# Syntheses and Thermal Behaviour of 9-Substituted 9-Thia-10-azaphenanthrenes

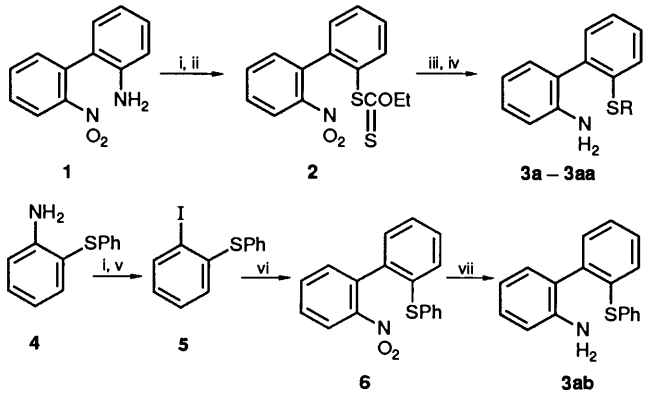
**Hiroshi Shimizu, Koji Ikedo, Koji Hamada, Michinori Ozawa, Harutoshi Matsumoto, Kunihiro Kamata, Haruhiko Nakamura, Min Ji, Tadashi Kataoka and Mikio Hori** *
*Gifu Pharmaceutical University, 6-1, Mitahora-higashi 5-chome, Gifu 502, Japan*

Synthetic approaches to a variety of 9-thia-10-azaphenanthrenes having various kinds of substituent at the 9-position were investigated. Their thermal stabilities were found to depend strongly upon the nature of the substituents on the sulphur atom. Several 9-alkyl and 9-phenyl derivatives are quite stable at room temperature; in particular, the phenyl derivative was too stable to undergo thermal degradation. Refluxing in xylene for many hours effected some change of the 9-phenyl derivative **7ab** to result in the formation of 1,4-rearranged **11** and N–S bond-cleaved **3ab** products, while 9-alkyl derivatives **3c–3f** were easily decomposed in refluxing benzene to undergo β-elimination to give 6*H*-dibenzo[*c*,*e*][1,2]thiazine **9** as major product. 9-Benzyl, 9-(4-substituted benzyl), 9-fluoren-9-yl and 9-cyanomethyl derivatives underwent, even at below room temperature, 1,2-rearrangement of the 9-substituent to afford the corresponding 6-substituted 6*H*-dibenzo[*c*,*e*][1,2]thiazines **10g–10o**, **10w**, which are very rarely observed in sulphilimine chemistry. A 9-silyl-group-substituted derivative was also too unstable to be isolated and caused a 1,2-imino shift to give the ring-expanded product **18**. 9-Acylmethyl derivatives underwent Sommelet–Hauser-type rearrangement to afford benzothienoindole derivatives **24**.

In our previous papers, we reported the first synthesis of novel cyclic sulphilimines (so-called azathiabenzenes), azathianaphthalenes and azathiaphenanthrenes.[1,2] The ylidic properties of the azathiabenzenes were revealed by spectral and some chemical evidence. Azathiabenzenes were shown to be good starting materials for the construction of novel sulphur- and nitrogen-containing heterocyclic compounds based on their reactions with some electrophiles.[2,3] Moody *et al.* also independently reported the preparation and properties of other azathiabenzene derivatives.[4] In our continuous studies on the chemistry in this class of novel heterocycles, we have investigated the synthesis of their derivatives. We now report here on the preparation of various kinds of 9-substituted 9-thia-10-azaphenanthrenes and their thermal stabilities.

## Results and Discussion

*Synthesis of 2-Alkylthio- (or 2-Arylthio)-2′-aminobiphenyls* **3**, *Precursors of 9-Substituted 9-Thia-10-azaphenanthrenes* **7**.—In our earlier report,[2] we prepared 2-amino-2′-methylthio- (or ethylthio-) biphenyl as a precursor of 9-methyl- (or ethyl-) 9-thia-10-azaphenanthrene by Ullmann coupling between 2-iodonitrobenzene and 2-iodophenyl methyl (or ethyl) sulphide, followed by reduction of the nitro group. The major disadvantage of this method was the rather poor yield because of the formation of self-coupling products, 2,2′-dinitrobiphenyl and 2,2′-bis(alkylthio)biphenyls, whose separation was not easy. Therefore, we planned to develop an alternative preparation method, which would be useful and convenient for the synthesis of several types of alkylthiobiphenyls *via* a common intermediate. We selected 2-amino-2′-mercaptobiphenyl as a common intermediate. The successful synthetic route to the many kinds of 2-alkylthio-2′-aminobiphenyls **3** is shown in Scheme 1. 2-Amino-2′-nitrobiphenyl **1**[5] was diazotized in the usual way, followed by treatment with potassium *O*-ethyl dithiocarbonate to give 2-[ethoxy(thiocarbonyl)thio-]-2′-nitrobiphenyl **2** in 54–60% yield. The biphenyl **2** was submitted to reduction with an excess of $LiAlH_4$ in tetrahydrofuran (THF). After decomposition of an excess of $LiAlH_4$ with ethanol, appropriate organohalides such as alkyl, aralkyl, allyl halides, *etc.* were added to give the corresponding 2-alkylthio-2′-aminobiphenyls **3a–3aa** in good yield. Refluxing for 1–2.5 h was necessary to complete the reaction with cyclohexyl bromide, trimethylsilyl (TMS) chloride, 4-methoxybenzyl bromide, 4-bromobenzyl bromide, and 4-nitrobenzyl bromide. The results are summarized in Tables 1–3. This method is very convenient in that there is no necessity in isolating the mercaptobiphenyl, during the simultaneous reduction of the nitro group to amino group. However, phenylthiobiphenyl derivative **3ab** was prepared by our previous method [2] using Ullmann coupling as shown in Scheme 1, because the above method could not be applied to the preparation of the arylthiobiphenyl derivatives. Diazotization of 2-aminophenyl phenyl sulphide **4**[6] in the usual way, followed by treatment with potassium iodide, gave 2-iodophenyl phenyl sulphide **5**. The sulphide **5** was then allowed to react with 2-iodonitrobenzene under the Ullmann coupling conditions in the presence of copper catalyst to give 2-nitro-2′-phenylthiobiphenyl **6** in 59% yield. The nitro compound **6** was readily reduced with metallic zinc in the aq. ethanol to the amino compound **3ab** in 94% yield.




**Scheme 1** *Reagents and conditions:* i, $NaNO_2$, HCl; ii, KSC(=S)OEt, $CH_2Cl_2$; iii, excess of $LiAlH_4$, THF; iv, RX; v, KI, water; vi, 2-$IC_6H_4NO_2$, Cu, 210 °C; vii, Zn, $CaCl_2$, 80% EtOH

**Table 1** Preparation of 2-alkylthio-2′-aminobiphenyls **3a**–**3aa**

| Compound | R | X of RX | Reaction conditions[a] | Yield (%)[b] | Isolation method[c] |
|---|---|---|---|---|---|
| **3a** | Me | I | r.t. | 55 | A, Hexane–$Et_2O$ (1:1) |
| **3b** | Et | I | r.t. | 60 | A, Hexane–EtOAc (5:1) |
| **3c** | Pr | I | r.t. | 64 | A, Hexane–EtOAc (5:1) |
| **3d** | $Pr^i$ | I | r.t. | 59 | B, Hexane–$CH_2Cl_2$ (5:1) |
| **3e** | $Bu^s$ | Br | r.t. | 47 | B, Hexane–$Et_2O$ (5:1) |
| **3f** | c-$C_6H_{11}$ | Br | reflux (2.5 h) | 42 | B, Hexane–$Et_2O$ (4:1) |
| **3g** | $PhCH_2$ | Br | r.t. | 96 | B, Hexane–$Et_2O$ (5:1) |
| **3h** | 4-$MeC_6H_4CH_2$ | Br | r.t. | 83 | B, Hexane–$Et_2O$ (10:1) |
| **3i** | 4-$MeOC_6H_4CH_2$ | Cl | reflux (1 h) | 87 | C |
| **3j** | 4-$FC_6H_4CH_2$ | Cl | r.t. | 71 | C |
| **3k** | 4-$ClC_6H_4CH_2$ | Cl | r.t. | 71 | C |
| **3l** | 2,4-$Cl_2C_6H_3CH_2$ | Cl | r.t. | 80 | C |
| **3m** | 4-$BrC_6H_4CH_2$ | Br | reflux (1 h) | 76 | B, Hexane–$Et_2O$ (10:1) |
| **3n** | 4-$NO_2C_6H_4CH_2$ | Br | reflux (2 h) | 82 | B, Hexane–$Et_2O$ (5:1) |
| **3o** | Fluoren-9-yl | Br | r.t. | 66 | B, Hexane–$Et_2O$ (5:1) |
| **3p** | $Me_3SiCH_2$ | Cl | reflux (2.5 h) | 73 | B, Hexane–$Et_2O$ (10:1) |
| **3q** | $H_2C{=}CHCH_2$ | Br | r.t. | 80 | B, Hexane–$Et_2O$ (5:1) |
| **3r** | $MeCH{=}CHCH_2$ | Br | r.t. | 84 | B, Hexane–$Et_2O$ (5:1) |
| **3s** | $Me_2C{=}CHCH_2$ | Br | r.t. | 79 | B, Hexane–$Et_2O$ (5:1) |
| **3t** | $PhCH{=}CHCH_2$ | Cl | r.t. | 86 | B, Hexane–$Et_2O$ (5:1) |
| **3u** | $HC{\equiv}CCH_2$ | Br | r.t. | 85 | B, Hexane–$Et_2O$ (5:1) |
| **3v** | $CF_3CH_2$ | Cl | r.t. | 74 | B, Hexane–$Et_2O$ (5:1) |
| **3w** | $NCCH_2$ | Br | r.t. | 80 | C |
| **3x** | $EtOCOCH_2$ | Cl | r.t. | 62 | B, Hexane–$Et_2O$ (2:1) |
| **3y** | $PhCOCH_2$ | Br | r.t. | 61 | C |
| **3z** | $MeSCH_2$ | Cl | r.t. | 65 | B, Hexane–$Et_2O$ (3:1) |
| **3aa** | $MeOCH_2$ | Cl | r.t. | 55 | B, Hexane–$Et_2O$ (2:1) |

[a] Reaction temperature after addition of organohalide to the thiolate compound. r.t.: room temperature. [b] Isolated yield. [c] A, TLC on silica gel; B, Column chromatography on silica gel; C, Recrystallization.

**Table 2** Physical properties for compounds **3a**–**3aa**

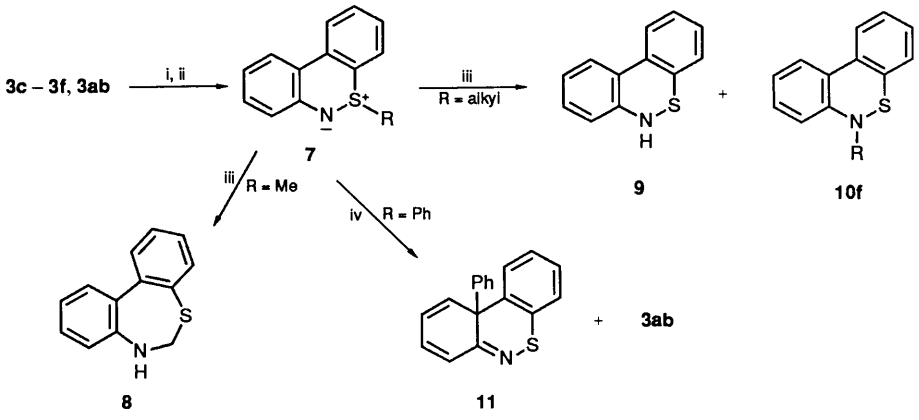
| | | | | | Microanalysis Found % (Required %) | | |
|---|---|---|---|---|---|---|---|
| Compound | Appearance | Recryst. solvent | M.p. (°C) | Formula | C | H | N |
| **3a**[a] | Columns | Hexane–benzene | 83–85 | $C_{13}H_{13}NS$ | 72.5 (72.5) | 6.1 (6.1) | 6.4 (6.5) |
| **3b**[a] | Prisms | Hexane–$Et_2O$ | 45–46 | $C_{14}H_{15}NS$ | 73.1 (73.3) | 6.6 (6.6) | 6.0 (6.1) |
| **3c** | Prisms | Hexane–$Et_2O$ | 30.5–31.5 | $C_{15}H_{17}NS$ | 73.8 (74.0) | 7.2 (7.0) | 5.7 (5.8) |
| **3d** | Yellow oil | | | $C_{15}H_{17}NS$ | High resolution MS 243.1068 (243.1088) | | |
| **3e** | Yellow oil | | | $C_{16}H_{19}NS$ | High resolution MS 257.1260 (257.1239) | | |
| **3f** | Yellow oil | | | $C_{18}H_{21}NS$ | High-resolution MS 283.1371 (283.1394) | | |
| **3g** | Prisms | Hexane–$CH_2Cl_2$ | 113–114 | $C_{19}H_{17}NS$ | 78.1 (78.3) | 6.0 (5.9) | 4.8 (4.8) |
| **3h** | Prisms | Hexane–$CH_2Cl_2$ | 91–92 | $C_{20}H_{19}NS$ | 78.8 (78.65) | 6.4 (7.3) | 4.6 (4.6) |
| **3i** | Prisms | Hexane–$CH_2Cl_2$ | 160–161 | $C_{20}H_{19}NOS$ | 74.5 (74.7) | 6.0 (6.0) | 4.4 (4.4) |
| **3j** | Prisms | Hexane–$CH_2Cl_2$ | 115–116 | $C_{19}H_{16}FNS$ | 73.5 (73.8) | 5.2 (5.2) | 4.5 (4.5) |
| **3k** | Prisms | Hexane–$CH_2Cl_2$ | 91 92 | $C_{19}H_{16}ClNS$ | 70.2 (70.0) | 5.0 (4.95) | 4.25 (4.3) |
| **3l** | Prisms | Hexane–$CH_2Cl_2$ | 115–116 | $C_{19}H_{15}Cl_2NS$ | 63.05 (63.3) | 4.2 (4.2) | 3.9 (3.9) |
| **3m** | Prisms | Hexane–$CH_2Cl_2$ | 111–113 | $C_{19}H_{16}BrNS$ | 61.6 (61.6) | 4.4 (4.4) | 3.8 (3.8) |
| **3n** | Yellow prisms | Hexane–$CH_2Cl_2$ | 119–121 | $C_{19}H_{16}N_2O_2S$ | 67.6 (67.8) | 4.7 (4.8) | 8.3 (8.3) |
| **3o** | Pale yellow plates | Hexane–$CH_2Cl_2$ | 141–142 | $C_{25}H_{19}NS$ | 81.9 (82.2) | 5.2 (5.2) | 3.8 (3.8) |
| **3p** | Prisms | Hexane–benzene | 63–64 | $C_{16}H_{21}NSSi$ | 66.6 (66.8) | 7.45 (7.4) | 4.9 (4.9) |
| **3q** | Yellow oil (yellow prisms)[b] | $Et_2O$–$CH_2Cl_2$[b] | 125–126[b] | $C_{21}H_{18}N_4O_7S$[b] | 53.4 (53.6) | 4.0 (3.9) | 11.9 (11.9)[b] |
| **3r** | Pale orange columns | Hexane–$CH_2Cl_2$ | 69–70 | $C_{16}H_{17}NS$ | 75.3 (75.1) | 6.8 (6.7) | 5.5 (5.5) |
| **3s** | Pale orange columns | Hexane–$CH_2Cl_2$ | 69–70 | $C_{17}H_{19}NS$ | 75.5 (75.8) | 7.2 (7.1) | 5.2 (5.2) |
| **3t** | Pale brown needles | Hexane–$CH_2Cl_2$ | 136–138 | $C_{21}H_{19}NS$ | 79.2 (79.5) | 6.0 (6.0) | 4.4 (4.4) |
| **3u** | Yellow oil (yellow prisms)[b] | Hexane–$Et_2O$[b] | 134–136 (decomp.)[b] | $C_{21}H_{16}N_4O_7S$[b] | 53.75 (53.8) | 3.5 (3.4) | 11.9 (12.0)[b] |
| **3v** | Yellow oil | | | $C_{14}H_{12}F_3NS$ | High-resolution MS 283.0651 (283.0643) | | |
| **3w** | Yellow prisms | Hexane–$CH_2Cl_2$ | 107–109 | $C_{14}H_{12}N_2S$ | 69.7 (70.0) | 5.05 (5.0) | 11.7 (11.7) |
| **3x** | Pale yellow prisms | Hexane–$CH_2Cl_2$ | 61–62 | $C_{16}H_{17}NO_2S$ | 66.6 (66.9) | 6.05 (6.0) | 5.0 (4.9) |
| **3y** | Plates | Hexane–$CH_2Cl_2$ | 132–134 | $C_{20}H_{17}NOS$ | 74.9 (75.2) | 5.4 (5.4) | 4.4 (4.4) |
| **3z** | Prisms | Hexane–$CH_2Cl_2$ | 72–73 | $C_{14}H_{15}NS_2$ | 64.2 (64.3) | 6.05 (5.8) | 5.1 (5.4) |
| **3aa** | Pale yellow columns | Hexane–$CH_2Cl_2$ | 73–74 | $C_{14}H_{15}NOS$ | 68.3 (68.5) | 6.15 (6.2) | 5.7 (5.7) |

[a] The data for compounds **3a** and **3b** have already been reported.[2] [b] Picrate derivative of the corresponding aminobiphenyl.

**Table 3** Spectral data for compounds **3a–3aa**

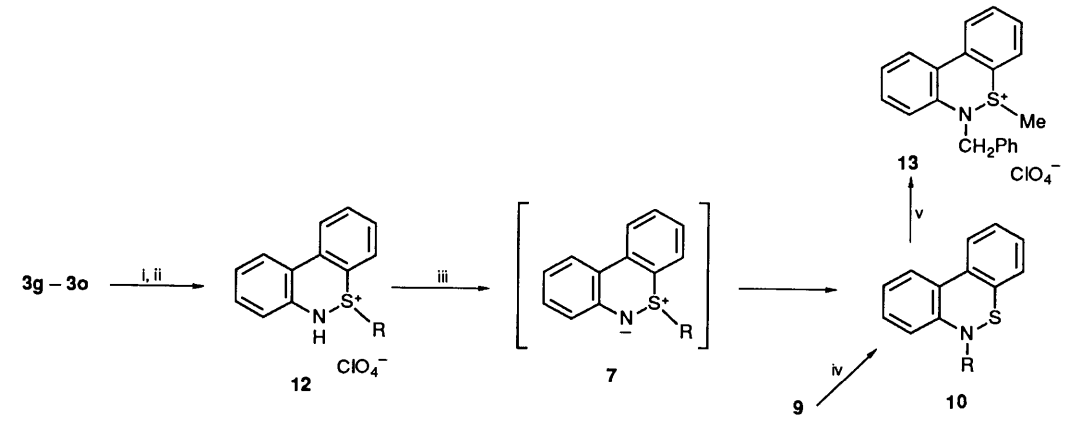
| Compound | $\nu_{max}$/cm$^{-1}$ [a] | $\delta_H$(CDCl$_3$) [b] | *m/z* |
|---|---|---|---|
| **3a** [c] | 3450, 3360 ($NH_2$) | 2.32 (3 H, s, Me), 3.41 (2 H, br, $NH_2$), 6.58–7.90 (8 H, m, ArH) | 215 ($M^+$), 168 (base) |
| **3b** [c] | 3430, 3370 ($NH_2$) | 1.24 (3 H, t, *J* 7, $CH_2$*Me*), 2.82 (2 H, q, *J* 7, $CH_2$Me), 3.33 (2 H, br, $NH_2$), 6.60–7.70 (8 H, **m**, ArH) | 229 ($M^+$), 168 (base) |
| **3c** | 3480, 3370 ($NH_2$) | 0.95 (3 H, t, *J* 7, $CH_2CH_2$*Me*), 1.33–1.90 (2 H, m, $CH_2CH_2$Me), 2.77 (2 H, t, *J* 7, $CH_2CH_2$Me), 6.55–7.40 (8 H, m, ArH) | 243 ($M^+$) |
| **3d** | 3450, 3360 ($NH_2$) | 1.71 (6 H, d, *J* 7, 2 × Me), 3.05–3.75 (3 H, m, $NH_2$ and CH), 6.57–7.55 (8 H, m, ArH) | 243 ($M^+$) |
| **3e** | 3460, 3370 ($NH_2$) | 0.89 (3 H, t, *J* 7, Me), 1.19 (3 H, d, *J* 6, Me), 1.45 (2 H, m, $CH_2$), 3.04 (1 H, m, CH), 3.53 (2 H, br, $NH_2$), 6.74–7.46 (8 H, **m**, ArH) | 257 ($M^+$), 168 (base) |
| **3f** | 3460, 3370 ($NH_2$) | 1.21–1.89 (10 H, m, $CH_2$ of cyclohexane), 3.02 (1 H, **m**, CH of cyclohexane), 3.42 (2 H, br, $NH_2$), 6.69–7.45 (8 H, m, ArH) | 283 ($M^+$), 168 (base) |
| **3g** | 3470, 3370 ($NH_2$) | 3.20–3.60 (2 H, br, $NH_2$), 4.02 (2 H, s, $CH_2$), 6.70–7.40 (13 H, m, ArH) | 291 ($M^+$) |
| **3h** | 3460, 3360 ($NH_2$) | 2.28 (3 H, s, Me), 2.90–3.50 (2 H, br, $NH_2$), 3.97 (2 H, s, $CH_2$), 6.65–7.45 (12 H, m, ArH) | 305 ($M^+$), 200 (base) |
| **3i** | 3475, 3380 ($NH_2$) | 2.90–3.40 (2 H, br, $NH_2$), 3.76 (3 H, s, OMe), 3.97 (2 H, s, $CH_2$), 6.60–7.45 (12 H, m, ArH) | 321 ($M^+$) |
| **3j** | 3450, 3350 ($NH_2$) | 3.25–3.75 (2 H, br, $NH_2$), 3.93 (2 H, s, $CH_2$), 6.63–7.40 (12 H, m, ArH) | 309 ($M^+$), 109 (base) |
| **3k** | 3420, 3350 ($NH_2$) | 3.10–3.70 (2 H, br, $NH_2$), 3.90 (2 H, s, $CH_2$), 6.65–7.33 (12 H, m, ArH) | 325 ($M^+$), 200 (base) |
| **3l** | 3450, 3350 ($NH_2$) | 3.30–3.75 (2 H, br, $NH_2$), 4.05 (2 H, s, $CH_2$), 6.70–7.28 (11 H, m, ArH) | 359 ($M^+$), 200 (base) |
| **3m** | 3480, 3380 ($NH_2$) | 3.00–3.60 (2 H, br, $NH_2$), 3.93 (2 H, s, $CH_2$), 6.70–7.48 (12 H, m, ArH) | 371 ($M^+$), 369 ($M^+ - 2$) |
| **3n** | 3480, 3380 ($NH_2$), 1510, 1345 ($NO_2$) | 3.30–3.80 (2 H, br, $NH_2$), 4.01 (2 H, s, $CH_2$), 6.75–7.44 (10 H, m, ArH), 8.00–8.22 (2 H, m, ArH) | 336 ($M^+$), 200 (base) |
| **3o** | 3440, 3350 ($NH_2$) | 3.50 (2 H, br, $NH_2$), 5.13 (1 H, s, CH), 6.73–7.66 (16 H, m, ArH) | 365 ($M^+$), 165 (base) |
| **3p** | 3470, 3370 ($NH_2$) | 0.05 (9 H, s, $SiMe_3$), 2.03 (2 H, s, $CH_2$), 3.35–3.75 (2 H, br, $NH_2$), 6.70–7.50 (8 H, m, ArH) | 287 ($M^+$) |
| **3q** | 3460, 3360 ($NH_2$) | 3.00–4.00 (2 H, br, $NH_2$), 3.35–3.50 (2 H, m, $CH_2CH{=}CH_2$), 4.95–5.35 (2 H, m, $=CH_2$), 5.55–6.20 (1 H, m, –CH=), 6.70–7.50 (8 H, m, ArH) | 241 ($M^+$) |
| **3r** | 3470, 3370 ($NH_2$) | 1.62 (3 H, d, *J* 6, Me), 3.41 (2 H, d, *J* 6, $CH_2$), 3.52 (2 H, br, $NH_2$), 5.38–5.65 (2 H, m, CH=CH), 6.75–7.40 (8 H, m, ArH) | 255 ($M^+$), 200 (base) |
| **3s** | 3450, 3370 ($NH_2$) | 1.58 (3 H, s, Me), 1.66 (3 H, s, Me), 3.42 (2 H, d, *J* 8, $CH_2$), 3.53 (2 H, br, $NH_2$), 5.22 (1 H, t, *J* 8, –CH=), 6.74–7.45 (8 H, m, ArH) | 269 ($M^+$), 184 (base) |
| **3t** | 3470, 3380 ($NH_2$) | 3.59 (2 H, d, *J* 7, $CH_2$), 3.51 (2 H, br, $NH_2$), 6.08–6.19 (1 H, m, –CH=), 6.41 (1 H, d, *J* 15, =C*H*Ph), 6.75–7.46 (13 H, m, ArH) | 317 ($M^+$), 117 (base) |
| **3u** | 3460, 3360 ($NH_2$), 3280, 2100 (C≡CH) | 2.15 (1 H, t, *J* 3, C≡CH), 3.47 (2 H, d, *J* 3, $CH_2$), 2.90–3.90 (2 H, br, $NH_2$), 6.70–7.70 (8 H, m, ArH) | 239 ($M^+$), 199 (base) |
| **3v** | 3470, 3380 ($NH_2$) | 3.24 (2 H, dd, *J* 2 and 10, $CH_2$), 3.50 (2 H, br, $NH_2$), 6.75–7.58 (8 H, m, ArH) | 283 ($M^+$), 168 (base) |
| **3w** | 3450, 3350 ($NH_2$), 2250 (CN) | 3.35 (2 H, s, $CH_2$), 3.50–4.75 (2 H, br, $NH_2$), 6.70–7.80 (8 H, m, ArH) | 240 ($M^+$), 168 (base) |
| **3x** | 3440, 3350 ($NH_2$), 1720 (CO) | 1.18 (3 H, t, *J* 7, $CH_2$*Me*), 3.48 (2 H, ABq, *J* 6, $CH_2$), 3.60 (2 H, br, $NH_2$), 4.09 (2 H, q, *J* 7, $CH_2$Me), 6.71–6.81 (6 H, m, ArH) | 287 ($M^+$), 168 (base) |
| **3y** | 3450, 3350 ($NH_2$), 1690 (CO) | 3.30–3.70 (2 H, br, $NH_2$), 4.08 (2 H, s, $CH_2$), 6.60–7.53 (11 H, m, ArH), 7.73–7.92 (2 H, m, ArH) | 319 ($M^+$), 181 (base) |
| **3z** | 3480, 3360 ($NH_2$) | 2.08 (3 H, s, SMe), 3.80 (2 H, s, $CH_2$), 6.65–7.50 (8 H, m, ArH), 3.40 (2 H, br, $NH_2$) | 261 ($M^+$), 181 (base) |
| **3aa** | 3450, 3360 ($NH_2$) | 3.31 (3 H, s, Me), 3.52 (2 H, br, $NH_2$), 4.84 (2 H, s, $CH_2$), 6.72–7.69 (8 H, m, ArH) | 245 ($M^+$), 45 (base) |

[a] KBr disk for the crystals and NaCl plate for the oil. [b] Chemical shifts are reported in ppm downfield from $SiMe_4$ as internal standard. [c] Spectral data for compounds **3a** and **3b** have already been reported.[2]




**Scheme 2** *Reagents and conditions:* i, NCS or Bu$^t$OCl, $CH_2Cl_2$, −78 to −65 °C; ii, aq. NaOH, 0 °C; iii, reflux in benzene; iv, reflux in xylene

*Preparation and Thermal Reactions of 9-Substituted 9-Thia-10-azaphenanthrenes* **7c–f** *and* **7ab**.—Treatment of 2-alkylthio-2′-aminobiphenyls **3c–f** or 2-amino-2′-phenylthiobiphenyl **3ab** with *N*-chlorosuccinimide (NCS) or t-butyl hypochlorite in dichloromethane at −78 to −50 °C, followed by deprotonation with aq. NaOH or KOH at 0 °C gave the corresponding 9-alkyl-**7c–7f** or 9-phenyl-9-thia-10-azaphenanthrenes **7ab** in good yield (Scheme 2). These azathiaphenanthrenes were stable at room temperature. We previously described an interesting contrast in the thermal reaction between the 9-methyl (**7a**;




**Scheme 3** *Reagents:* i, NCS or Bu$^t$OCl, $CH_2Cl_2$; ii, $AgClO_4$; iii, BuLi or NaOH or KOH; iv, NaH, RBr, THF; v, MeI, $AgClO_4$

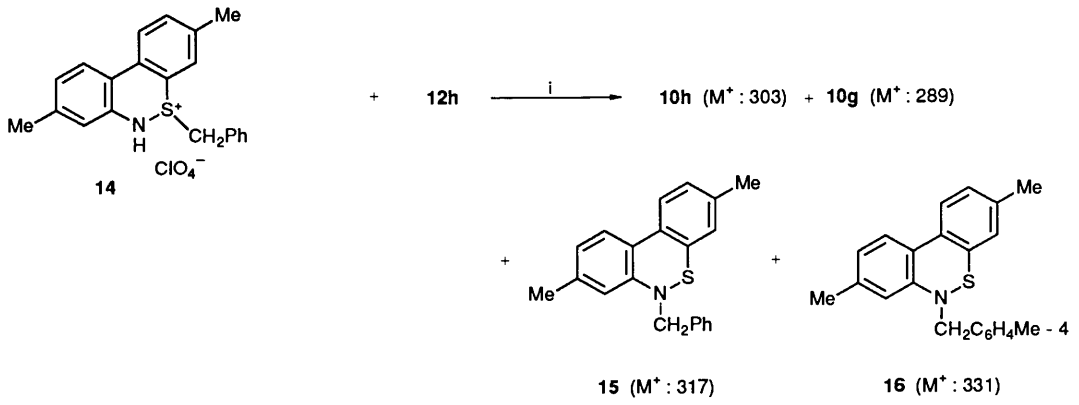
**Table 4** Generation and subsequent 1,2-rearrangement of 9-substituted 9-thia-10-azaphenanthrenes **7g–7o** and **7w**

| Biphenyl 3 | Chlorinating agent | Yield (%) of the perchlorate 12 | Base | Yield (%) of the thiaazaphenanthrene 10 |
|---|---|---|---|---|
| **3g** | NCS | 63 | BuLi | 50[b] |
| **3h** | NCS | 69 | BuLi | 57[b] |
| **3i** | Bu$^t$OCl | 46 | NaOH | 21[c] |
| **3j** | Bu$^t$OCl | *a* | NaOH | 28 |
| **3k** | Bu$^t$OCl | *a* | NaOH | 28 |
| **3l** | Bu$^t$OCl | *a* | NaOH | 40 |
| **3m** | Bu$^t$OCl | 90 | NaOH | 56[c] |
| **3n** | Bu$^t$OCl | *a* | NaOH | 57 |
| **3o** | Bu$^t$OCl | 95 | NaOH | 58[c] |
| **3w** | Bu$^t$OCl | *a* | NaOH | 22[c] |

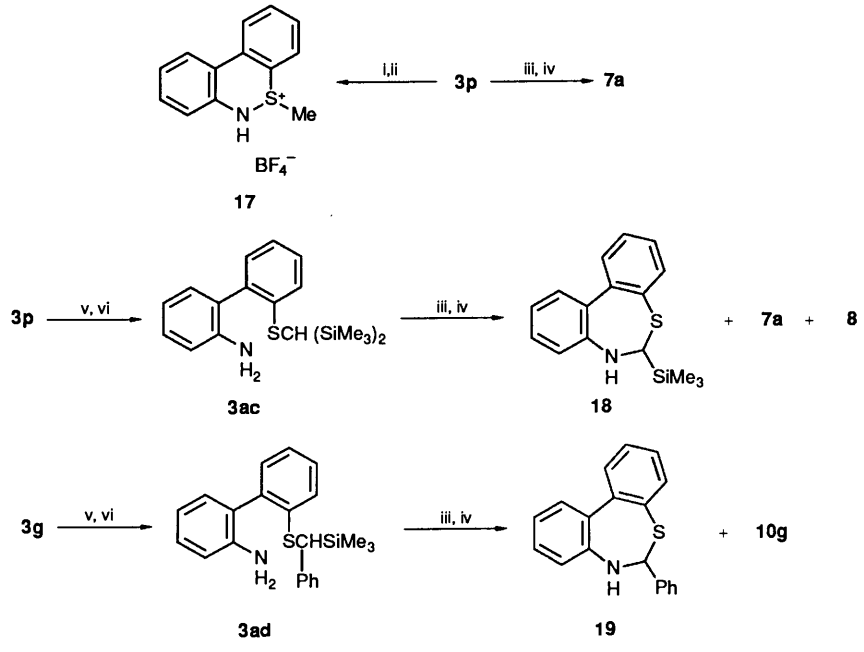
[a] No isolation of the perchlorate **12**. [b] Yield based on the perchlorate **12** used. [c] Yield based on the biphenyl **3** used.

R = Me) and 9-ethyl derivatives (**7b**; R = Et):[2] compound **7a** underwent ring expansion to give 6,7-dihydrodibenzo[*d*,*f*]-[1,3]thiazepine **8**, while compound **7b** underwent dealkylation with cycloelimination *via* a five-membered transition state to furnish 6*H*-dibenzo[*c*,*e*][1,2]thiazine **9**. When heated with reflux in benzene, 9-alkyl derivatives **7c–7e** prepared above underwent dealkylation to yield 1,2-thiazine derivative **9** as in the case of the 9-ethyl derivative **7b**. Under similar conditions, interestingly, the 9-cyclohexyl derivative **7f** yielded 10% of the 1,2-rearranged product **10f** in addition to compound **9** as a major product. The formation of compound **10f** by 1,2-alkyl migration from sulphur to nitrogen is quite interesting from the mechanistic point of view, because this simple 1,2-migration is rarely observed in sulphilimine chemistry.[7] In contrast, the 9-phenyl derivative **7ab** was quite stable, and even if it was refluxed in benzene no decomposition took place, the substrate being completely recovered. However, prolonged refluxing in xylene effected some change, giving a product for which we propose the structure **11** and S–N bond-cleaved product **3ab** in 18 and 24% yield, respectively. The structure of compound **11** is unique from the point of disruption of the benzenoid aromaticity and was determined mainly on the basis of its spectral properties. In particular, the $^1$H NMR spectrum showed olefinic proton peaks at $\delta$ 6.18–6.82, and the $^{13}$C NMR spectrum revealed the absorption of the sp$^3$-quaternary carbon attributable to the C-10a at $\delta$ 53.52. 1,4-Aryl migration itself is considered formally to be a 1,4-sigmatropic rearrangement involving six electrons, and has been observed in thiabenzenes by our group[8] and by Mislow's group.[9] However, there was no observation of 1,4-aryl migration of benzo-fused *S*-aryl thiaazabenzenes, a process which would destroy the benzenoid aromaticity, although the corresponding aryl migration of thiphene- or furan-fused *S*-aryl thiaazabenzenes was observed by Gairns *et al.*[4b] An S–N bond fission similar to that above was observed in the pyrolysis (at 300 °C) of an cyclic sulphilimine (*S*,*S*-diphenyl-*N*-tosylsulphilimine) by Atkins and Lentz.[10]

*Attempted Preparation of 9-Benzyl (and 4-Substituted Benzyl) 9-Thia-10-azaphenanthrenes* **7g–7o**—*An Easy 1,2-Rearrangement of 9-Benzyl Substituents.*—With the intention of preparing 9-benzyl-9-thia-10-azaphenanthrene **7g**, we carried out the cyclization of 2-amino-2′-benzylthiobiphenyl **3g** under similar conditions to those used in the preparation of 9-alkyl derivatives as described above. However, we could not prepare the expected compound **7g**, but instead isolated the 6-benzyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine **10g** in 39% yield (Scheme 3). This suggested that the 9-benzyl derivative **7g** initially formed was too unstable to be isolated and readily underwent thermal 1,2-rearrangement of the *S*-benzyl group. In order to verify this, we conducted the deprotonation of the isolated 5-benzyl-6*H*-dibenzo[*c*,*e*][1,2]thiazin-5-ium perchlorate **12g**, which was easily prepared in 63% yield by addition of silver perchlorate to the reaction mixture of compound **3g** and NCS, to give the 6-benzyl derivative **10g** in 50% yield. The structure of compound **10g** was confirmed by analytical and spectroscopic means and was further established by comparison of the spectral data with those of an authentic specimen prepared by *N*-benzylation of the 1,2-thiazine **9** after treatment with sodium hydride in THF as shown in Scheme 3. In addition to this, compound **10g** was methylated by treatment with methyl iodide in the presence of silver perchlorate to afford 6-benzyl-5-methyl-6*H*-dibenzo[*c*,*e*]-[1,2]thiazin-5-ium perchlorate **13** in 30% yield. Similarly, other 2-amino-2′-[(4-substituted benzyl)thio]biphenyl derivatives **3h–3n** were treated with NCS or Bu$^t$OCl for the cyclization, followed by deprotonation with base at 0 °C to give the corresponding 1,2-benzyl rearranged products **10h–10n** *via* unstable thiaazaphenanthrenes **7h–7n** in moderate-to-good yield. The aminobiphenyl **3o**, having a bulky fluorenyl group at the 2′-position, also resulted in 1,2-rearrangement to give 1,2-thiazine **10o**. Butyllithium was used for the deprotonation for the isolated azasulphonium perchlorates **12g** and **12h** in dry THF. Aq. NaOH was also effectively used for the deprotonation of other azasulphonium salts in dichloromethane. The results are summarized in Table 4. This type of ready 1,2-shift of the substituent on sulphur to nitrogen is quite rare in sulphilimines, although the 1,2-imino shifts[7,11] from the sulphur atom to the α-methylene carbon atom or Sommelet–Hauser-type 2,3-sigmatropic rearrangements[12] of *N*-aryl sulphilimines are well known. The 1,2-imino shifts are believed to occur after proton transfer from the α-carbon atom to the nitrogen atom, generating the sulphonium ylide intermediate. The ring-




**Scheme 4** *Reagents and conditions:* i, BuLi, THF, −70 to 0 °C

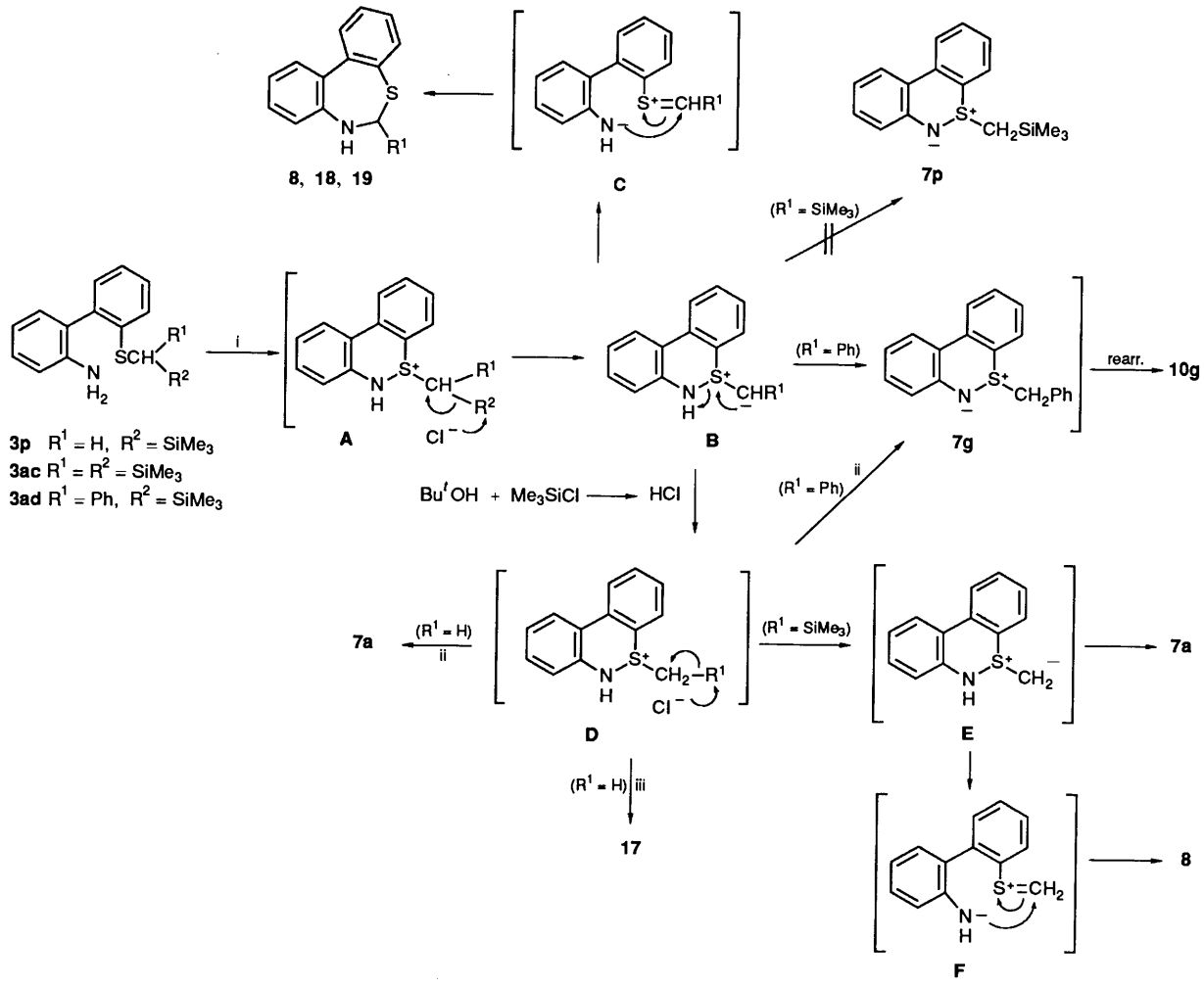



**Scheme 5** *Reagents and conditions:* i, NCS, $CH_2Cl_2$, −50 °C; ii, $AgBF_4$; iii, NCS or Bu$^t$OCl, $CH_2Cl_2$, −78 to −50 °C; iv, aq. NaOH or KOH, 0 °C; v, BuLi, TMEDA, −78 °C; vi, $Me_3SiCl$

expansion reaction of compound **7a** to compound **8** is understandable in terms of this 1,2-imino shift. To our knowledge, there is a single recent report on the thermal (60 °C) 1,2-alkyl shift of highly strained four-membered-ring exocyclic sulphilimines, in which the high ring strain is considered to cause the S–C bond fission, making the 1,2-alkyl shift possible.[13] There have been some reports postulating a 1,2-alkyl-shifted intermediate in a reaction mechanism for the formation of final products resulting from thermal decomposition (180 °C, sealed tube) of acyclic *N*-tosylsulphilimines[14,15] or thermal decomposition (reflux in bromobenzene) of an *S*-methyl thiophene-fused thiaazabenzene.[4b]

In order to obtain information concerning the mechanism of this interesting 1,2-rearrangement of thiaazaphenanthrenes, we investigated the cross-over experiment between 5-benzyl-3,8-dimethyl-6*H*-dibenzo[*c*,*e*][1,2]thiazin-5-ium perchlorate **14** and 5-(4-methylbenzyl)-6*H*-dibenzo[*c*,*e*][1,2]thiazin-5-ium perchlorate **12h** as shown in Scheme 4. The azasulphonium salt **14** was prepared by a similar synthetic sequence to that for the preparation of compounds **12** described above, *via* 2-amino-4,4′-dimethyl-2′-nitrobiphenyl which was synthesized as follows: Ullmann coupling of 2-chloro-5-methylnitrobenzene afforded 4,4′-dimethyl-2,2′-dinitrobiphenyl in 53% yield, which was submitted to reduction with sodium hydrogen sulphide in methanol. A mixture of azasulphonium perchlorates **12h** and **14** was allowed to react with butyllithium in THF at −70 °C. After usual work-up, the reaction mixture was subjected to mass spectroscopy. Molecular-ion peaks attributable to crossed products **10g** and **16** were observed at *m*/*z* 289 and 331, respectively, together with those of the intramolecularly rearranged products **10h** and **15** at *m*/*z* 303 and 317, respectively, suggesting that the 1,2-rearrangement of the benzyl substituent proceeded intermolecularly. The 1,2-rearrangement is similar to the Stevens rearrangement of an isoelectronic sulphonium ylide and is closely related to that process in occurring *via* initial formation of a cation-radical intermediate.

*Attempted Preparations of 9-Trimethylsilylmethyl-9-thia-10-azaphenanthren-9-ium-10-ide* **7p**—*Desilylation Reactions.*—2-Amino-2′-trimethylsilylmethylthiobiphenyl **3p** was subjected to sequential reaction with a chlorinating agent and base to afford none of the expected 9-trimethylsilylmethyl-9-thia-10-azaphenanthren-9-ium-10-ide **7p** but instead the desilylated product **7a** was obtained in 79% yield (Scheme 5). In order to determine the stage of desilylation, we tried to isolate the azasulphonium salt intermediate by adding silver tetrafluoroborate to the reaction mixture of substrate **3p** and chlorinating agent (NCS or Bu$^t$OCl) before the treatment with base. However, we could not isolate the corresponding 5-trimethylsilylmethyl-6*H*-dibenzo[*c*,*e*][1,2]thiazin-5-ium tetrafluoro-



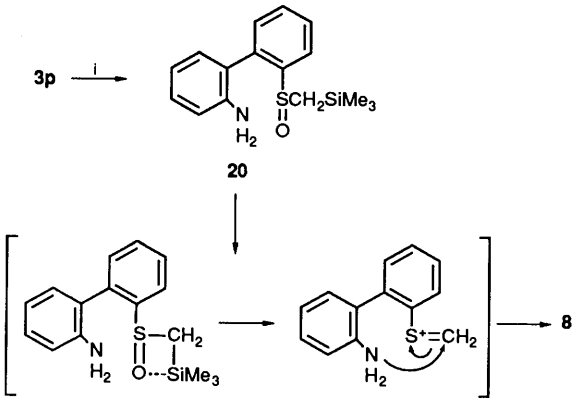

**Scheme 6** *Reagents:* i, Bu'OCl; ii, NaOH; iii, $AgBF_4$

borate, but only the desilylated thiazinium tetrafluoroborate **17** in 33% yield. This suggested that desilylation might occur during cyclization of the aminobiphenyl **3p**. This was confirmed by the successful isolation of 5-methyl-6*H*-dibenzo[*c*,*e*][1,2]-thiazin-5-ium chloride as very hygroscopic material from the reaction mixture of compound **3p** and Bu'OCl. In this case, we could also obtain ring-expanded product **8** in 7% yield. Judging from this desilylation reaction, we considered that if we performed the cyclization of 2-amino-2′-[bis(trimethylsilyl)-methylthio]biphenyl **3ac**, we would prepare the thiaazaphen-anthrene **7p** after desilylation of one of two trimethylsilyl groups during the cyclization with Bu'OCl. Hence, we next carried out the cyclization of compound **3ac**, which was prepared by the trimethylsilylation of compound **3p** after treatment with butyllithium in the presence of tetramethyl-ethylenediamine (TMEDA) (Scheme 5). However, we did not obtain the expected product **7p**, but instead the monodesilylated and seven-membered-ring product **18** in 62% yield together with compounds **7a** (8%) and **8** (6%) as shown in Scheme 5. Even if this reaction was performed without treatment with base, compound **18** was also obtained in 52% yield along with a trace amount of the product **7a**. When this interesting desilylation reaction was applied to 2-amino-2′-[(α-trimethyl-silyl)benzylthio]biphenyl **3ad**, which was prepared in 79% yield by trimethylsilylation of compound **3g**, seven-membered-ring product **19** and 1,2-thiazine derivative **10g** were obtained in 39 and 7% yield, respectively. When treatment with base was omitted in this reaction, compound **19** was again obtained, in 25% yield, together with a trace of compound **10g**.

We propose the following mechanism for these desilylation reactions of 2-amino-2′-trimethylsilylmethylbiphenyl deriva-tives **3p**, **3ac** and **3ad** with chlorinating agents (Bu'OCl as a representative) as shown in Scheme 6. Biphenyls **3p**, **3ac** and **3ad** cyclize to give azasulphonium chloride **A**, whose chloride counterion next attacks nucleophilically on the silicon atom to afford the *exo*-sulphonium ylide intermediate **B** along with trimethylsilyl chloride. The sulphonium ylide intermediate **B** collapses to give ring-expanded products **8**, **18** and **19** *via* the intermediate **C**. This process is rationalized as a 1,2-imino shift. Our first expectation, that intermediate **B** might be converted into the expected 9-trimethylsilylmethyl-9-thia-10-azaphenan-threne **7p** *via* 1,3-proton shift, was in vain. In contrast, a portion of intermediate **B**; $R^1$ = Ph, probably undergoes a 1,3-proton shift to give the 9-benzylthiaazaphenanthrene **7g**, which then undergoes easy 1,2-benzyl migration to furnish compound **10g**. On the other hand, most of intermediate **B** is protonated with hydrogen chloride generated from the reaction of Bu'OH and trimethylsilyl chloride formed *in situ* to give azasulphonium chloride **D**. In the case where $R^1$ = H, treatment of the azasulphonium salt **D** with base gives compound **7a**, and addition of silver tetrafluoroborate to **D** causes exchange of the counterion to give the tetrafluoroborate **17**. In the case where $R^1$ = Ph, action of base on intermediate **D** forms the 9-benzylthiaazaphenanthrene **7g** which is easily converted into compound **10g**. When $R^1$ = TMS, chloride ion from the intermediate **D** again attacks the silicon atom to give the methylide intermediate **E**, which undergoes a 1,2-imino shift to lead to the formation of compound **8** *via* intermediate **F**. A

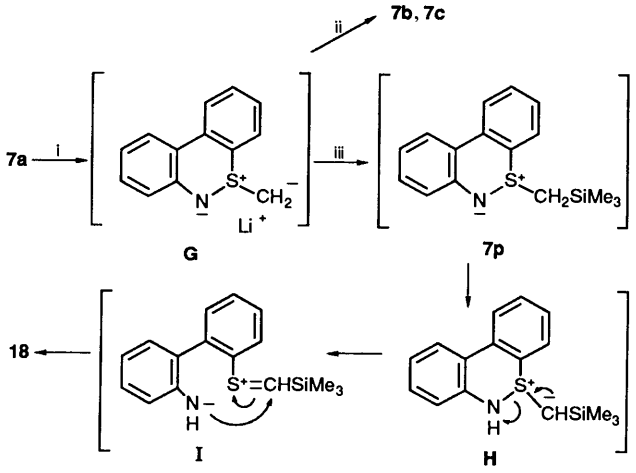
portion of intermediate **E** undergoes a 1,3-proton shift to result in the formation of **7a**.

The above results forced us to develop other methods for the synthesis of compound **7p**. We first planned to adopt a dehydration reaction between an amino compound and the sulphoxide moiety, which is one of the well known methods for the convenient preparation of sulphilimines.[16] However, 2-amino-2′-(trimethylsilylmethylsulphinyl)biphenyl **20**, prepared by *m*-chloroperbenzoic acid (MCPBA) oxidation of the biphenyl **3p**, was very unstable at room temperature and readily converted into compound **8** in 87% yield, presumably *via* an intramolecular Sila–Pummerer rearrangement as shown in Scheme 7. Since the methyl hydrogen of 9-methylthia-




**Scheme 7** *Reagent:* i, MCPBA

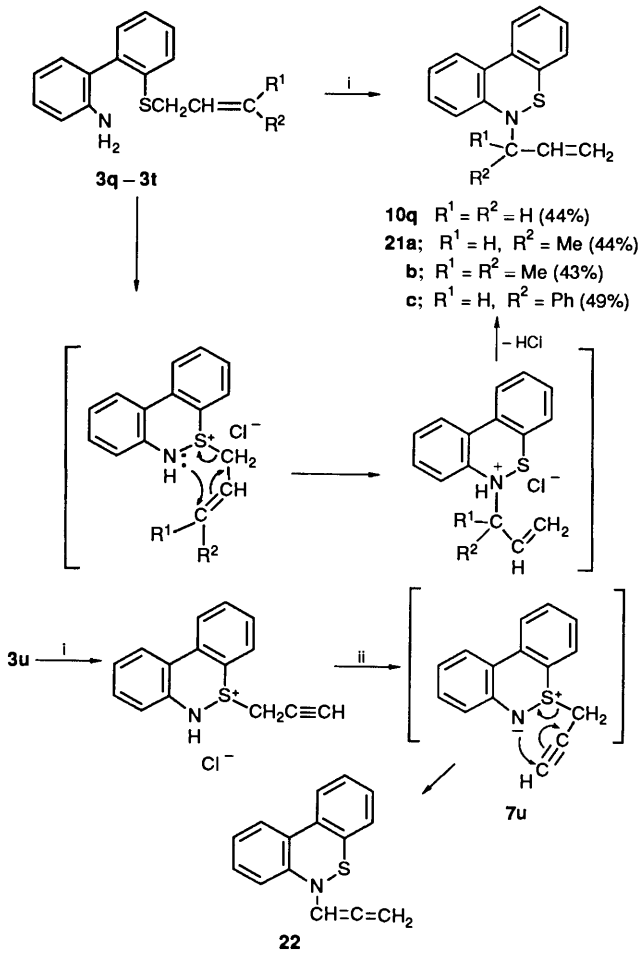
azaphenanthrene **7a** is considered to be acidic due to the positive sulphur atom,[17] we next conducted a deprotonation of the methyl group with butyllithium to give a red coloured solution of the anion **G**, which was then quenched with methyl or ethyl iodide to afford 9-alkylthiaazaphenanthrene derivative **7b** or **7c**, respectively, in 31 or 44% yield (Scheme 8).




**Scheme 8** *Reagents:* i, BuLi, THF; ii, MeI or EtI; iii, $Me_3SiCl$

We then carried out the quenching of the red solution with TMSCl, but the expected trimethylsilylated thiaazaphenanthrene **7p** was not obtained. Instead, ring-expanded product **18** was formed in 27% yield, presumably *via* sulphonium ylide intermediate **H** derived from the expected compound **7p** by 1,3-proton shift. This result shows clearly that intermediate **H** is thermally more stable than is **7p**, explaining well the lack of conversion of the intermediate **B** ($R^1$ = TMS) into zwitterion **7p** as discussed in Scheme 6.

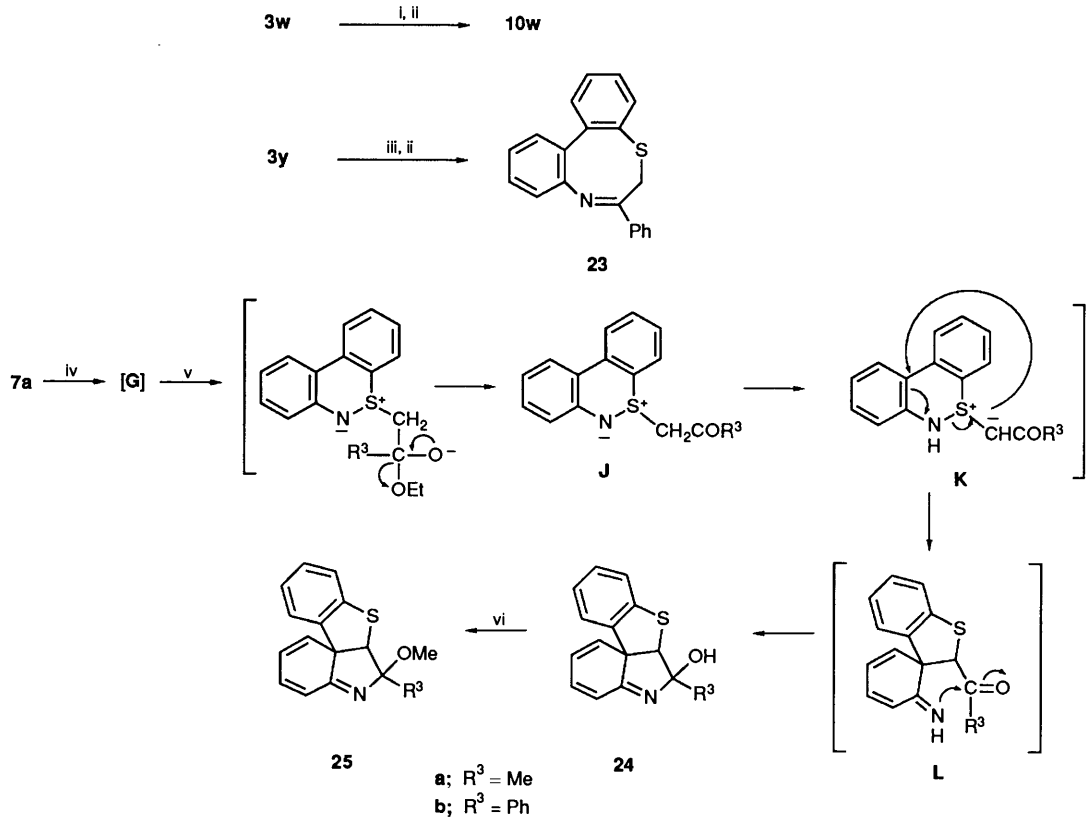
*Synthetic Approaches to 9-Allyl- or 9-Prop-2-ynyl-9-thia-10-azaphenanthrenes.*—2-Allylthio-2′-aminobiphenyl **3q** was allowed to react with Bu$^t$OCl to afford (surprisingly) no corresponding dibenzothiazinium salt, but instead the dibenzothiazine derivative **10q** in which the allyl group has rearranged from the sulphur to the nitrogen. In order to clarify the rearrangement mode of the allyl group, the same reactions of other biphenyls **3r–3t** bearing a methyl- or phenyl-substituted allylthio group were performed and they afforded similar dibenzothiazine derivatives, compounds **21a**, **21b** and **21c** respectively, in moderate yield, by rearrangement of the $sp^2$-carbon of the allyl group. Since the rearrangement of the allyl group from sulphur to nitrogen took place without the presence of base, it is difficult to understand the formation of 9-allylthiaazaphenanthrenes and their successive 2,3-sigmatropic rearrangement as observed in acyclic allylsulphilimines generally.[7,11] Therefore, we think that this interesting rearrangement proceeds *via* the process shown in Scheme 9. On




**Scheme 9** *Reagents and conditions:* i, Bu$^t$OCl, $CH_2Cl_2$, −78 °C to room temp.; ii, aq. NaOH, $CH_2Cl_2$, 0 °C

the other hand, 2-amino-2′-(prop-2-ynylthio)biphenyl **3u** precipitated 5-(prop-2-ynyl)dibenzothiazinium chloride after treatment with Bu$^t$OCl, which in turn was successively treated with NaOH to afford 6-(propa-1,2-dienyl)dibenzo[1,2]thiazine **22** as an unstable oil in 40% yield, presumably *via* the 2,3-sigmatropic rearrangement of the unstable 9-(prop-2-ynyl)thiaazaphenanthrene **7u** as shown in Scheme 9.

*Synthetic Approaches to Thiaazaphenanthrenes bearing an Electron-withdrawing Group at the 9-Position.*—The preparation of thiaazaphenanthrenes having an electron-withdrawing group at the 9-position was then attempted (Scheme 10). The




**Scheme 10** *Reagents and conditions:* i, Bu$^t$OCl, $CH_2Cl_2$, −78 °C; ii, aq. NaOH, 0 °C; iii, NCS, $CH_2Cl_2$; iv, LDA, THF; v, $R^3CO_2Et$; vi, NaH, MeI, THF

sequential reaction of 2-amino-2′-cyanomethylbiphenyl **3w** with Bu$^t$OCl and base gave the 6-cyanomethyldibenzo[1,2]-thiazine derivative **10w** in 22% yield by 1,2-migration of the 9-substituent of the initially formed thiaazaphenanthrene **7w**, together with a very complex mixture of other products. In contrast, similar reaction of the 2-amino-2′-ethoxy-carbonylmethylthiobiphenyl **3x** or the 2′-(2,2,2-trifluoroethyl-thio) derivative **3v** did not afford the desired thiaazaphenan-threne, but instead only undetermined complex mixtures. On the other hand, the cyclization of 2-amino-2′-phenacylthiobiphenyl **3y** with chlorinating agent (NCS), followed by treatment with aq. NaOH, gave quite different results, and yielded only eight-membered-ring compound **23** in low yield together with unchanged starting material. Therefore, we next tried the acylation of the anion **G** with a carboxylic ester for the preparation of acylmethyl-group-substituted thiaazaphenan-threnes. A solution of the anion **G** generated by treatment of substrate **3a** with lithium diisopropylamide (LDA) in THF was allowed to react with ethyl acetate to result in the formation of benzothienoindole derivative **24a**, m.p. 203–205 °C, as prisms in 48% yield. The structure of this novel compound was determined on the basis of analytical and spectral data. Elemental analysis and mass spectral data [*m/z* 255 ($M^+$)] indicate a molecular formula of $C_{15}H_{13}NOS$ for this compound. The IR spectrum showed a characteristic absorption band at 3130 $cm^{-1}$ for the hydroxy group. The $^1H$ NMR spectrum ($CDCl_3$) showed a singlet for the methyl group at $\delta$ 1.07 and a singlet for the methine proton at $\delta$ 3.85. The $^{13}C$ NMR spectrum showed two quaternary carbon signals at $\delta$ 69.5 and 100.8, which are assignable to the spiro carbon and tertiary alcoholic carbon atoms, respectively, and an $sp^3$-tertiary carbon signal assigned to CHS at $\delta$ 66.3. The reaction of the anion **G** with ethyl benzoate similarly gave the corresponding benzothienoindole derivative **24b**, m.p. 187–189 °C, as pale yellow prisms in 39% yield. The hydroxy groups of the spiro compounds **24a** and **24b** were easily methylated by quenching with methyl iodide after treatment with sodium hydride to give methoxy compounds **25a** and **25b**, respectively.

A plausible mechanism for the formation of spiro compounds **24** is also depicted in Scheme 10. Nucleophilic attack of the carbanion **G** on the carbonyl group of the ester forms our expected 9-acylmethylthiaazaphenanthrene **J** by the loss of ethoxide ion. However, intermediate **J** readily led to the *exo*-sulphonium ylide intermediate **K**, *via* 1,3-proton shift, whose carbanion attacks the aromatic carbon (C-10a) accompanied by the cleavage of the S–N bond to give intermediate **L** (Sommelet–Hauser-type rearrangement).

Finally, the nitrogen atom of the intermediate **L** attacks the proximate carbonyl group to give the final product **24**. This type of Sommelet–Hauser rearrangement of acyclic aryl sulphilimines bearing an acylmethyl group on the sulphur atom to give indole derivatives was reported by Gassman *et al.*[18]

Attempts to lead 2-amino-2′-methylthiomethylthio- **3z** or -2′-methoxymethylthiobiphenyl **3aa** to the corresponding thia-azaphenanthrene failed and resulted in complex mixtures.

In summary, we have demonstrated that the thermal behaviour of several types of 9-substituted 9-thia-10-aza-phenanthrenes depended greatly upon the nature of the substituent on the sulphur atom. The most fascinating result is that 9-benzyl and 9-cyanomethyl derivatives underwent a rarely observed 1,2-rearrangement to afford the corresponding 6-substituted 6*H*-dibenzo[*c*,*e*][1,2]thiazines.

## Experimental

M.p.s were measured on a Yanagimoto micro melting point apparatus, and are uncorrected. IR spectra were measured on a JASCO A-1 spectrophotometer. $^1H$ NMR spectra were recorded on a Hitachi R-20B (60 MHz) or a JEOL GX-270

(270 MHz) spectrometer with tetramethylsilane as internal standard. The coupling constants (*J*) are in Hz. $^{13}C$ NMR spectra were obtained using a JEOL GX-270 spectrometer. Mass spectra were obtained using a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. Analytical and preparative TLC (PLC) were performed on E. M. Merck silica gel 60PF-254 plates.

2-[*Ethoxy(thiocarbonyl)thio*]-2′-*nitrobiphenyl* **2**.—2-Amino-2′-nitrobiphenyl hydrochloride **1**[5] (20 g, 79.78 mmol) was suspended in a mixture of conc. HCl (8.5 $cm^3$) and ice–water (100 $cm^3$). A solution of sodium nitrite (6.06 g, 87.76 mmol) in water (20 $cm^3$) was slowly added to the above stirred suspension at 0–5 °C and the mixture was further stirred for 2 h at the same temperature. The resulting orange diazonium salt solution was slowly added to a stirred solution of potassium *O*-ethyl dithiocarbonate (15.35 g, 95.74 mmol) in water (20 $cm^3$), dichloromethane (20 $cm^3$) was added to dissolve the precipitated sticky product, the mixture was stirred overnight before being extracted with dichloromethane, and the extract was washed with water, dried ($CaCl_2$), and evaporated to dryness. The residual oil was purified by silica gel column chromatography with hexane–diethyl ether (10:1) as solvent to give the *title compound* (12.9 g, 54.4%) as yellow prisms after recrystallization from dichloromethane–hexane, m.p. 65–67 °C; $\nu_{max}/cm^{-1}$ 1530 and 1350 ($NO_2$); $\delta_H(CDCl_3)$ 1.27 (3 H, t, *J* 7.5, $CH_2Me$), 4.50 (2 H, q, *J* 7.5, $CH_2Me$) and 7.25–8.25 (8 H, m, ArH); *m/z* 319 ($M^+$) (Found: C, 56.1; H, 4.2; N, 4.3. $C_{15}H_{13}NO_3S_2$ requires C, 56.4; H, 4.1; N, 4.4%).

*General Procedure for the Preparation of* 2-*Alkylthio*-2′-*aminobiphenyls* **3**.—2-*Amino*-2′-*methylthiobiphenyl* **3a**. A solution of the nitrobiphenyl **2** (1.08 mg, 3.38 mmol) in dry THF (5 $cm^3$) was slowly added to a stirred suspension of $LiAlH_4$ (640 mg, 16.9 mmol) in dry THF (30 $cm^3$). After the mixture had been stirred for 2 h, ethanol was slowly added to destroy excess of $LiAlH_4$, and then methyl iodide (960 mg, 6.76 mmol) was added and the mixture was stirred overnight. Water (20 $cm^3$) was added to the reaction mixture which was stirred then for 30 min and filtered to remove the solid. The filtrate was extracted with diethyl ether and the extract was washed with water, dried ($MgSO_4$), and evaporated to dryness under reduced pressure. The residue was purified by PLC on silica gel with hexane–diethyl ether (1:1) as solvent to give the *title biphenyl* (398 mg, 54.7%) as columns after recrystallization from hexane–benzene.

In a similar manner to that above, other 2-alkylthio-2′-aminobiphenyls (**3b**–**3aa**) were prepared from compound **2** and appropriate organohalides. The results are summarized in Table 1. The physicochemical and analytical data of the products are shown in Table 2 and their spectral data are summarized in Table 3.

*Preparation of* 9-*Alkyl*-9-*thia*-10-*azaphenanthren*-9-*ium*-10-*ides* **7**.—(*a*) 9-*Propyl*-9-*thia*-10-*azaphenanthren*-9-*ium*-10-*ide* **7c**. A solution of NCS (1.63 g, 12.2 mmol) in dry dichloromethane (40 $cm^3$) was added dropwise during 1 h to a stirred solution of the biphenyl **3c** (2.7 g, 11.09 mmol) in dry dichloromethane (50 $cm^3$) at −50 °C, and the mixture was stirred for 1 h at the same temperature, and then for a further 13 h during which time the temperature was gradually raised to 0 °C. The reaction mixture was extracted with dil. aq. KOH [KOH (3.11 g) in water (60 $cm^3$)] and the organic layer was separated, dried ($MgSO_4$), and evaporated to give the *title compound* (2.13 g, 79.4%). Recrystallization of this from diethyl ether–hexane afforded yellow prisms, m.p. 58–59 °C (decomp.); $\delta_H(CDCl_3)$ 0.93 (3 H, t, *J* 8, $CH_2CH_2Me$), 1.15–1.85 (2 H, m, $CH_2CH_2Me$), 2.10–2.30 (2 H, m, $CH_2CH_2Me$) and 6.70–8.05 (8 H, m, ArH); *m/z* 241 ($M^+$) (Found: C, 74.4: H, 6.4; N, 5.6. $C_{15}H_{15}NS$ requires C, 74.6; H, 6.3; N, 5.8%).

(*b*) 9-*Isopropyl*-9-*thia*-10-*azaphenanthren*-9-*ium*-10-*ide* **7d**. A solution of $Bu^tOCl$ (250 mg, 2.32 mmol) in dry dichloromethane (10 $cm^3$) was added dropwise to a stirred solution of the biphenyl **3d** (540 mg, 2.22 mmol) in dry dichloromethane (20 $cm^3$) at −78 °C and the mixture was stirred for 2 h at −78 °C and then overnight during which time the temperature was raised to ambient. Aq. NaOH (93 mg, 2.3 mmol in water, 2.5 $cm^3$) was added to the above reaction mixture at 0 °C and the mixture was stirred for 30 min. The reaction mixture was extracted with dichloromethane and the extract was washed with water, dried ($MgSO_4$), and evaporated under reduced pressure. The residual oil was passed through silica gel with diethyl ether–hexane (2:1) as solvent to afford the *title thiaazaphenanthrene* (487 mg, 91%) as a yellow oil; $\delta_H(CDCl_3)$ 0.95 (3 H, d, *J* 7, Me), 1.18 (3 H, d, *J* 7, Me), 3.32 (1 H, m, CH) and 6.60–8.02 (8 H, m, ArH); *m/z* 241 ($M^+$) and 198 (base) (Found: $M^+$, 241.0910. $C_{15}H_{15}NS$ requires M, 241.0924).

In a similar manner to that above, the following thiazaphenanthrenes were prepared.

9-sec-*Butyl*-9-*thia*-10-*azaphenanthren*-9-*ium*-10-*ide* **7e**, from the biphenyl **3e**, as a red oil (86.5%); $\delta_H(CDCl_3)$ 0.87 (6 H, m, 2 × Me), 1.42 (2 H, m, $CH_2$), 3.20 (1 H, m, CH) and 6.90–7.90 (8 H, m, ArH); $\delta_C(CDCl_3)$ 9.7 (q), 12.5 (q), 22.4 (t), 50.4 (d), 119.0 (d), 121.3 (s), 121.4 (s), 123.9 (d), 124.3 (d), 124.8 (d), 126.6 (d), 127.0 (d), 130.0 (d), 131.4 (d), 132.9 (s) and 149.7 (s); *m/z* 255 ($M^+$) and 198 (base) (Found: $M^+$, 255.1068. $C_{16}H_{17}NS$ requires M, 255.1081).

9-*Cyclohexyl*-9-*thia*-10-*azaphenanthren*-9-*ium*-10-*ide* **7f**, from the biphenyl **3f**, as an orange oil (75%); $\delta_H(CDCl_3)$ 1.03–1.65 (10 H, m, 5 × $CH_2$ of cyclohexane), 2.84–3.21 (1 H, m, CH of cyclohexane) and 6.88–7.90 (8 H, m, ArH); $\delta_C(CDCl_3)$ 22.4 (t), 22.6 (t), 25.2 (t), 25.8 (t), 26.3 (t), 52.9 (d), 118.9 (d), 120.7 (s), 121.5 (s), 123.9 (d), 124.3 (d), 124.9 (d), 126.6 (d), 126.9 (d), 130.0 (d), 131.5 (d), 132.9 (s) and 149.9 (s); *m/z* 281 ($M^+$) and 198 (base) (Found: $M^+$, 281.1248. $C_{18}H_{19}NS$ requires M, 281.1238).

2-*Iodophenyl Phenyl Sulphide* **5**.—2-Aminophenyl phenyl sulphide **4**[6] (6.28 g, 31.2 mmol) was dissolved in conc. HCl (22 $cm^3$) and ice–water (100 $cm^3$) was added. Aq. sodium nitrite (3.04 g, 44 mmol in water, 20 $cm^3$) was slowly added to the above solution at 0–5 °C and the mixture was stirred for 2.5 h at the same temperature. The resulting diazonium salt solution was slowly added to aq. potassium iodide (13.28 g, 80 mmol in 100 $cm^3$) and the mixture was stirred overnight at room temperature. The reaction mixture was extracted with diethyl ether, and the extract was washed successively with aq. sodium thiosulphinate and water, dried ($MgSO_4$), and evaporated to dryness. The residue was purified by silica gel column chromatography with hexane–dichloromethane (3:1) as solvent to give the *title sulphide* (9.21 g, 94.5%) as a powder, m.p. 45–47 °C; $\delta_H(CDCl_3)$ 6.90–7.98 (m, ArH); *m/z* 312 ($M^+$) (Found: C, 46.2; H, 2.95. $C_{12}H_9IS$ requires C, 46.2; H, 2.9%).

2-*Nitro*-2′-*phenylthiobiphenyl* **6**.—A mixture of 2-iodonitrobenzene (16 g, 64 mmol), the sulphide **5** (20 g, 64 mmol), and copper powder (16.3 g) was heated at 190–200 °C and vigorously stirred for 1.5 h. Benzene was added to the cooled reaction mixture, which was then stirred for 30 min. The solids were filtered off and washed well with benzene. The combined washings and filtrates were evaporated to dryness. The residue was separated by column chromatography on silica gel with hexane–dichloromethane (3:1) as solvent to give the *title compound* (7.12 g, 59.4%) as an oil; $\nu_{max}/cm^{-1}$ 1522 and 1350 ($NO_2$); $\delta_H(CDCl_3)$ 7.10–8.15 (m, ArH); *m/z* 307 ($M^+$) and 261

(base) (Found: $M^+$, 307.0650. $C_{18}H_{13}NO_2S$ requires M, 307.0666).

2-*Amino*-2′-*phenylthiobiphenyl* **3ab**.—A mixture of compound **6** (1.69 g, 5.5 mmol), Zn powder (2.15 g, 33 mmol), and $CaCl_2$ (1.81 g, 16.5 mmol) in 80% ethanol (50 $cm^3$) was refluxed for 3 h. The hot reaction mixture was filtered to remove solids, and the solids were well washed with hot ethanol. The combined ethanolic solution was poured into water and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residual oil was purified by column chromatography on silica gel with dichloromethane–hexane (1:1) as solvent to yield the *title compound* (1.43 g, 94.2%) as needles after recrystallization from dichloromethane–hexane, m.p. 69–71 °C; $\nu_{max}/cm^{-1}$ 3470 and 3380 ($NH_2$); $\delta_H$ 3.37 (2 H, br, $NH_2$) and 6.55–7.40 (13 H, m, ArH); *m/z* 277 ($M^+$) and 168 (base) (Found: C, 77.9; H, 5.5; N, 4.9. $C_{18}H_{15}NS$ requires C, 77.9; H, 5.45; N, 5.05%).

9-*Phenyl*-9-*thia*-10-*azaphenanthren*-9-*ium*-10-*ide* **7ab**.—This compound was prepared by reaction of the biphenyl **3ab** (1.96 g, 7.07 mmol) with Bu$^t$OCl (828 mg, 7.63 mmol) in dry dichloromethane (120 $cm^3$), followed by treatment with aq. NaOH and work-up as described for compound **7d**; yellow prisms, m.p. 110–112 °C (from hexane–dichloromethane) (1.78 g, 91.6%); $\delta_H(CDCl_3)$ 6.86–7.98 (m, ArH); $\delta_C(CDCl_3)$ 119.45 (d), 121.44 (s), 121.89 (s), 124.02 (d), 124.85 (d), 125.45 (d), 125.98 (d), 126.44 (d), 127.05 (d), 128.76 (d), 128.87 (d), 129.96 (d), 131.79 (d), 133.35 (s), 140.71 (s) and 149.89 (s); *m/z* 275 ($M^+$) and 198 (base) (Found: $M^+$, 275.0749. $C_{18}H_{13}NS$ requires M, 275.0768) (Found: C, 76.6; H, 4.65; N, 4.9. $C_{18}H_{13}NS{\cdot}0.1CH_2Cl_2$ requires C, 76.6; H, 4.65; N, 4.9%).

*Thermal Reactions of* 9-*Alkyl*-9-*thia*-10-*azaphenanthren*-9-*ium*-10-*ides* **7**.—*Thermolysis of* 9-*propyl*-9-*thia*-10-*phenanthren*-9-*ium*-10-*ide* **7c**. A solution of compound **7c** (500 mg) in dry benzene (30 $cm^3$) was refluxed for 10 h under nitrogen. Benzene was evaporated off to give an oil, which was separated by PLC on silica gel with hexane–diethyl ether (5:1) to afford 6*H*-dibenzo[*c*,*e*][1,2]thiazine **9** (293 mg, 71%) as an oil. All spectral data of the product **9** were perfectly identical with those of an authentic sample obtained from the thermal reaction of 9-ethyl-9-thia-10-azaphenanthren-9-ium-10-ide **7b**, which was described in our previous report.[2] Thermolysis of compound **7c** in xylene under reflux for 30 min afforded compound **9** in 66.6% yield.

Thermolysis of other thiaazaphenenthrenes **7d** and **7e** also gave compound **9**, in 45.1 and 44% yield, respectively.

*Thermolysis of* 9-*cyclohexyl*-9-*thia*-10-*azaphenanthren*-9-*ium*-10-*ide* **7f**. A solution of compound **7f** (334 mg) in dry benzene (20 $cm^3$) was refluxed for 2.5 h under nitrogen. The solvent was removed and the residue was then separated by PLC on silica gel with hexane–ethyl acetate (9:1) to afford the product **9** (81 mg, 34%), 6-*cyclohexyl*-6H-*dibenzo*[c,e][1,2]*thiazine* **10f** (32 mg, 10%), and unchanged starting compound **7f** (98 mg, 29% recovery). The product **10f** was a yellow oil; $\delta_H(CDCl_3)$ 1.02–1.67 (10 H, m, 5 × $CH_2$ of cyclohexane), 2.83–2.95 (1 H, m, CH of cyclohexane), 7.17–7.30 (6 H, m, ArH) and 7.72–7.77 (2 H, m, ArH); $\delta_C(CDCl_3)$ 25.5 (t), 31.4 (t), 67.3 (d), 124.3 (d), 124.6 (d), 125.3 (d), 125.5 (d), 126.7 (d), 126.9 (d), 127.9 (d), 128.1 (d), 131.7 (s), 133.1 (s), 137.0 (s) and 147.1 (s); *m/z* 281 ($M^+$) and 198 (base) (Found: $M^+$, 281.1251. $C_{18}H_{19}NS$ requires M, 281.1234).

*Thermolysis of* 9-*phenyl*-9-*thia*-10-*azaphenanthren*-9-*ium*-10-*ide* **7ab**. A solution of compound **7ab** (543 mg) in xylene (35 $cm^3$) was refluxed for 55 h. The reaction mixture was concentrated to dryness and the residual oil was separated by PLC on silica gel with ethyl acetate–hexane (1:2) as solvent to afford 10a-*phenyl*-10a*H*-*dibenzo*[c,e][1,2]*thiazine* **11** (96 mg, 17.7%), the ring-opened product **3ab** (129 mg, 23.8%), and unchanged starting compound **7ab** (161 mg, 29.7%) was recovered. The product **11** was obtained as yellow prisms, m.p. 83–85 °C (from hexane); $\delta_H(CDCl_3)$ 6.18–6.82 (4 H, m, olefinic H) and 6.90–7.68 (9 H, m, ArH); $\delta_C(CDCl_3)$ 53.52 (s), 119.91 (d), 122.80 (d), 126.27 (d), 126.70 (d), 127.20 (d), 127.32 (d), 127.53 (d), 128.19 (d), 129.03 (d), 130.01 (s), 134.51 (s), 137.66 (d), 138.74 (s) and 164.88 (s); *m/z* 275 ($M^+$) and 198 (base) (Found: C, 78.7; H, 4.8; N, 5.05. $C_{18}H_{13}NS$ requires C, 78.5; H, 4.8; N, 5.1%).

5-*Benzyl*-6H-*dibenzo*[c,e][1,2]*thiazin*-5-*ium Perchlorate* **12g**.—The biphenyl **3g** (1.56 g, 5.34 mmol) was dissolved in dry dichloromethane (50 $cm^3$). The solution was cooled to −50 °C and stirred while a solution of NCS (784 mg, 5.87 mmol) in dry dichloromethane (30 $cm^3$) was added dropwise during 30 min. The mixture was stirred for a further 15 h during which time the temperature was gradually raised to −5 °C. Silver perchlorate (1.11 g, 5.34 mmol) was added to the reaction mixture, which was then stirred for 3 h. The precipitated silver chloride was filtered off and washed several times with dichloromethane. Dry diethyl ether was added to the filtrate to precipitate crystals, which were collected and recrystallized from dichloromethane–diethyl ether to afford the title thiazinium perchlorate (1.31 g, 63%) as prisms, m.p. 171–173 °C (decomp.); $\nu_{max}/cm^{-1}$ 1050–1150 ($ClO_4^-$); $\delta_H(CF_3CO_2H)$ 4.01 (2 H, ABq, *J* 12, $\Delta\nu$ 14 Hz, $CH_2$) and 6.47–7.90 (13 H, m, ArH) (Found: C, 58.7; H, 4.1; N, 3.6. $C_{19}H_{16}ClNO_4S$ requires C, 58.5; H, 4.1; N, 3.6%).

5-(4-*Methylbenzyl*)-6H-*dibenzo*[c,e][1,2]*thiazin*-5-*ium Perchlorate* **12h**.—This compound was prepared, by a similar manner to that described for **12g**, from the reaction of the biphenyl **3h** (0.8 g, 2.62 mmol) with NCS (384.7 mg, 2.88 mmol) in dry dichloromethane (70 $cm^3$), followed by treatment with silver perchlorate (593.3 mg, 2.88 mmol). The *title product* (733 mg, 69.3%) was obtained as prisms, m.p. 169–171 °C (decomp.) (from acetonitrile–diethyl ether); $\nu_{max}/cm^{-1}$ 1090–1120 ($ClO_4^-$); $\delta_H(CF_3CO_2H)$ 2.35 (3 H, s, Me), 4.46 (2 H, ABq, *J* 12, $\Delta\nu$ 14 Hz, $CH_2$) and 6.83–8.35 (12 H, m, ArH and NH) (Found: C, 59.5; H, 4.5; N, 3.5. $C_{20}H_{18}ClNO_4S$ requires C, 59.5; H, 4.5; N, 3.5%).

5-(4-*Bromobenzyl*)-6H-*dibenzo*[c,e][1,2]*thiazin*-5-*ium Perchlorate* **12m**.—A solution of Bu$^t$OCl (294 mg, 2.71 mmol) in dry dichloromethane (12 $cm^3$) was added dropwise to a stirred solution of the biphenyl **3m** (1 g, 2.70 mmol) in dry dichloromethane (12 $cm^3$) at −78 °C and the mixture was stirred for 4 h at −65 to −70 °C and then overnight during which time the temperature rose to ambient. 90% Silver perchlorate (626.4 mg, 2.71 mmol) was added to the reaction mixture, which was then stirred for 2 h. Work-up as described for compound **12g** gave the *title compound* (1.14 g, 90.3%) as columns after recrystallization from dichloromethane–hexane, m.p. 180 °C (decomp.); $\nu_{max}/cm^{-1}$ 1070–1120 ($ClO_4^-$); $\delta_H(CDCl_3)$ 4.38 (2 H, s, $CH_2$) and 6.78–8.35 (12 H, m, ArH) (Found: C, 48.4; H, 3.3; N, 2.9. $C_{19}H_{15}BrClNO_4S$ requires C, 48.7; H, 3.2; N, 3.0%).

The following compounds were prepared in a similar manner to that above.

5-(4-*Methoxybenzyl*)-6H-*dibenzo*[c,e][1,2]*thiazin*-5-*ium Perchlorate* **12i**, from the reaction of the biphenyl **3i** (500 mg, 1.56 mmol) with Bu$^t$OCl (200 mg, 1.87 mmol) in dry dichloromethane (45 $cm^3$), followed by treatment with silver perchlorate (350 mg, 1.71 mmol), and was obtained as a pale purple powder (300 mg, 45.9%), m.p. 133–135 °C (decomp.) (from acetonitrile–diethyl ether); $\nu_{max}/cm^{-1}$ 1020–1120 ($ClO_4^-$); $\delta_H[(CD_3)_2SO]$ 3.80 (3 H, s, OMe), 4.50 (2 H, s, $CH_2$) and 6.88–8.53 (12 H, m, ArH) (Found: C, 57.0; H, 4.3; N, 3.3. $C_{20}H_{18}ClNO_5S$ requires C, 57.2; H, 4.3; N, 3.3%).

5-(*Fluoren*-9-*yl*)-6H-*dibenzo*[c,e][1,2]*thiazin*-5-*ium Perchlorate* **12o**, from the reaction of the biphenyl **3o** (500 mg, 1.37

mmol) with Bu$^t$OCl (163 mg, 1.50 mmol) in dry dichloromethane (20 $cm^3$), followed by treatment with silver perchlorate (346 mg, 1.51 mmol), and was obtained as pale violet prisms (766 mg, 95%), m.p. 180–183 °C (decomp.) (from acetone–diethyl ether); $\nu_{max}/cm^{-1}$ 1100 ($ClO_4^-$); $\delta_H(CF_3CO_2H)$ 5.77 (1 H, s, CH) and 6.76–8.17 (16 H, m, ArH) (Found: C, 64.6; H, 4.05; N, 3.0. $C_{25}H_{18}ClNO_4S$ requires C, 64.7; H, 3.9; N, 3.0%).

*Attempts to Prepare 9-Benzyl-9-thia-10-azaphenanthrenes.*—*1,2-Rearrangement of 9-benzyl group.* (*a*) An ether solution of butyllithium (1 mol $dm^{-3}$; 2.6 $cm^3$) was added to a stirred suspension of compound **12g** (1 g, 2.57 mmol) in dry THF (20 $cm^3$) at −60 °C, and the mixture was stirred for 3 h during which time the temperature was gradually raised to 0 °C. The reaction mixture was poured into ice–water and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to dryness under reduced pressure. The residue was subjected to PLC on silica gel with hexane–ethyl acetate (3:1) as solvent to give 6-*benzyl*-6H-*dibenzo*[c,e][1,2]*thiazine* **10g** (371 mg, 50%) as a yellow oil; $\delta_H(CDCl_3)$ 4.09 (2 H, s, $CH_2$) and 7.05–7.90 (13 H, m, ArH); *m/z* 289 ($M^+$) and 198 (base) (Found: $M^+$, 289.0920. $C_{19}H_{15}NS$ requires M, 289.0925).

In a similar manner to that above, reaction of compound **12h** (600 mg, 1.49 mmol) with butyllithium (1.49 $cm^3$) afforded 6-(4-*methylbenzyl*)-6H-*dibenzo*[c,e][1,2]*thiazine* **10h** (259 mg, 57.4%) as a pale yellow oil; $\delta_H(CDCl_3)$ 2.30 (3 H, s, Me), 4.02 (2 H, s, $CH_2$) and 7.00–7.90 (12 H, m, ArH); *m/z* 303 ($M^+$) and 198 (base) (Found: $M^+$, 303.1069. $C_{20}H_{17}NS$ requires M, 303.1081).

(*b*) A solution of Bu$^t$OCl (136 mg, 1.25 mmol) in dry dichloromethane (5 $cm^3$) was slowly added to a stirred solution of the biphenyl **3n** (419 mg, 1.25 mmol) at −65 to −70 °C, and the mixture was stirred at the same temperature overnight, during which time the temperature was raised to ambient. The reaction mixture was cooled (ice) and aq. NaOH [NaOH (82 mg) in water (5 $cm^3$)] was added, and the mixture was stirred for 1 h. The organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to give an oil, which was separated by PLC on silica gel with hexane–ethyl acetate (4:1) to afford 6-(4-*nitrobenzyl*)-6H-*dibenzo*[c,e][1,2]-*thiazine* **10n** (237 mg, 56.9%) as pale yellow prisms, after recrystallization from hexane–dichloromethane, m.p. 96–98 °C; $\nu_{max}/cm^{-1}$ 1518 and 1340 ($NO_2$); $\delta_H(CDCl_3)$ 4.17 (2 H, s, $CH_2$) and 7.11–8.11 (12 H, m, ArH); $\delta_C(CDCl_3)$ 62.92 (t), 123.31 (d), 124.59 (d), 125.32 (d), 125.89 (d), 125.99 (d), 126.56 (d), 127.37 (d), 128.20 (d), 128.89 (d), 130.05 (d), 130.81 (s), 131.90 (s), 133.03 (s), 144.62 (s), 147.15 (s) and 147.40 (s); *m/z* 334 ($M^+$) and 198 (base) (Found: C, 68.4; H, 4.2; N, 8.4. $C_{19}H_{14}N_2O_2S$ requires C, 68.3; H, 4.2; N, 8.4%).

In a similar manner to that above, the other biphenyl derivatives **3i**–**3m** and **3o** afforded the following 1,2-rearranged products, **10i**–**10m** and **10o**, respectively.

6-(4-*Methoxybenzyl*)-6H-*dibenzo*[c,e][1,2]*thiazine* **10i**, from the biphenyl **3i**, as a yellow oil (21%); $\delta_H(CDCl_3)$ 3.78 (3 H, s, OMe), 3.99 (2 H, s, $CH_2$), 6.79 (2 H, d, *J* 8.5, ArH), 7.11 (2 H, d, *J* 8.5, ArH), 7.04–7.08 (1 H, m, ArH), 7.22–7.32 (5 H, m, ArH) and 7.75–7.82 (2 H, m, ArH); $\delta_C(CDCl_3)$ 55.23 (q), 62.89 (t), 113.49 (d), 124.43 (d), 125.73 (d), 125.94 (d), 126.03 (d), 126.12 (d), 127.05 (d), 128.03 (d), 128.53 (d), 129.59 (s), 130.77 (s), 130.84 (d), 132.15 (s), 133.56 (s), 147.73 (s) and 159.12 (s); *m/z* 319 ($M^+$) and 198 (base) (Found: $M^+$, 319.1048. $C_{20}H_{17}NOS$ requires M, 319.1030).

6-(4-*Bromobenzyl*)-6H-*dibenzo*[c,e][1,2]*thiazine* **10m**, from the biphenyl **3m**, as a pale brown oil (56.3%); $\delta_H(CDCl_3)$ 3.99 (2 H, s, $CH_2$), 7.02–7.08 (3 H, m, ArH), 7.19–7.37 (7 H, m, ArH) and 7.72–7.77 (2 H, m, ArH); $\delta_C(CDCl_3)$ 62.88 (t), 121.59 (s), 124.47 (d), 125.60 (d), 125.76 (d), 125.96 (d), 126.26 (d), 127.12 (d), 128.06 (d), 128.65 (d), 130.71 (s), 131.11 (d), 131.17 (d), 131.96 (s), 133.27 (s), 136.28 (s) and 147.41 (s); *m/z* 369 ($M^+$ + 2), 367 ($M^+$) and 198 (base) (Found: $M^+$, 367.0055. $C_{19}H_{14}BrNS$ requires M, 367.0030).

6-(4-*Chlorobenzyl*)-6H-*dibenzo*[c,e][1,2]*thiazine* **10k**, from the biphenyl **3k**, as a yellow oil (28%); $\delta_H(CDCl_3)$ 4.01 (2 H, s, $CH_2$), 7.05–7.30 (10 H, m, ArH) and 7.73–7.78 (2 H, m, ArH); $\delta_C(CDCl_3)$ 62.88 (t), 124.48 (d), 125.64 (d), 125.76 (d), 125.97 (d), 126.26 (d), 127.14 (d), 128.07 (d), 128.23 (d), 128.65 (d), 130.76 (s), 130.79 (d), 132.02 (s), 133.35 (s), 133.41 (s), 135.82 (s) and 147.45 (s); *m/z* 323 ($M^+$) and 198 (base) (Found: $M^+$, 323.0553. $C_{19}H_{14}ClNS$ requires M, 323.0537).

6-(4-*Fluorobenzyl*)-6H-*dibenzo*[c,e][1,2]*thiazine* **10j**, from the biphenyl **3j**, as a yellow oil (28.1%); $\delta_H(CDCl_3)$ 4.01 (2 H, s, $CH_2$), 6.88–7.30 (10 H, m, ArH) and 7.70–7.80 (2 H, m, ArH); $\delta_C(CDCl_3)$ 62.81 (t), 114.72 (d), 115.03 (d), 124.43 (d), 125.74 (d), 126.20 (d), 127.11 (d), 128.04 (d), 128.58 (d), 130.77 (s), 133.11 (s), 133.41 (s), 147.43 (s) and 160.50 (s); *m/z* 307 ($M^+$) and 198 (base) (Found: $M^+$, 307.0855. $C_{19}H_{14}FNS$ requires M, 307.0832).

6-(2,4-*Dichlorobenzyl*)-6H-*dibenzo*[c,e][1,2]*thiazine* **10l**, from the biphenyl **3l**, as a yellow oil (39.8%); $\delta_H(CDCl_3)$ 4.10 (2 H, s, $CH_2$), 7.05–7.32 (10 H, m, ArH) and 7.55–7.81 (2 H, m, ArH); $\delta_C(CDCl_3)$ 59.47 (t), 124.51 (d), 125.37 (d), 125.73 (d), 126.17 (d), 126.40 (d), 126.65 (d), 127.28 (d), 128.11 (d), 128.73 (d), 129.24 (d), 130.67 (s), 132.00 (s), 132.85 (d), 133.24 (s), 133.58 (s), 134.11 (s), 135.56 (s) and 147.51 (s); *m/z* 357 ($M^+$) and 198 (base) (Found: $M^+$, 357.0199. $C_{19}H_{13}Cl_2NS$ requires M, 357.0146).

6-(*Fluoren-9-yl*)-6H-*dibenzo*[c,e][1,2]*thiazine* **10o**, from the biphenyl **3o**, as pale yellow prisms (58%), m.p. 147–148 °C (from hexane–dichloromethane); $\delta_H(CDCl_3)$ 5.40 (1 H, s, CH) and 6.66–7.73 (16 H, m, ArH); $\delta_C(CDCl_3)$ 74.4 (d), 119.4 (d), 124.3 (d), 124.4 (d), 124.9 (d), 125.0 (d), 125.2 (d), 125.6 (d), 126.8 (d), 127.0 (d), 127.6 (d), 128.4 (d), 128.6 (d), 131.5 (s), 133.2 (s), 136.6 (s), 140.8 (s), 143.3 (s) and 148.0 (s); *m/z* 362 ($M^+$), 198 and 165 (base) (Found: C, 82.7; H, 4.7; N, 3.9. $C_{25}H_{17}NS$ requires C, 82.6; H, 4.7; N, 3.85%).

*Alternative Preparation of 6-Benzyl-6H-dibenzo*[c,e][1,2]*thiazine* **10g**.—Sodium hydride (60% dispersion in mineral oil; 66.2 mg, 2.76 mmol) was added to a stirred, ice-cooled solution of the 1,2-thiazine **9** (550 mg, 2.76 mmol) in dry THF (20 $cm^3$) and the mixture was stirred for 1 h at room temperature. Benzyl bromide (472 mg, 2.76 mmol) was added to this stirred mixture which, after being stirred overnight, was poured into water and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residual oil was separated by PLC on silica gel with hexane–ethyl acetate (5:1) to give the title compound (183 mg, 22.9%) as a yellow oil, whose spectral data were in complete accord with those of the product **10g** obtained from the reaction of compound **12g** with base.

*Methylation of Compound* **10g**.—Silver perchlorate (161.2 mg, 0.78 mmol) was added to a stirred solution of compound **10g** (225 mg, 0.78 mmol) and methyl iodide (220.7 mg, 1.56 mmol) in dry dichloromethane (20 $cm^3$) and the mixture was stirred for 7 days. The precipitates were filtered off and the filtrate was diluted with diethyl ether to precipitate 6-*benzyl*-5-*methyl*-6H-*dibenzo*[c,e][1,2]*thiazin*-5-*ium perchlorate* **13** (97 mg, 30.9%) as prisms after recrystallization from dichloromethane–diethyl ether, m.p. 150–152 °C (decomp.); $\nu_{max}/cm^{-1}$ 1090 ($ClO_4^-$); $\delta_H(CF_3CO_2H)$ 2.93 (3 H, s, Me), 5.03 (2 H, s, $CH_2$) and 7.10–8.25 (13 H, m, ArH) (Found: C, 59.3; H, 4.4; N, 3.4. $C_{20}H_{18}ClNO_4S$ requires C, 59.5; H, 4.5; N, 3.5%).

4,4′-*Dimethyl*-2,2′-*dinitrobiphenyl*.—A mixture of 4-chloro-3-nitrotoluene (25 g, 146 mmol) and quartz sand (35 g) was stirred and heated at 200 °C. Active copper powder[19] (25 g) was slowly added to the above mixture during 1 h. The mixture was stirred vigorously for 5.5 h at 220–230 °C. Dichloromethane was added

to the cooled reaction mixture and insoluble materials were filtered off. The filtrate was concentrated to give the *title compound* (11 g, 53.4%), which was recrystallized from ethanol to afford dark brown needles, m.p. 140–142 °C; $\nu_{max}$/cm$^{-1}$ 1525 and 1350 ($NO_2$); $\delta_H$($CDCl_3$) 2.45 (6 H, s, 2 × Me), 7.12 (2 H, d, *J* 7.5, ArH), 7.28–7.60 (2 H, m, ArH) and 7.87–8.04 (2 H, m, ArH); *m*/*z* 272 ($M^+$) (Found: C, 61.6; H, 4.4; N, 10.1. $C_{14}H_{12}N_2O_4$ requires C, 61.8; H, 4.4; N, 10.3%).

2-*Amino*-4,4′-*dimethyl*-2′-*nitrobiphenyl Hydrochloride*.—A methanol solution of NaSH [prepared from $Na_2S$·$9H_2O$ (13.9 g) and $NaHCO_3$ (4.36 g) by the reported method [20]] was slowly added to a stirred, refluxing solution of 4,4′-dimethyl-2,2′-dinitrobiphenyl (7.76 g, 28.5 mmol) in methanol (450 cm$^3$). The mixture was refluxed for a further 30 min and was then kept overnight at room temperature before being poured into ice–water (1 dm$^3$) and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residual oil was dissolved in ether and a diethyl ether–HCl solution was added, sufficient to precipitate the hydrochloride (4.64 g, 58.4%) as a powder, whose IR spectrum (KBr) showed the absorption bands due to $-\overset{+}{N}H_3$ at 3200–2150 cm$^{-1}$ and $-NO_2$ at 1535 and 1350 cm$^{-1}$. This compound was used for the next reaction without further purification or characterization.

2-*Ethoxy*(*thiocarbonyl*)*thio*-4,4′-*dimethyl*-2′-*nitrobiphenyl*.—This compound was prepared by a similar method to that described for compound **2**: diazotization of 2-amino-4,4′-dimethyl-2′-nitrobiphenyl hydrochloride (3.80 g, 13.6 mmol), followed by treatment with potassium *O*-ethyl dithiocarbonate (3.08 g, 16.3 mmol) to give the *title compound* (1.82 g, 38.4%) as a yellow oil after column chromatography on silica gel with hexane–dichloromethane (2.5:1–1:1) as solvent; $\nu_{max}$/cm$^{-1}$ 1530 and 1350 ($NO_2$); $\delta_H$($CDCl_3$) 1.30 (3 H, t, *J* 6.8, $CH_2$*Me*), 2.41 (3 H, s, Me), 2.45 (3 H, s, Me), 4.48 (2 H, q, *J* 6.8, *C*$H_2$Me), 7.08–7.55 (5 H, m, ArH) and 7.81 (1 H, m, ArH); *m*/*z* 347 ($M^+$) and 212 (base) (Found: $M^+$, 347.0619. $C_{17}H_{17}NO_3S_2$ requires M, 347.0622).

2-*Amino*-2′-*benzylthio*-4,4′-*dimethylbiphenyl*.—This compound was prepared in a similar manner to that described for compound **3**: 2-ethoxy(thiocarbonyl)thio-4,4′-dimethyl-2′-nitrobiphenyl (1.64 g, 4.71 mmol) was reduced with $LiAlH_4$ (890 mg, 23.45 mmol) in dry THF (75 cm$^3$) and was then treated with benzyl bromide (996 mg, 5.65 mmol) to give the *title compound* (896 mg, 59.6%) as a yellow oil; $\nu_{max}$/cm$^{-1}$ 3460 and 3370 ($NH_2$); $\delta_H$($CDCl_3$) 2.24 (3 H, s, Me), 2.26 (3 H, s, Me), 3.09–3.53 (2 H, br, $NH_2$), 3.93 (2 H, s, $CH_2$), 6.43–7.20 (6 H, m, ArH) and 7.13 (5 H, s, ArH); *m*/*z* 319 ($M^+$) and 196 (base) (Found: $M^+$, 319.1421. $C_{21}H_{21}NS$ requires M, 319.1395).

5-*Benzyl*-3,8-*dimethyl*-6H-*dibenzo*[c,e][1,2]*thiazin*-5-*ium Perchlorate* **14**.—This compound was prepared by a similar method to that described for the thiazinium perchlorate **12g**, from reaction of 2-amino-2′-benzylthio-4,4′-dimethylbiphenyl (400 mg, 1.25 mmol) with Bu$^t$OCl (136 mg, 1.25 mmol) in dry dichloromethane (11 cm$^3$), followed by treatment with silver perchlorate (289 mg, 1.25 mmol), and was obtained as a pale purple powder (239 mg, 4.71%), m.p. 160–161 °C (from diethyl ether–dichloromethane); $\nu_{max}$/cm$^{-1}$ 1000–1190 ($ClO_4^-$); $\delta_H$($CF_3CO_2H$) 2.35 (3 H, s, Me), 2.46 (3 H, s, Me), 4.43 (2 H, ABq, *J* 12, $\Delta\nu$ 14 Hz, $CH_2$) and 6.85–8.19 (11 H, m, ArH) (Found: C, 59.8; H, 4.8; N, 3.2. $C_{21}H_{20}ClNO_4S$ requires C, 60.4; H, 4.8; N, 3.4%).

*Cross-over Experiment. Treatment of a Mixture of Thiazinium Perchlorates* **12h** *and* **14** *with Butyllithium*.—A mixture of compound **12h** (96.6 mg, 0.24 mmol) and compound **14** (100 mg, 0.24 mmol) in dry THF (10 cm$^3$) was cooled at −70 °C in solid $CO_2$–ethanol. A hexane solution of butyllithium (1.6 mol dm$^{-3}$; 0.3 cm$^3$) was added by syringe to the above stirred mixture. The mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient. The reaction mixture was poured into ice–water, and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to give an oil. The oil was subjected to MS measurement to show ion peaks at *m*/*z* 289, 303, 317 and 331 which are attributed to the molecular-ion peaks of 6-benzyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine **10g**, 6-(4-methylbenzyl)-6*H*-dibenzo[*c*,*e*][1,2]thiazine **10h**, 6-benzyl-3,8-dimethyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine **15** and 6-(4-methylbenzyl)-3,8-dimethyl-6*H*-dibenzo[*c*,*e*][1,2]thiazine **16**, respectively.

*Attempted Preparation of* 9-*Trimethylsilylmethyl*-9-*thia*-10-*azaphenanthren*-9-*ium*-10-*ide* **7p**.—(*a*) The biphenyl **3p** (990 mg, 3.44 mmol) was allowed to react with NCS (505.8 mg, 3.79 mmol) in dry dichloromethane (70 cm$^3$) and the mixture was worked up as described for the preparation of the thiaazaphenanthrene **7c** to give 9-methyl-9-thia-10-azaphenanthren-9-ium-10-ide **7a** (582 mg, 79.2%), whose structure was completely determined by comparison of the spectral data with those of an authentic specimen.[2] On the other hand, after cyclization of compound **3p** (1.05 g, 3.65 mmol) with NCS (536.5 mg, 4.02 mmol) in dry dichloromethane (60 cm$^3$) as described above, addition of silver tetrafluoroborate (97% purity; 733 mg, 3.65 mmol) to the reaction mixture afforded 5-*methyl*-6H-*dibenzo*[c,e][1,2]*thiazin*-5-*ium tetrafluoroborate* **17** (359 mg, 33%) as needles after recrystallization from dichloromethane–diethyl ether, m.p. 155–157 °C; $\nu_{max}$/cm$^{-1}$ 1060–1120 ($BF_4^-$); $\delta_H$[$(CD_3)_2SO$] 2.93 (3 H, s, Me), 3.75 (1 H, br, NH) and 7.26–8.46 (8 H, m, ArH) (Found: C, 51.9; H, 4.0; N, 4.65. $C_{13}H_{12}BF_4NS$ requires C, 51.6; H, 4.1; N, 4.55%).

(*b*) *Cyclization of compound* **3p** *with* Bu$^t$OCl. A solution of the biphenyl **3p** (500 mg, 1.74 mmol) in dry dichloromethane (20 cm$^3$) was allowed to react with Bu$^t$OCl (189 mg, 1.74 mmol) in dichloromethane (8 cm$^3$) at −78 °C in the usual manner. The reaction mixture was poured into water and the organic layer was separated, dried ($MgSO_4$), and evaporated. The residue was separated by PLC on silica gel with hexane–ethyl acetate (5:1) as solvent to afford compound **8** (26 mg, 7%). The aqueous layer was basified with dil. aq. NaOH and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to yield compound **7a** (253 mg, 68.2%) as yellow crystals.

5-*Methyl*-6H-*dibenzo*[c,e][1,2]*thiazin*-5-*ium Chloride*.—Diethyl ether saturated with dry hydrogen chloride was added slowly to a stirred solution of compound **7a** (100 mg, 0.47 mmol) in dry diethyl ether (50 cm$^3$). The precipitate was collected and washed with dry diethyl ether to give the title compound (98 mg, 83.6%) as a very hygroscopic powder; $\delta_H$($CDCl_3$) 3.15 (3 H, s, Me) and 7.10–8.67 (8 H, m, ArH); *m*/*z* 213 ($M^+$ − HCl) and 199 (base).

2-*Amino*-2′-[*bis*(*trimethylsilyl*)*methylthio*]*biphenyl* **3ac**.—TMEDA (5.25 cm$^3$, 3.48 mmol) was added to a hexane solution of butyllithium (1.6 mol dm$^{-3}$; 6.52 cm$^3$, 10.43 mmol) at 0 °C under nitrogen, and the mixture was stirred for 30 min. To the above solution was added a solution of compound **3p** (1 g, 3.48 mmol) in dry THF (20 cm$^3$), and the mixture was stirred for 1 h. TMSCl (450 mg, 4.14 mmol) was added to the mixture, which was stirred for 3 h before being poured into ice–water and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residual oil was subjected to PLC on silica gel with ethyl acetate–hexane (1:6) as solvent to give the *title compound* (945 mg, 75.5%) as an orange oil together with unchanged starting material (196 mg

recovery). The biphenyl **3ac** showed $\nu_{max}/cm^{-1}$ 3470 and 3380 ($NH_2$); $\delta_H(CDCl_3)$ 0.0 (18 H, 2 × $SiMe_3$), 1.48 (1 H, s, CH), 3.35–3.85 (2 H, br, $NH_2$) and 6.63–7.60 (8 H, m, ArH); *m/z* 359 ($M^+$) (Found: $M^+$, 359.1576. $C_{19}H_{29}NSSi_2$ requires M, 359.1559).

*2-Amino-2′-[α-(trimethylsilyl)benzylthio]biphenyl* **3ad**.—A hexane solution of butyllithium (1.62 mol $dm^{-3}$; 2 $cm^3$, 1.54 mmol) was added under nitrogen to a stirred solution of the biphenyl **3g** (450 mg, 1.54 mmol) in dry THF (30 $cm^3$) at −78 °C. After the mixture had been stirred for 30 min, TMSCl (0.2 $cm^3$) was added and the mixture was stirred for 5 h, during which time the temperature was gradually raised to ambient. Aq. $NH_4Cl$ was added to the reaction mixture, which was then extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated to dryness. The residual oil was purified by PLC on silica gel with hexane–ethyl acetate (5:1) to afford the *title biphenyl* (441 mg, 79%) as a yellow oil; $\nu_{max}/cm^{-1}$ 3470 and 3380 ($NH_2$); $\delta_H(CDCl_3)$ 0.02 (3 H, s, Me), 0.03 (3 H, s, Me), 0.07 (3 H, s, Me), 3.55 (2 H, br, $NH_2$), 3.61 (1 H, s, CH), 6.81–6.91 (1 H, m, ArH) and 7.06–7.31 (12 H, m, ArH); $\delta_C(CDCl_3)$ −2.68 (q), 40.7 (d), 115.5 (d), 123.2 (d), 125.3 (d), 125.9 (d), 126.5 (s), 127.6 (d), 127.9 (d), 128.1 (d), 128.7 (d), 128.8 (d), 130.5 (d), 130.8 (d), 137.5 (s), 139.5 (s), 141.2 (s) and 143.8 (s); *m/z* 363 ($M^+$) and 73 (base) (Found: $M^+$, 363.1501. $C_{22}H_{25}NSSi$ requires M, 363.1477).

*Cyclization of Compound* **3ac** *with* Bu$^t$OCl.—The biphenyl **3ac** (400 mg, 1.11 mmol) in dry dichloromethane (15 $cm^3$) was allowed to react at −78 °C with Bu$^t$OCl (120.7 mg, 1.11 mmol) in dry dichloromethane (6 $cm^3$), and was then treated with aq. NaOH in the usual manner. The reaction mixture was separated by PLC on silica gel with hexane–dichloromethane (3:1) to afford the following three products. *6-Trimethylsilyl-6,7-dihydrodibenzo[d,f][1,3]thiazepine* **18** (196 mg, 61.7%) as a yellow oil; $\nu_{max}/cm^{-1}$ 3380 (NH); $\delta_H(CDCl_3)$ 0.17 (9 H, s, 3 × Me), 3.60–3.80 (1 H, br, NH), 4.24 (1 H, s, CH) and 7.02–7.54 (8 H, m, ArH); *m/z* 285 ($M^+$) and 184 (base); $\delta_C(CDCl_3)$ −3.09 (q), 68.63 (d), 122.90 (d), 123.37 (d), 127.36 (d), 128.49 (d), 128.96 (d), 131.05 (d), 132.36 (d), 133.88 (d), 134.74 (s), 136.78 (s), 144.30 (s) and 146.09 (s) (Found: $M^+$, 285.0990. $C_{16}H_{19}NSSi$ requires M, 285.1006); 6,7-dihydrodibenzo[d,f][1,3]thiazine, **8** (14 mg, 6%); and compound **7a** (19 mg, 8%).

When the above reaction mixture, obtained before treatment with base, was concentrated and then subjected to PLC on silica gel, compound **18** (52.3%) and a trace of compound **7a** were obtained.

*Cyclization of Compound* **3ad** *with* Bu$^t$OCl.—The biphenyl **3ad** (364 mg, 1 mmol) in dry dichloromethane (15 $cm^3$) was treated at −78 °C with Bu$^t$OCl (130 mg, 1.20 mmol), and was then treated with aq. NaOH (40 mg, 1 mmol), and worked up as above. The residue was separated by PLC on silica gel with hexane–ethyl acetate (4:1) to afford the compound **10g** (19 mg, 6.5%) and *6-phenyl-6,7-dihydrodibenzo[d,f][1,3]thiazepine* **19** (112 mg, 39%) as a yellow oil; $\nu_{max}/cm^{-1}$ 3320 (NH); $\delta_H(CDCl_3)$ 3.93 (1 H, br, NH), 5.80 (1 H, s, CH) and 7.01–7.58 (13 H, m, ArH); $\delta_C(CDCl_3)$ 78.2 (d), 124.0 (d), 124.4 (d), 126.4 (d), 128.3 (d), 128.6 (d), 128.7 (d), 128.8 (d), 129.1 (d), 130.4 (d), 130.8 (d), 132.8 (s), 134.8 (d), 135.5 (s), 141.9 (s), 143.8 (s) and 144.4 (s) (Found: $M^+$, 289.0950. $C_{19}H_{15}NS$ requires M, 289.0925).

When the above reaction mixture, obtained before treatment with base, was concentrated and then separated by PLC, compounds **19** (25%) and **10g** (trace) were obtained.

*Synthesis of the 9-Alkyl-9-thia-10-azaphenanthren-9-ium-10-ides* **7b** *and* **7c** via *Alkylation of an Anion of the Thiaazaphenanthrene* **7a**.—An ethereal solution of butyllithium (1 mol $dm^{-3}$; 2.34 $cm^3$) was added to a stirred solution of compound **7a** (500 mg, 2.34 mmol) in dry THF (20 $cm^3$) under nitrogen and the mixture was stirred for 30 min. Methyl iodide (333 mg, 2.34 mmol) was added to the above solution and the mixture was stirred for 2 h at room temperature. The reaction mixture was poured into ice–water and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residual oil was purified by PLC on silica gel with ethyl acetate–triethylamine (10:1) to give 9-ethyl-9-thia-10-azaphenanthren-9-ium-10-ide **7b**[2] (164 mg, 30.78%).

In a similar manner, 9-propyl-9-thia-10-azaphenanthren-9-ium-10-ide **7c**[2] was prepared in 43.84% yield by addition of ethyl iodide, instead of methyl iodide, to the anion of the thiaazaphenanthreniumide **7a**.

*Reaction of the Anion of Compound* **7a** *with Trimethylsilyl Chloride*.—A hexane solution of butyllithium (1.32 mol $dm^{-3}$; 1.6 $cm^3$) was added to a solution of compound **7a** (540 mg, 2.53 mmol) in dry THF (15 $cm^3$) at −50 °C under nitrogen and the mixture was stirred for 30 min. To this solution was added dropwise a solution of TMSCl (280 mg, 2.54 mmol) in dry THF (10 $cm^3$) and the mixture was stirred overnight during which time the temperature was raised to ambient. The reaction mixture was worked up as above to give an oil, which was subjected to PLC on silica gel with ethyl acetate to afford the compound **18** (200 mg, 26.8%) as yellow oil.

*Formation of 6,7-Dihydrodibenzo[d,f][1,3]thiazepine* **8** *by Oxidation of Compound* **3p** *with* MCPBA.—MCPBA (80% purity; 763 mg, 3.54 mmol) was added slowly to a stirred solution of the biphenyl **3p** (1.02 g, 3.54 mmol) in dichloromethane (33 $cm^3$), and the mixture was stirred until compound **3p** disappeared (TLC). The reaction mixture was basified by addition of aq. $NaHCO_3$ and the organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by PLC on silica gel with hexane–dichloromethane (1:2) to afford the title compound **8** (658 mg, 87.3%).

*Reactions of the 2-Allylthio-2′-aminobiphenyls* **3q–3t** *with* Bu$^t$OCl.—A solution of the biphenyl **3q** (500 mg, 2.07 mmol) in dry dichloromethane (20 $cm^3$) was treated with a solution of Bu$^t$OCl (225 mg, 2.07 mmol) in dichloromethane (10 $cm^3$) at −78 °C in the usual way. After being stirred overnight the mixture was concentrated under reduced pressure and the residue was separated by PLC on silica gel with hexane–ethyl acetate (10:1) to give *6-allyl-6H-dibenzo[c,e][1,2]thiazine* **10q** (218 mg, 44%) as a yellow oil; $\delta_H(CDCl_3)$ 3.55–3.58 (2 H, m, $CH_2$), 4.96–5.09 (2 H, m, $=CH_2$), 5.79–5.93 (1 H, m, –CH=) and 7.16–7.80 (8 H, m, ArH); $\delta_C(CDCl_3)$ 62.6 (t), 118.3 (t), 124.4 (d), 125.7 (d), 125.8 (d), 126.0 (d), 127.1 (d), 128.0 (d), 128.5 (d), 130.6 (s), 132.1 (s), 133.8 (s), 134.4 (d) and 147.7 (s); *m/z* 239 ($M^+$) and 198 (base) (Found: $M^+$, 239.0753. $C_{15}H_{13}NS$ requires M, 239.0768).

Under similar conditions to those above, the following 1,2-thiazine derivatives were obtained from the reaction of the biphenyls **3r–3t** and Bu$^t$OCl, respectively.

*6-(1-Methylprop-2-enyl)-6H-dibenzo[c,e][1,2]thiazine* **21a**, from the biphenyl **3r** (44.5%), was obtained as a yellow oil, after PLC on silica gel with hexane–ethyl acetate (15:1) as solvent; $\delta_H(CDCl_3)$ 1.13 (3 H, d, *J* 6, Me), 3.60–3.70 (1 H, m, NCH), 4.79–4.87 (2 H, m, $=CH_2$), 5.66–5.78 (1 H, m, –CH=), 7.16–7.31 (6 H, m, ArH) and 7.72–7.76 (2 H, m, ArH); $\delta_C(CDCl_3)$ 19.1 (q), 65.8 (d), 115.6 (t), 124.3 (d), 124.8 (d), 125.5 (d), 125.7 (d), 126.7 (d), 127.0 (d), 127.9 (d), 128.1 (d), 131.5 (s), 133.0 (s), 135.9 (s), 139.4 (d) and 146.7 (s); *m/z* 253 ($M^+$) and 198 (base) (Found: $M^+$, 253.0939. $C_{16}H_{15}NS$ requires M, 253.0925).

*6-(1,1-Dimethylprop-2-enyl)-6H-dibenzo[c,e][1,2]thiazine* **21b**, from the biphenyl **3s** (43%), was obtained as an orange oil,

after PLC on silica gel with hexane–ethyl acetate (15:1) as solvent; $\delta_H(CDCl_3)$ 1.12 (6 H, s, 2 × Me), 4.75–4.84 (2 H, m, $=CH_2$), 5.79 (1 H, dd, *J* 17 and 11, –CH=), 7.17–7.22 (6 H, m, ArH) and 7.67–7.72 (2 H, m, ArH); $\delta_C(CDCl_3)$ 25.7 (q), 25.9 (q), 65.6 (s), 122.4 (t), 124.1 (d), 125.7 (d), 125.8 (d), 126.6 (d), 127.0 (d), 127.6 (d), 129.1 (d), 133.3 (s), 133.8 (s), 138.7 (s), 143.7 (s) and 144.1 (d); *m/z* 267 ($M^+$) and 198 (base) (Found: $M^+$, 267.1096. $C_{17}H_{17}NS$ requires M, 267.1082).

6-(1-*Phenylprop*-2-*enyl*)-6H-*dibenzo*[c,e][1,2]*thiazine* **21c**, from the biphenyl **3t** (49%), was obtained as a yellow oil after PLC on silica gel with hexane–ethyl acetate (10:1) as solvent; $\delta_H(CDCl_3)$ 4.43 (1 H, d, *J* 8, >CH–), 4.47 (1 H, d, *J* 17, =CH*H*), 4.89 (1 H, d, *J* 11, =C*H*H), 6.03 (1 H, ddd, *J* 17, 11 and 8, –CH=) and 6.98–7.74 (13 H, m, ArH); $\delta_C(CDCl_3)$ 73.5 (d), 117.5 (t), 124.2 (d), 125.4 (d), 125.6 (d), 125.9 (d), 126.9 (d), 127.1 (d), 127.5 (d), 127.7 (d), 127.8 (d), 128.1 (d), 128.3 (d), 131.4 (s), 132.7 (s), 134.2 (s), 137.6 (d), 140.6 (s) and 146.3 (s); *m/z* 315 ($M^+$) and 198 (base) (Found: $M^+$, 315.1093. $C_{21}H_{17}NS$ requires M, 315.1083).

6-(*Propa*-1,2-*dienyl*)-6H-*dibenzo*[c,e][1,2]*thiazine* **22**.—A solution of 2-amino-2′-prop-2-ynylthiobiphenyl **3u** (500 mg, 2.09 mmol) in dry dichloromethane (20 $cm^3$) was allowed to react at −78 °C with Bu$^t$OCl (227 mg, 2.09 mmol) in dry dichloromethane (10 $cm^3$), and was then treated at 0 °C with aq. NaOH (84 mg, 2.01 mmol). Work-up was as usual, and the resulting oil was purified by column chromatography on silica gel with hexane–ethyl acetate (10:1) to afford the *title compound* (198 mg, 40%) as a yellow oil; $\nu_{max}/cm^{-1}$ 1950 (C=C=C); $\delta_H(CDCl_3)$ 4.98 (2 H, d, *J* 6, $=CH_2$), 6.19 (1 H, t, *J* 6, =CH–) and 7.19–7.81 (8 H, m, ArH); $\delta_C(CDCl_3)$ 87.2 (t), 112.5 (d), 124.8 (d), 125.1 (d), 125.5 (d), 125.7 (d), 126.2 (d), 127.5 (d), 127.9 (d), 128.1 (d), 131.1 (s), 132.5 (s), 134.7 (s), 144.9 (s) and 203.1 (s); *m/z* 237 ($M^+$) and 198 (base) (Found: $M^+$, 237.0611. $C_{15}H_{11}NS$ requires M, 237.0612).

*Cyclization of* 2-*Amino*-2′-(*cyanomethylthio*)*biphenyl* **3w**.—The biphenyl **3w** (300 mg, 1.25 mmol) was allowed to react with Bu$^t$OCl (136 mg, 1.25 mmol) in dry dichloromethane (10 $cm^3$), followed by treatment with aq. NaOH (84 mg) in the usual way to give 6-*cyanomethyl*-6H-*dibenzo*[c,e][1,2]*thiazine* **10w** (73 mg, 22%) as an oil after PLC on silica gel with hexane–ethyl acetate (2:1); $\delta_H(CDCl_3)$ 3.89 (2 H, s, $CH_2$), 7.31–7.41 (6 H, m, ArH) and 7.79–7.87 (2 H, m, ArH); $\delta_C(CDCl_3)$ 48.29 (t), 115.71 (s), 124.85 (d), 125.37 (d), 126.10 (d), 126.17 (d), 127.60 (d), 128.04 (d), 128.65 (d), 129.21 (d), 130.44 (s), 131.26 (s), 131.66 (s) and 144.86 (s); *m/z* 238 ($M^+$) and 198 (base) (Found: $M^+$, 238.0557. $C_{14}H_{10}N_2O$ requires M, 238.0563).

*Alternative Synthesis of Compound* **10w**.—Sodium hydride (60% dispersion in mineral oil; 76.3 mg, 1.91 mmol) was added to a solution of compound **9** (380 mg, 1.91 mmol) in dry THF (10 $cm^3$) cooled in an ice-bath under nitrogen. After being stirred for 10 min, the mixture was treated with a solution of bromoacetonitrile (229 mg, 1.91 mmol) in dry THF (3 $cm^3$) and was then stirred for 2 h before being worked up as for compound **10g**. The resulting oil was separated by PLC on silica gel with hexane–ethyl acetate (5:1) to afford the title compound (130 mg, 28.6%). The starting material **9** was recovered unchanged (16.3% recovery).

*Cyclization of* 2-*Amino*-2′-*phenacylthiobiphenyl* **3y**.—The biphenyl **3y** (1 g, 3.14 mmol) was allowed to react with NCS (417 mg, 3.12 mmol) in dry dichloromethane (130 $cm^3$) at −50 °C as described for compound **7c**, and the reaction mixture was treated with aq. KOH (931 mg). Work-up gave an oil, which was submitted to PLC on silica gel with hexane–ethyl acetate (3:1) to give unchanged starting material (164 mg recovery) and 7-*phenyl*-6H-*dibenzo*[e,g][1,4]*thiazocine* **23** (119 mg, 12.59%) as orange plates after recrystallization from hexane–dichloromethane, m.p. 125–128 °C; $\delta_H(CDCl_3)$ 3.84 (2 H, ABq, *J* 9.6, $CH_2$), 6.70–7.42 (11 H, m, ArH) and 7.73–8.00 (2 H, m, ArH); *m/z* 301 ($M^+$) (Found: $M^+$, 301.0918. $C_{20}H_{15}NS$ requires M, 301.0924).

*Reaction of the Anion of the Thiaazaphenanthreniumide* **7a** *with a Carboxylic Ester*.—A solution of compound **7a** (500 mg, 2.34 mmol) in dry THF (10 $cm^3$) was added dropwise at −78 °C to a stirred solution of LDA prepared from diisopropylamine (400 mg) and butyllithium (1.62 mol $dm^{-3}$; 2 $cm^3$) in dry THF (40 $cm^3$) under nitrogen, and the mixture was stirred for 50 min. Dry ethyl acetate (0.5 $cm^3$, 5.10 mmol) was added by syringe to the above reaction mixture. After being stirred overnight, the mixture was treated with aq. $NH_4Cl$ and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to afford 6-*methyl*-6,6a-*dihydro*[1]*benzothieno*[2,3-c]*indol*-6-*ol* **24a** (287 mg, 48%) as prisms after recrystallization from ethanol, m.p. 203–205 °C; $\nu_{max}/cm^{-1}$ 3130 (OH); $\delta_H(CDCl_3)$ 1.07 (3 H, s, Me), 2.15 (1 H, s, OH), 3.85 (1 H, s, CH), 6.02–6.08 (1 H, m, olefinic H), 6.31–6.36 (1 H, m, olefinic H), 6.64–6.73 (2 H, m, olefinic H) and 6.95–7.36 (4 H, m, ArH); $\delta_C[(CD_3)_2SO]$ 24.1 (q), 66.3 (d), 69.5 (s), 100.8 (s), 120.4 (d), 122.2 (d), 123.0 (d), 123.8 (d), 125.5 (d), 129.2 (d), 135.4 (d), 135.5 (d), 136.3 (s), 139.5 (s) and 169.6 (s); *m/z* 255 ($M^+$) and 197 (base) (Found: C, 70.35; H, 5.1; N, 5.5. $C_{15}H_{13}NOS$ requires C, 70.6; H, 5.1; N, 5.5%).

In a similar manner, the anion of compound **7a** was treated with ethyl benzoate to give 6-*phenyl*-6,6a-*dihydro*[1]*benzothieno*[2,3-c]*indol*-6-*ol* **24b** (287 mg, 39%) as pale yellow prisms after recrystallization from ethanol, m.p. 187–189 °C; $\nu_{max}/cm^{-1}$ 3060 (OH); $\delta_H(CDCl_3)$ 1.73 (1 H, br, OH), 3.93 (1 H, s, CH), 6.01–6.08 (1 H, m, olefinic H), 6.26–6.33 (1 H, m, olefinic H) and 6.53–7.49 (11 H, m, olefinic and ArH); $\delta_C(CDCl_3)$ 65.8 (d), 71.1 (s), 104.6 (s), 120.5 (d), 122.3 (d), 123.4 (d), 124.1 (d), 125.0 (d), 126.3 (d), 127.8 (d), 128.4 (d), 129.2 (d), 136.4 (d), 136.5 (d), 136.9 (s), 140.0 (s), 145.2 (s) and 177.7 (s); *m/z* 317 ($M^+$) and 105 (base) (Found: C, 75.75; H, 4.8; N, 4.4. $C_{20}H_{15}NOS$ requires C, 75.7; H, 4.8; N, 4.4%).

*Methylation of the Alcohol* **24a**.—Sodium hydride (60% dispersion in mineral oil; 34. mg, 0.85 mmol) was added to a stirred suspension of the alcohol **24a** (200 mg, 0.78 mmol) in dry THF (40 $cm^3$) at 0 °C and the mixture was further stirred for 6 h. Methyl iodide (122 mg, 0.86 mmol) was added to this solution by syringe and the mixture was stirred for 48 h at room temperature, poured into water, and extracted with dichloromethane. The extract was separated, washed with water, dried ($MgSO_4$), and evaporated to give 6-*methoxy*-6-*methyl*-6,6a-*dihydro*[1]*benzothieno*[2,3-c]*indole* **25a** (102 mg, 48%), which was recrystallized from ethanol as yellow prisms, m.p. 79–80 °C; $\delta_H(CDCl_3)$ 1.28 (3 H, s, Me), 3.14 (3 H, s, OMe), 3.97 (1 H, s, CH), 6.03–6.08 (1 H, m, olefinic H), 6.29–6.33 (1 H, m, olefinic H), 6.68–6.70 (2 H, m, olefinic H) and 6.94–7.28 (4 H, m, ArH); $\delta_C(CDCl_3)$ 20.6 (q), 50.4 (q), 63.8 (d), 70.3 (s), 105.0 (s), 120.2 (d), 122.1 (d), 123.3 (d), 123.8 (d), 125.4 (d), 129.1 (d), 135.6 (d), 135.9 (d), 136.1 (s), 140.3 (s) and 172.6 (s); *m/z* 269 ($M^+$) and 197 (base) (Found: C, 71.1; H, 5.7; N, 5.15. $C_{16}H_{15}NOS$ requires C, 71.3; H, 5.6; N, 5.2%).

*Methylation of the Alcohol* **24b**.—Sodium hydride (60% dispersion in mineral oil; 14 mg, 0.35 mmol) was added to a stirred suspension of the alcohol **24b** (100 mg, 0.32 mmol) in dry THF (20 $cm^3$) at 0 °C and the mixture was stirred for 6 h at the same temperature. Methyl iodide (54 mg, 0.38 mmol) was added to this solution by syringe and the mixture was stirred for 24 h at room temperature. Work-up as above afforded 6-*methoxy*-6-*phenyl*-6,6a-*dihydro*[1]*benzothieno*[2,3-c]*indole* **25b** (101 mg, 94%), which was recrystallized from ethanol as pale yellow

prisms, m.p. 128–130 °C; $\delta_H(CDCl_3)$ 3.42 (3 H, s, OMe), 4.07 (1 H, s, CH), 5.99–6.11 (1 H, m, olefinic H), 6.28–6.31 (1 H, m, olefinic H), 6.51–6.54 (1 H, m, olefinic H) and 6.75–7.56 (10 H, m, olefinic and ArH); $\delta_C(CDCl_3)$ 52.3 (q), 67.4 (d), 70.1 (s), 108.9 (s), 120.2 (d), 122.0 (d), 122.5 (d), 123.8 (d), 124.9 (d), 125.7 (s), 126.2 (d), 127.5 (d), 128.0 (d), 128.5 (s), 128.6 (d), 136.1 (d), 136.4 (d), 139.5 (s) and 175.6 (s); *m/z* 331 ($M^+$) and 229 (base) (Found: C, 75.9; H, 5.2; N, 4.2. $C_{21}H_{17}NOS$ requires C, 76.1; H, 5.2; N, 4.2%).

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