, respectively. The formation of **5** and **7** indicates that the 6- and 3-positions of the

phenanthryl radicals of **13** and **14** are bonded to the *ortho* position of the anilino group to give **15** and **16**, respectively. Thus, the position of the cyclization depends on the length of the methylene chain. The aromatization of **15** to **6**, followed by the photochemical addition of the NH group of **6** to the C(7)–C(8) double bond, leads to the formation of **5**. On the other hand, **16** also undergoes intramolecular cyclization by a similar process to give **7**.

#### Experimental

Mps were determined with a Yanaco micromelting point apparatus (MP-500) and are uncorrected. Spectra were recorded on a Shimadzu UV-160A spectrophotometer (UV), on a Hitachi 215 spectrophotometer or on a Perkin-Elmer FT-IR type-1600 spectrophotometer (IR), and on a JNM-GX270 spectrometer (<sup>1</sup>HNMR) which was used tetramethylsilane as internal standard. Photoirradiation was carried out using a 300W high-pressure mercury lamp (Eikosha PIH-300).

X-Ray diffraction data were collected by using a Rigaku AFC5R diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) and an 18 kW rotating anode generator. Cell dimensions were obtained by least-squares fitting from 25 high angle reflections. All computations for the structure determination were carried out on VAX station 3100 using a crystallographic program package TEXSAN.<sup>10</sup>

#### Materials

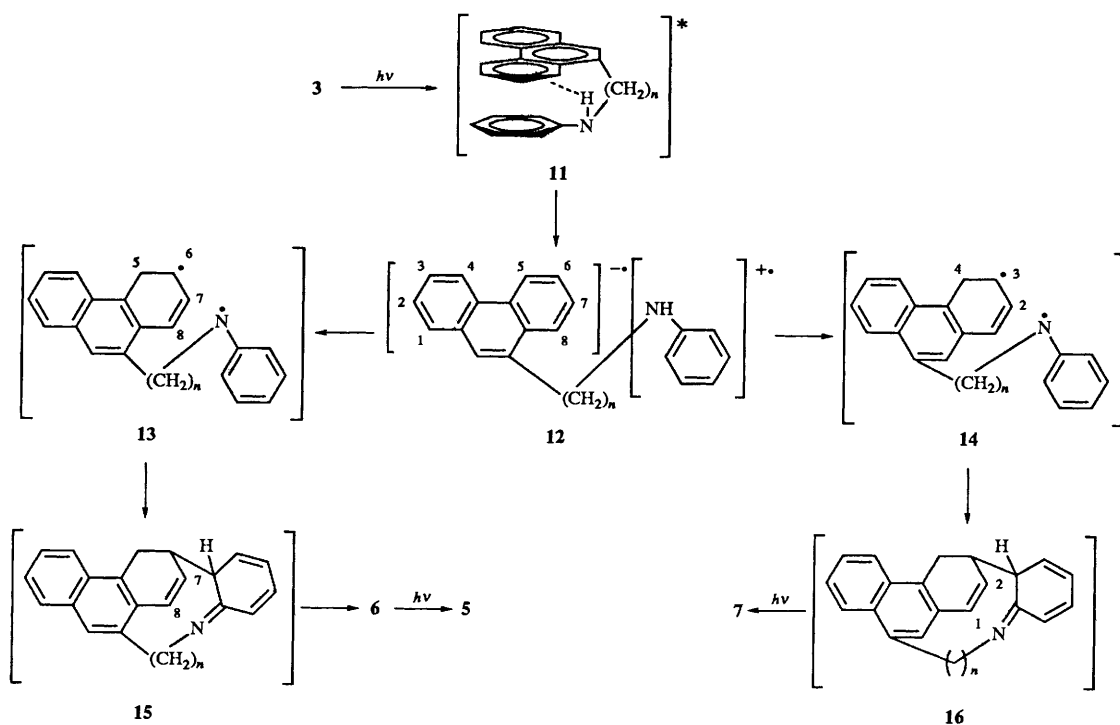
Aniline derivatives **3** ( $n = 6$ ) and **3** ( $n = 10$ ) and the corresponding bromides have been reported earlier.<sup>5</sup> Other phenanthrylalkyl bromides and anilinoalkylphenanthrenes were prepared according to the method described in an earlier paper.<sup>5</sup>

**7**-(9-Phenanthryl)heptyl bromide.—Mp 67–68 °C (hexane), 51% yield (Found: C, 71.1; H, 6.6. C<sub>21</sub>H<sub>23</sub>Br requires C, 71.0; H, 6.5%);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.26–1.52 (6 H, m), 1.76–1.90 (4 H, m), 3.07–3.13 (2 H, t), 3.37–3.42 (2 H, t), 7.53–7.67 (5 H, m), 7.80–7.84 (1 H, m), 8.07–8.11 (1 H, m) and 8.63–8.76 (2 H, m).

**8**-(9-Phenanthryl)octyl bromide.—Mp 70–72 °C (hexane), 81% yield (Found: C, 71.2; H, 7.1. C<sub>22</sub>H<sub>25</sub>Br requires C, 71.5; H, 6.8%);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.26–1.51 (8 H, m), 1.76–1.90 (4 H, m), 3.08–3.14 (2 H, t), 3.37–3.42 (2 H, t), 7.53–7.68 (5 H, m), 7.81–7.84 (1 H, m), 8.09–8.12 (1 H, m) and 8.64–8.75 (2 H, m).

**9**-(9-Phenanthryl)nonyl bromide.—Mp 75.5–77 °C (hexane), 38% yield (Found: C, 71.9; H, 7.2. C<sub>23</sub>H<sub>27</sub>Br requires C, 72.1; H, 7.1%);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.32–1.54 (10 H, m), 1.75–1.89 (4 H, m),

<sup>§</sup>Prolonged irradiation gave a 7-membered cyclic product, 1'-phenylspiro[9, 10-dihydrophenanthrene-9,2'-azepane], **4** ( $n = 5$ ).<sup>5</sup>



Scheme 3

3.07–3.13 (2 H, t), 3.37–3.42 (2 H, t), 7.53–7.68 (5 H, m), 7.80–7.84 (1 H, m), 8.08–8.12 (1 H, m) and 8.63–8.75 (2 H, m).

**12-(9-Phenanthryl)dodecyl bromide.**—Mp 85–86 °C (hexane), 48% yield (Found: C, 73.2; H, 8.0.  $C_{26}H_{33}Br$  requires C, 73.4; H, 7.8%);  $\delta_H(CDCl_3)$  1.28–1.51 (16 H, m), 1.79–1.87 (4 H, m), 3.08–3.13 (2 H, t), 3.38–3.42 (2 H, t), 7.56–7.66 (5 H, m), 7.81–7.84 (1 H, m), 8.09–8.13 (1 H, m) and 8.64–8.75 (2 H, m).

**9-(7-Anilinoheptyl)phenanthrene 3** ( $n = 7$ ).—Mp 82–83 °C (hexane), 74% yield (Found: C, 88.2; H, 7.9; N, 3.7.  $C_{27}H_{29}N$  requires C, 88.2; H, 7.95; N, 3.8%);  $\lambda_{max}(\text{hexane})/nm$  223 (log  $\epsilon$  4.44), 252 (4.85) and 298 (4.18);  $\nu_{max}(KBr)/cm^{-1}$  3400 (NH);  $\delta_H(CDCl_3)$  1.42–1.84 (10 H, m), 3.06–3.13 (4 H, m), 3.55 (1 H, br s, NH), 6.57–6.70 (3 H, m), 7.13–7.19 (2 H, m), 7.53–7.68 (5 H, m), 7.80–7.83 (1 H, m), 8.08–8.11 (1 H, m) and 8.63–8.75 (2 H, m);  $m/z$  367 ( $M^+$ , 30%) and 106 (100).

**9-(8-Anilinoheptyl)phenanthrene 3** ( $n = 8$ ).—Mp 73–75 °C (hexane), 76% yield (Found: C, 88.3; H, 8.5; N, 3.7.  $C_{28}H_{31}N$  requires C, 88.1; H, 8.2; N, 3.7%);  $\lambda_{max}(\text{cyclohexane})/nm$  253 (log  $\epsilon$  4.71), 278 (4.05), 287 (3.97) and 299 (4.04);  $\nu_{max}(KBr)/cm^{-1}$  3380 (NH);  $\delta_H(CDCl_3)$  1.26–1.63 (10 H, m), 1.76–1.88 (2 H, m), 3.07–3.14 (4 H, m), 3.57 (1 H, br s, NH), 6.57–6.71 (3 H, m), 7.13–7.20 (2 H, m), 7.54–7.69 (5 H, m), 7.81–7.84 (1 H, m), 8.09–8.13 (1 H, m) and 8.64–8.76 (2 H, m).

**9-(9-Anilinoheptyl)phenanthrene 3** ( $n = 9$ ).—Mp 80–81.5 °C (hexane), 79% yield (Found: C, 88.0; H, 8.6; N, 3.6.  $C_{29}H_{33}N$  requires C, 88.05; H, 8.4; N, 3.5%);  $\lambda_{max}(\text{hexane})/nm$  222 (log  $\epsilon$  4.43), 252 (4.84) and 297 (4.17);  $\nu_{max}(KBr)/cm^{-1}$  3420 (NH);  $\delta_H(CDCl_3)$  1.34–1.62 (12 H, m), 1.76–1.84 (2 H, m), 3.06–3.13 (4 H, m), 3.59 (1 H, br s, NH), 6.60–6.71 (3 H, m), 7.13–7.19 (2 H, m), 7.53–7.68 (5 H, m), 7.81–7.84 (1 H, m), 8.09–8.12 (1 H, m) and 8.63–8.75 (2 H, m).

**9-(12-Anilinoheptyl)phenanthrene 3** ( $n = 12$ ).—Mp 67–68.5 °C (hexane), 78% yield (Found: C, 87.6; H, 9.2; N, 3.2.  $C_{32}H_{39}N$  requires C, 87.8; H, 9.0; N, 3.2%);  $\lambda_{max}(\text{hexane})/nm$  222 (log  $\epsilon$  4.43), 252 (4.84) and 297 (4.16);  $\nu_{max}(KBr)/cm^{-1}$  3420 (NH);  $\delta_H(CDCl_3)$  1.21–1.63 (18 H, m), 1.79–1.84 (2 H, m), 3.06–3.13 (4 H, m), 3.60 (1 H, br s, NH), 6.58–6.71 (3 H, m), 7.13–7.19 (2 H, m), 7.55–7.66 (5 H, m), 7.81–7.84 (1 H, m), 8.09–8.13 (1 H, m) and 8.64–8.75 (2 H, m).

***N,N'*-Bis[7-(9-phenanthryl)heptyl]hydrazobenzene 9** ( $n = 7$ ). A solution of butyllithium (15% solution in hexane; 0.7 cm<sup>3</sup>, 1.13 mmol) was added dropwise to a stirred solution of hydrazobenzene (218 mg, 1.18 mmol) in dimethyl sulfoxide (DMSO) (10 cm<sup>3</sup>). To this reaction mixture was added a solution of 9-(7-bromoheptyl)phenanthrene (422 mg, 1.19 mmol) in DMSO (40 cm<sup>3</sup>) over 20 min and the mixture was stirred for 1 h. To this mixture was added a solution of butyllithium (15% solution in hexane; 1.4 cm<sup>3</sup>, 2.26 mmol) followed by a solution of 9-(7-bromoheptyl)phenanthrene (411 mg, 1.16 mmol) in DMSO (40 cm<sup>3</sup>) over 15 min. After being stirred for 1 h, the reaction mixture was extracted with ether. Evaporation of the extract gave a solid which was separated by chromatography on silica gel with hexane–benzene (1 : 1, v/v) to afford the title compound **9** ( $n = 7$ ) (44 mg, 5%) as a colourless solid (in the second fraction), mp 141–144 °C (from hexane–benzene) (Found: C, 88.2; H, 7.7; N, 3.7.  $C_{54}H_{56}N_2$  requires C, 88.5; H, 7.7; N, 3.8%);  $\lambda_{max}(CH_2Cl_2)/nm$  255 (log  $\epsilon$  5.11), 278 (4.47), 288 (4.36) and 300 (4.41);  $\delta_H(CDCl_3)$  1.27–1.78 (20 H, m, CH<sub>2</sub>), 3.07 (4 H, t, CH<sub>2</sub>), 3.40 (4 H, t, NCH<sub>2</sub>), 6.68–6.77 (6 H, m, ArH), 7.16–7.22 (4 H, m, ArH), 7.51–7.65 (10 H, m, ArH), 7.77–7.81 (2 H, m, ArH), 8.05–8.09 (2 H, m, ArH) and 8.62–8.73 (4 H, m, ArH).

***N*-[7-(9-Phenanthryl)heptyl]hydrazobenzene** was obtained from the third fraction (347 mg, 64%), mp 68–72 °C (Found: C, 86.35; H, 7.55; N, 6.4.  $C_{33}H_{34}N_2$  requires C, 86.4; H, 7.5; N, 6.1%);  $\delta_H(CDCl_3)$  1.26–1.77 (10 H, m, CH<sub>2</sub>), 3.02 (2 H, t, CH<sub>2</sub>), 3.39 (2 H, t, CH<sub>2</sub>), 5.43 (1 H, s, NH), 6.70–6.86 (6 H, m, ArH), 7.07–7.21 (4 H, m, ArH), 7.50–7.60 (5 H, m, ArH), 7.76 (1 H, t, ArH), 8.04 (1 H, t, ArH) and 8.56–8.68 (2 H, m, ArH); starting bromide was recovered from the first fraction (522 mg).

#### Preparative photoirradiation

A typical preparative irradiation in a Pyrex vessel (internal irradiation) is described for compound **3** ( $n = 8$ ). Argon was bubbled through a solution of 9-(8-anilinoheptyl)phenanthrene **3** ( $n = 8$ ) (1.16 g, 3.0 mmol) in benzene (190 cm<sup>3</sup>) in a Pyrex vessel for 30 min after which it was irradiated with continuous passage of argon. After irradiation for 8 h, the mixture was evaporated

under reduced pressure and the residue was chromatographed on silica gel with benzene-hexane (1:3, v/v) as eluent. The first fraction gave a cyclic product **5** ( $n = 8$ ) as a colourless solid (92 mg); the second afforded a cyclic product **7** ( $n = 8$ ) (colourless, 131 mg) and the third a precursor to **5** ( $n = 8$ ) [ $=6$  ( $n = 8$ )] (45 mg). Unchanged amine **3** ( $n = 8$ ) was in the 5th fraction (405 mg).

**6,7,8,9,10,11,12,13,21,22-Decahydro-22,5,14,20[1,2,3]prop-  
anetriyl[3]ylidenedibenzo[*b,g*]azacyclooctadecine 5** ( $n = 8$ ). Mp 199–201 °C (hexane) (Found: 87.9; H, 8.3; N, 3.8.  $C_{28}H_{31}N$  requires C, 88.1; H, 8.2; N, 3.7%);  $\lambda_{\max}$ (hexane)/nm 234 (log  $\epsilon$  4.90) and 253 (4.01);  $\delta_H$ ( $CDCl_3$ ) 1.21–1.91 (10 H, m), 2.06–2.35 (4 H, m), 2.49–2.60 (1 H, m), 3.05–3.16 (1 H, m), 3.33–3.50 (5 H, m), 4.67–4.69 (1 H, t), 6.71–6.77 (2 H, m), 6.97–7.04 (1 H, m), 7.12–7.15 (1 H, d  $J$  7.93), 7.31–7.40 (2 H, m), 7.54 (1 H, s), 7.64–7.67 (1 H, m) and 7.88–7.91 (1 H, m).

**6,7,8,9,10,11,12,13,20,21-Decahydro-21,5,19,14[1,2]butane-  
diyl[3,4]diylidenedibenzo[*b,g*]azacycloheptadecine 7** ( $n = 8$ ). Mp 204–207 °C (hexane) (Found: C, 87.8; H, 8.2; N, 3.5.  $C_{28}H_{31}N$  requires C, 88.1; H, 8.2; N, 3.7%);  $\lambda_{\max}$ (hexane)/nm 214 (log  $\epsilon$  4.64), 234 (4.76) and 259 (4.18);  $\delta_H$ ( $CDCl_3$ ) 0.92–1.88 (14 H, m), 2.04–2.14 (3 H, m), 2.83–2.92 (1 H, m), 3.33–3.67 (6 H, m), 4.36 (1 H, s), 6.55–6.62 (2 H, m), 6.94–7.01 (1 H, m), 7.12–7.16 (1 H, m), 7.36 (1 H, s), 7.40–7.58 (2 H, m) and 7.90–7.98 (2 H, m).

***N,N'*-Bis[8-(9-phenanthryl)octyl]hydrazobenzene 9** ( $n = 8$ ). This was obtained in the third chromatographic fraction (yield: 1%) of irradiation mixture at high-concentration (0.11 mol  $dm^{-3}$ ) as a yellow oil;  $\delta_H$ ( $CDCl_3$ ) 1.25–1.80 (24 H, m), 3.07 (4 H, t), 3.40 (4 H, t), 6.58–6.78 (6 H, m), 7.13–7.22 (4 H, m), 7.43–7.66 (10 H, m), 7.79 (2 H, t), 8.07 (2 H, t) and 8.62–8.73 (4 H, m).

**6,7,8,9,10,11,12,13,21,22-Decahydro-5*H*-22,14,20[1,3]prop-  
1-enediyl[3]ylidenedibenzo[*b,g*]azacyclooctadecine 6** ( $n = 8$ ). Mp 165–167.5 °C (from hexane) (Found: C, 87.8; H, 8.2; N, 3.4.  $C_{28}H_{31}N$  requires C, 88.1; H, 8.2; N, 3.7%);  $\lambda_{\max}$ (hexane)/nm 242 (log  $\epsilon$  4.19), 251 (4.28), 260 (4.41) and 270 (4.48);  $\nu_{\max}$ (KBr)/ $cm^{-1}$  3393 (NH);  $\delta_H$ ( $CDCl_3$ ) 0.77–1.95 (12 H, m), 2.63–2.73 (1 H, m), 3.00–3.18 (2 H, m), 3.25–3.32 (1 H, m), 3.38–3.57 (1 H, m), 3.77–3.88 (1 H, m), 4.09–4.20 (1 H, m), 4.46 (1 H, br s), 6.00–6.05 (1 H, m), 6.66–6.73 (2 H, m), 6.93–6.98 (1 H, m), 7.09–7.18 (1 H, m), 7.21–7.24 (1 H, m), 7.36–7.43 (3 H, m), 7.69–7.75 (1 H, m) and 7.86–7.90 (1 H, m).

#### Photoreaction of **3** ( $n = 6$ )

A solution of **3** ( $n = 6$ ) (750 mg, 2.12 mmol) in benzene (130  $cm^3$ ) was irradiated for 1.5 h. Chromatography of the irradiation mixture with hexane-benzene (1:3, v/v) as eluent gave the cyclic product **5** ( $n = 6$ ) in the first fraction (126 mg),<sup>6</sup> **9** ( $n = 6$ ) in the second fraction, **6** ( $n = 6$ ) in the third, and **3** ( $n = 6$ ) in the fourth (recovery) (Table 1).

**6,7,8,9,10,11,19,20-Octahydro-5*H*-20,12,18[1,3]prop-1-  
enediyl[3]ylidenedibenzo[*b,g*]azacyclohexadecine 6** ( $n = 6$ ). Mp 199–201 °C (Found: C, 88.0; H, 7.7; N, 4.1.  $C_{26}H_{27}N$  requires C, 88.3; H, 7.7; N, 4.0%);  $\lambda_{\max}$ (hexane)/nm 242 (log  $\epsilon$  4.47), 251 (4.56), 260 (4.66) and 270 (4.65);  $\nu_{\max}$ (KBr)/ $cm^{-1}$  3425 (NH);  $\delta_H$ ( $CDCl_3$ ) 0.42–1.54 (6 H, m), 1.83–1.97 (2 H, m), 2.52–2.61 (1 H, m), 2.73–2.93 (2 H, m), 3.20–3.29 (1 H, m), 3.50–3.78 (2 H, m), 4.07–4.19 (1 H, m), 4.20 (1 H, br s), 6.09–6.15 (1 H, m), 6.46 (1 H, d), 6.59–6.64 (1 H, m), 7.03–7.25 (3 H, m), 7.28–7.42 (2 H, m), 7.53 (1 H, s), 7.70–7.73 (1 H, m) and 7.83–7.89 (1 H, m).

***N,N'*-Bis[6-(9-phenanthryl)hexyl]hydrazobenzene 9** ( $n = 6$ ). A yellow oil;  $\delta_H$ ( $CDCl_3$ ) 1.25–1.87 (16 H, m), 3.05 (4 H, t), 3.41 (4 H, t), 6.58–6.77 (6 H, m), 7.16–7.22 (4 H, m), 7.53–7.66 (10 H, m), 7.76–7.81 (2 H, m), 8.04–8.07 (2 H, m) and 8.61–8.75 (4 H, m).

#### Photoreaction of **3** ( $n = 7$ )

A solution of **3** ( $n = 7$ ) (1.12 g, 3.05 mmol) in benzene (190  $cm^3$ ) was irradiated for 7.5 h. Chromatography of the irradiation

mixture with hexane-benzene (3:1, v/v) as eluent gave a cyclic product **5** ( $n = 7$ ) (57 mg) in the first fraction, the cyclic product **7** ( $n = 7$ ) (67 mg) in the second, and unchanged amine **3** ( $n = 7$ ) (263 mg) in the third.

***N,N'*-Bis[7-(9-phenanthryl)heptyl]hydrazobenzene 9** ( $n = 7$ ) was obtained in the third chromatographic fraction (2%) of a mixture irradiated at high concentration in a sealed tube (0.16 mol  $dm^{-3}$ ).

**7,8,9,10,11,12,20,21-Octahydro-6*H*-21,5,13,19[1,2,3]prop-  
anetriyl[3]ylidenedibenzo[*b,g*]azacycloheptadecine 5** ( $n = 7$ ). Mp 159–161 °C (hexane) (Found: C, 88.0; H, 8.1; N, 3.6.  $C_{27}H_{29}N$  requires C, 88.2; H, 7.95; N, 3.8%);  $\lambda_{\max}$ (hexane)/nm 234 (log  $\epsilon$  4.92) and 255 (4.08);  $\delta_H$ ( $CDCl_3$ ) 1.54–1.97 (10 H, m), 2.09–2.11 (1 H, m), 2.26–2.33 (1 H, m), 2.60–2.65 (1 H, m), 3.29–3.55 (6 H, m), 4.81–4.83 (1 H, m), 6.68–6.73 (2 H, m), 6.96–7.03 (1 H, m), 7.15–7.18 (1 H, m), 7.35–7.39 (2 H, m), 7.53 (1 H, s), 7.65–7.69 (1 H, m) and 7.87–7.90 (1 H, m).

**7,8,9,10,11,12,19,20-Octahydro-6*H*-20,5,18,13[1,2]butane-  
diyl[3,4]diylidenedibenzo[*b,g*]azacyclohexadecine 7** ( $n = 7$ ). Mp 237–238 °C (hexane) (Found: C, 88.2; H, 8.2; N, 3.7.  $C_{27}H_{29}N$  requires C, 88.2; H, 7.95; N, 3.8%);  $\lambda_{\max}$ (hexane)/nm 214 (log  $\epsilon$  4.62), 233 (4.78) and 260 (4.19);  $\delta_H$ ( $CDCl_3$ ) 0.21–0.62 (2 H, m), 1.02–2.29 (10 H, m), 2.92–3.03 (1 H, m), 3.23–3.62 (5 H, m), 3.89–4.01 (1 H, m), 4.43–4.44 (1 H, t), 6.56–6.61 (2 H, m), 6.98–7.04 (1 H, m), 7.14–7.23 (1 H, m), 7.40–7.50 (3 H, m) and 7.93–8.01 (2 H, m).

**Compound 9** ( $n = 7$ ). Mp 143–145 °C (hexane);  $\lambda_{\max}$ ( $CH_2Cl_2$ )/nm 255 (log  $\epsilon$  5.10), 278 (4.45), 288 (4.33) and 300 (4.38);  $\delta_H$ ( $CDCl_3$ ) 1.25–1.80 (20 H, m,  $CH_2$ ), 3.07 (4 H, t,  $CH_2$ ), 3.40 (4 H, t,  $NCH_2$ ), 6.68–6.76 (6 H, m, ArH), 7.16–7.24 (4 H, m, ArH), 7.51–7.65 (10 H, m, ArH), 7.77–7.81 (2 H, m, ArH), 8.05–8.08 (2 H, m, ArH) and 8.61–8.73 (4 H, m, ArH).

#### Photoreaction of **3** ( $n = 9$ )

A solution of compound **3** ( $n = 9$ ) (0.80 g, 2.02 mmol) in benzene (125  $cm^3$ ) was irradiated for 3.6 h. Chromatography of the irradiation mixture with hexane-benzene (3:1, v/v) as eluent gave the cyclic product **5** ( $n = 9$ ) (9 mg) in the first fraction, the cyclic product **7** ( $n = 9$ ) (11 mg) in the second, the hydrazine derivative **9** ( $n = 9$ ) (11 mg) in the third and unchanged amine **3** ( $n = 9$ ) (465 mg) in the fourth. Prolonged irradiation gave rise to different yields of compounds **5** ( $n = 9$ ) (a trace) and **7** ( $n = 9$ ) (a trace), formation of the spiro compound **8** ( $n = 9$ ) (1%) and recovery of compound **3** ( $n = 9$ ) (39%).

**7,8,9,10,11,12,13,14,22,23-6*H*-Decahydro-23,5,15,21[1,2,3]-  
propanetriyl[3]ylidenedibenzo[*b,g*]azacyclononadecine 5** ( $n = 9$ ). Mp 180–182 °C (hexane) (Found: C, 87.7; H, 8.5; N, 3.6.  $C_{29}H_{33}N$  requires C, 88.05; H, 8.4; N, 3.5%);  $\lambda_{\max}$ (hexane)/nm 233 (log  $\epsilon$  4.90) and 255 (4.04);  $\delta_H$ ( $CDCl_3$ ) 1.50–2.28 (15 H, m), 2.91–3.57 (8 H, m), 4.75 (1 H, s), 6.68–6.76 (2 H, m), 6.98–7.04 (1 H, m), 7.15–7.18 (1 H, m), 7.35–7.41 (2 H, m), 7.53 (1 H, s), 7.65–7.70 (1 H, m) and 7.87–7.90 (1 H, m).

**7,8,9,10,11,12,13,14,21,22-Decahydro-6*H*-22,5,20,15[1,2]bu-  
tanediyl[3,4]diylidenedibenzo[*b,g*]azacyclooctadecine 7** ( $n = 9$ ).<sup>†</sup> Mp 210–212 °C (hexane) (Found: C, 87.65; H, 8.3; N, 3.1.  $C_{29}H_{33}N$  requires C, 88.05; H, 8.4; N, 3.5%);  $\lambda_{\max}$ (hexane)/nm 215 (log  $\epsilon$  4.61), 233 (4.75) and 259 (4.15);  $\delta_H$ ( $CDCl_3$ ) 1.11–2.21 (17 H, m), 2.75–2.86 (1 H, m), 3.30–3.54 (4 H, m), 3.80–3.89 (1 H, m), 4.43–4.44 (1 H, t), 6.52–6.62 (2 H, m), 7.00–7.07 (1 H, m), 7.17–7.20 (1 H, m), 7.25 (1 H, s), 7.29–7.49 (2 H, m) and 7.93–8.02 (2 H, m).

**Spiro[9,10-dihydrophenanthrene-9,10'-(1',2',3',4',5',6',7',8',  
9',10'-decahydro[1]benzazadodecine)] 8** ( $n = 9$ ). Mp 202.5–

<sup>†</sup> See footnote on p. 1597.

203.5 °C (hexane);  $\lambda_{\max}(\text{hexane})/\text{nm}$  209 (log  $\epsilon$  4.70) and 255 (4.23);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3440 (NH);  $\delta_{\text{H}}(\text{CDCl}_3)$  0.86–1.76 (15[18]H, s, m), 2.99 (1 H, d,  $J$  14.65), 2.89–3.00 (2 H, m), 3.27–3.33 (1 H, m), 3.63 (1 H, d,  $J$  14.65), 4.21 (1 H, br s, NH), 6.39–6.45 (1 H, m), 6.54 (1 H, t), 6.78–6.81 (1 H, m), 6.96–7.03 (1 H, m), 7.15–7.39 (5 H, m) and 7.57–7.75 (3 H, m).

***N,N'*-Bis[9-(9-phenanthryl)nonyl]hydrazobenzene, 9 ( $n = 9$ ).**  $\delta_{\text{H}}(\text{CDCl}_3)$  1.17–1.83 (28 H, m), 3.06 (4 H, t), 3.40 (4 H, t), 6.68–6.78 (6 H, m), 7.16–7.22 (4 H, m), 7.50–7.64 (10 H, m), 7.77–7.81 (2 H, m), 8.06–8.09 (2 H, m) and 8.60–8.72 (4 H, m).

#### Photoreaction of 3 ( $n = 10$ )

A solution of 3 ( $n = 10$ ) (1.08 g, 2.6 mmol) in benzene (165 cm<sup>3</sup>) was irradiated for 3.5 h. Chromatography of the irradiation mixture with hexane–benzene (3:1, v/v) gave the cyclic product 7 ( $n = 10$ ) (41 mg) in first fraction, cyclic product 5 ( $n = 10$ ) (11 mg) in the second, the precursor to 5 ( $n = 10$ ) (trace) in the third, the cyclic product 8 ( $n = 10$ ) (trace) in the 4th and unchanged amine 3 ( $n = 10$ ) (494 mg) in the 5th.

**6,7,8,9,10,11,12,13,14,15,23,24-Dodecahydro-24,5,16,22-[1,2,3]propanetriyl[3]ylidenedibenzo[*b,g*]azacycloicosine 5 ( $n = 10$ ).** Mp 165–166.5 °C (hexane) (Found: 88.0; H, 8.6; N, 3.1. C<sub>30</sub>H<sub>35</sub>N requires C, 88.0; H, 8.6; N, 3.4%);  $\lambda_{\max}(\text{hexane})/\text{nm}$  233 (log  $\epsilon$  4.80) and 256 (4.02);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.27–2.22 (17 H, m), 2.71–2.81 (1 H, m), 3.23–3.61 (7 H, m), 4.83 (1 H, s), 6.62–6.69 (2 H, m), 6.97–7.03 (1 H, m), 7.16 (1 H, d), 7.35–7.38 (2 H, m), 7.51 (1 H, s), 7.64–7.68 (1 H, m) and 7.86–7.89 (1 H, m).

**6,7,8,9,10,11,12,13,14,15,22,23-Dodecahydro-23,5,21,16-[1,2]butanediyl[3,4]diylidenedibenzo[*b,g*]azacyclononadecine 7 ( $n = 10$ ).** † Mp 230–231.5 °C (hexane),  $\lambda_{\max}(\text{hexane})/\text{nm}$  214 (log  $\epsilon$  4.58), 234 (4.69) and 258 (4.05);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.15–1.85 (16[21]H, s, m), 1.99–2.13 (2 H, m), 2.75–2.95 (1 H, m), 3.30–3.50 (6 H, m), 4.32–4.34 (1 H, t), 6.61–6.68 (2 H, m), 6.99–7.05 (1 H, m), 7.15–7.20 (2 H, m), 7.42–7.47 (2 H, m) and 7.91–8.02 (2 H, m).

**Spiro[9,10-dihydrophenanthrene-9,12'-(1',2',3',4',5',6',7',8',9',10',11',12'-dodecahydro[1]benzoazatetradecine)], 8 ( $n = 10$ ).** Mp 203–206 °C (hexane),  $\lambda_{\max}(\text{hexane})/\text{nm}$  208 (log  $\epsilon$  4.73) and 254 (4.20);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3350 (NH);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.13–1.83 (17[20]H, s, m), 2.78–2.94 (2 H, m), 3.03 (1 H, d), 3.22–3.26 (1 H, m), 3.57 (1 H, d), 4.04 (1 H, br s), 6.30–6.36 (1 H, m), 6.52–6.62 (2 H, m), 6.89–6.95 (1 H, m), 7.16–7.28 (3 H, m), 7.35–7.39 (2 H, m) and 7.59–7.76 (3 H, m).

**Compound 9 ( $n = 10$ ).** *N,N'*-Bis[10-(9-phenanthryl)decyl]hydrazobenzene, yellow oil, was obtained in the second fraction of the chromatography (2% yield) of the mixture irradiated at high concentration (0.16 mol dm<sup>-3</sup>);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.18–1.82 (32 H, m), 3.08 (4 H, t), 3.40 (4 H, t), 6.67–6.76 (6 H, m), 7.16–7.22 (4 H, m), 7.52–7.66 (10 H, m), 7.79–7.82 (2 H, m), 8.07–8.11 (2 H, m) and 8.62–8.74 (4 H, m).

#### Photoreaction of 3 ( $n = 12$ )

A solution of 3 ( $n = 12$ ) (0.62 g, 1.42 mmol) in benzene (90 cm<sup>3</sup>) was irradiated for 3.5 h. Chromatography of the irradiation mixture with hexane–benzene (3:1, v/v) gave the cyclic product 7 ( $n = 12$ ) (4 mg) in the second fraction, the cyclic product 5

( $n = 12$ ) (10 mg) in the third, spirocyclic derivative 8 ( $n = 12$ ) (15 mg) in the 4th, and unchanged amine 3 ( $n = 12$ ) (286 mg) in the 5th. Trace amounts of the hydrazine derivative 9 ( $n = 12$ ) were detected in the first fraction.

**6,7,8,9,10,11,12,13,14,15,16,17,25,26-Tetradecahydro-26,5,18,24[1,2,3]propanetriyl[3]ylidenedibenzo[*b,g*]azacyclodocosine 5 ( $n = 12$ ).** Mp 153–155 °C (hexane) (Found: 87.6; H, 9.1; N, 3.3. C<sub>32</sub>H<sub>39</sub>N requires C, 87.8; H, 9.0; N, 3.2%);  $\lambda_{\max}(\text{hexane})/\text{nm}$  233 (log  $\epsilon$  4.92) and 258 (4.13);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.03–1.80 (20 H, m), 2.04–2.18 (2 H, m), 2.47–2.85 (1 H, m), 3.06–3.24 (1 H, m), 3.38–3.72 (5 H, m), 4.72 (1 H, s), 6.61–6.73 (2 H, m), 6.96–7.03 (1 H, m), 7.14–7.23 (1 H, m), 7.33–7.40 (2 H, m), 7.50 (1 H, s), 7.63–7.68 (1 H, m) and 7.86–7.90 (1 H, m).

**6,7,8,9,10,11,12,13,14,15,16,17,24,25-Tetradecahydro-25,5,23,18[1,2]butanediyl[3,4]diylidenedibenzo[*b,g*]azacyclohenicosine 7 ( $n = 12$ ).** Mp 139–142 °C (hexane);  $\lambda_{\max}(\text{hexane})/\text{nm}$  214 (log  $\epsilon$  4.63), 233 (4.69) and 256 (4.19);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.21–1.95 (20[26]H, s, m), 2.05–2.18 (2 H, m), 2.76–2.87 (1 H, m), 3.13–3.24 (1 H, m), 3.32–3.59 (5 H, m), 4.41 (1 H, s), 6.54–6.64 (2 H, m), 6.97–7.04 (1 H, m), 7.14–7.17 (1 H, m), 7.20 (1 H, s), 7.42–7.47 (2 H, m) and 7.90–8.09 (1 H, m).

**Spiro[9,10-dihydrophenanthrene-9,14'-(1',2',3',4',5',6',7',8',9',10',11',12',13',14'-tetradecahydro[1]benzazahexadecine)] 8 ( $n = 12$ ).** † Mp 186–187.5 °C (hexane) (Found: C, 87.6; H, 9.2; N, 2.9. C<sub>32</sub>H<sub>39</sub>N requires C, 87.8; H, 9.0; N, 3.2%);  $\lambda_{\max}(\text{hexane})/\text{nm}$  209 (log  $\epsilon$  4.72) and 253 (4.16);  $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$  3449 (NH);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.27–1.62 (20 H, m), 2.13–2.23 (1 H, m), 2.56–2.47 (1 H, m), 2.91 (1 H, br s), 3.03–3.09 (2 H, d), 3.50–3.55 (1 H, d), 4.00 (1 H, br s), 6.34–6.40 (1 H, t), 6.48–6.51 (1 H, d), 6.75–6.79 (1 H, q), 6.90–6.96 (1 H, m), 7.15–7.21 (2 H, m), 7.23–7.27 (1 H, m), 7.28–7.39 (2 H, m) and 7.58–7.74 (3 H, m).

***N,N'*-Bis[12-(9-phenanthryl)dodecyl]hydrazobenzene, 9 ( $n = 12$ ).** Yellow oil;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.25–1.79 (40 H, m), 3.08 (4 H, t), 3.40 (4 H, t), 6.68–6.76 (6 H, m), 7.16–7.22 (4 H, m), 7.51–7.63 (10 H, m), 7.78–7.81 (2 H, m), 8.07–8.10 (2 H, m) and 8.61–8.72 (4 H, m).

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§ This compound may be contaminated by solvents which could not be removed; the integrated ratio of the <sup>1</sup>H NMR spectrum is shown in brackets.