Reactions of 9-Substituted 9-Thia-10-azaphenanthrenes with Electrophiles

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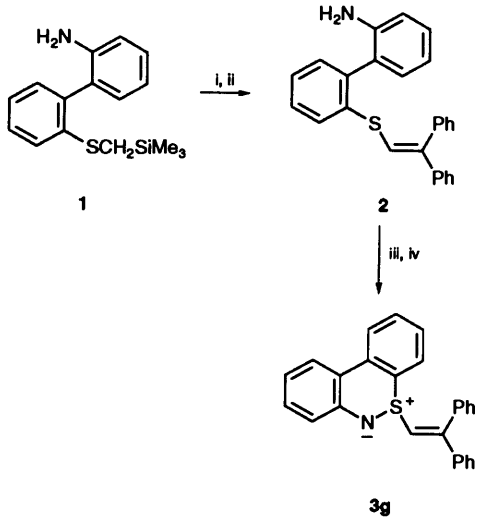
Reactions of 9-substituted 9-thia-10-azaphenanthrenes with several electrophiles have been investigated. Reaction of 9-alkyl-9-thia-10-azaphenanthrenes with dimethyl acetylenedicarboxylate (DMAD) afforded dibenzothiazonine derivatives **4** and **5**, dibenzothiazocine derivatives **6**, 2-alkylsulfinyl-2'-vinylaminobiphenyls **7**, and bis(biphenylylimino)ethane derivatives **8**. The product distribution was markedly influenced by the substituent on the sulfur atom. 9-Methyl **3a** and 9-isopropyl derivatives **3d** afforded predominantly dibenzothiazonine derivatives **5a** and **4d**, respectively, while 9-ethyl **3b**, 9-isopropyl **3c** and 9-cyclohexyl derivatives **3e** gave predominantly dibenzothiazocine derivatives **6** and alkylsulfinyl vinylaminobiphenyls **7**. In contrast, the reactions of 9-phenyl- **3f** or 9-vinyl-9-thia-10-azaphenanthrene **3g** with DMAD afforded only the corresponding dibenzothiazocine derivative **6**. Reactions of 9-alkylthiaazaphenanthrenes **3a–c** with methyl propiolate (MP) in benzene afforded dibenzothiazecine derivatives **12** as 1:2 adducts. Reactions of compounds **3a–c** with diphenylcyclopropenone in ethanol yielded the ring-opened products **13**, while the same reaction in benzene solvent afforded the 4-quinolone derivatives **14** *via* intramolecular cyclization of a ketene intermediate, **L**.

In our earlier paper, we both reported the first synthesis of novel cyclic sulfilimines (azathiabenzenes), in which a sulfur–nitrogen bond forms part of a cyclic conjugated ring system containing six π-electrons, and demonstrated their ylidic properties on the basis of spectral and chemical evidence.[1] Moody and co-workers have also independently both synthesized other azathiabenzene derivatives by an alternative method[2] and reported their thermal and nucleophilic reactions.[3] Recently, we reported the thermal behaviour of 9-thia-10-azaphenanthrenes having various substituents on the sulfur and described interesting rearrangements and ring transformations of the substituent.[4]

In continuing our study of the chemistry of 9-substituted 9-thia-10-azaphenanthrenes, we have investigated their ylidic nature as demonstrated by their reactions with several types of electrophiles, and found several novel ring transformations of the azathiaphenanthrene skeleton.

In this paper, we describe the full details of our new findings on the reactivities of 9-substituted 9-thia-10-azaphenanthrenes with electrophiles such as dimethyl acetylenedicarboxylate, methyl propiolate and diphenylcyclopropenone.



Scheme 1 *Reagents and conditions:* i, BuLi, TMEDA, THF; ii, Ph_2CO; iii, Bu^{t}OCl, CH_2Cl_2, −78 °C; iv, aq. NaOH, 0 °C

Results and Discussion

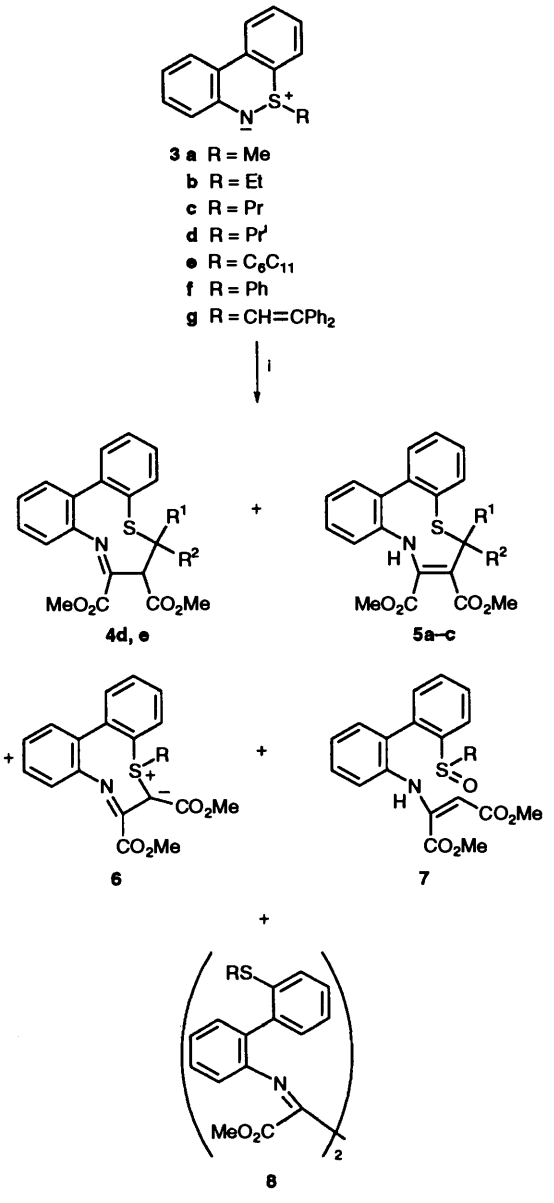
Synthesis of 9-(β-*Phenylstyryl*)-9-*thia*-10-*azaphenanthrene* **3g**.—The 9-substituted 9-thia-10-azaphenanthrenes used in the present studies are the 9-alkyl derivatives **3a–e**, the 9-phenyl derivative **3f**, whose synthesis was reported in our recent paper,[4c] and the 9-vinyl derivative **3g**. The last-mentioned compound was freshly prepared for the present studies by the method shown in Scheme 1. Treatment of 2-amino-2'-trimethylsilylmethylsulfanylbiphenyl **1** with BuLi in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA), followed by addition of benzophenone, gave 2-amino-2'-vinylsulfanylbiphenyl **2**. The biphenyl **2** was cyclized by treatment with *tert*-butyl hypochlorite (Bu^{t}OCl) in CH_2Cl_2 at −78 °C, and the product treated with aq. NaOH to afford 9-(β-phenylstyryl)-9-thia-10-azaphenanthrene **3g** as orange prisms.

Reactions of 9-*Substituted* 9-*Thia*-10-*azaphenanthrenes* **3a–g** *with Dimethyl Acetylenedicarboxylate (DMAD)*.—Treatment of 9-substituted 9-thia-10-azaphenanthrenes **3a–g** with DMAD in dry benzene at room temperature afforded the dibenzothiazonine derivatives **4** and **5**, the dibenzothiazocine derivatives **6**, the 2-alkylsulfinyl-2'-vinylaminobiphenyls **7**, and the bis(biphenylylimino)ethane derivatives **8**. Interestingly, the product distribution was markedly influenced by the substituent on the sulfur atom (see Scheme 2 and Table 1). The 9-methyl **3a** and 9-isopropyl **3d** derivatives afforded predominantly dibenzothiazonine skeleton products **4** and **5**, while the 9-ethyl **3b**, 9-propyl **3c** and 9-cyclohexyl **3e** derivatives gave this skeleton only as a minor product. In the case of **3b**, the pure dibenzothiazocine **6b** was gradually hydrolysed on the silica gel TLC plate to give the sulfoxide **7b**. Therefore, it is suggested that the other sulfoxides

Table 1 Reactions of 9-R-substituted 9-thia-10-azaphenanthrenes **3** with dimethyl acetylenedicarboxylate (DMAD)

Compound	R	Yield of product (%) 4	5	6	7	8
3a	Me	—	40.5 (R^1 = R^2 = H)	16	15	9.5
3b	Et	—	—	27	26	2.4
3c	Pr	—	16 (R^1 = H, R^2 = Et)	37	27	2
3d	Pr^i	42 (R^1 = R^2 = Me)	—	—	9.1	—
		35.6 (R^1 = R^2 = Me)[a]	—	—	11.2[a]	—
3e	C_6H_{11}	17 [R^1 = R^2 = $-(CH_2)_5-$]	—	—	62	—
3f	Ph	—	—	73	—	—
		—	—	83.4[a]	—	—
3g	$CH{=}CPh_2$	—	—	77	—	—

[a] Yield of the corresponding diethyl esters obtained from the reaction with diethyl acetylenedicarboxylate (DEAD).



Scheme 2 *Reagents:* i, DMAD, benzene

7a, **c–e** are also formed from the corresponding dibenzothiazocines **6a**, **c–e**, during separation of the reaction mixtures on TLC. It is noteworthy that the formation of dibenzothiazonines here contrasts with the absence of such products in the reaction of the bicyclic azathiabenzene, azathianaphthalene, with DMAD, with the formation of only benzothiazocines as stable compounds in our previous work[1b] and featured in the report of Moody's group.[3] Failure to isolate dibenzothiazocines from 9-isopropyl **3d** and 9-cyclohexyl derivatives **3e** is probably because of their instability, resulting in the formation of the corresponding sulfoxides **7d** and **7e**, respectively, by hydrolysis during preparative TLC (PLC) purification. The dibenzothiazocine derivatives **6f** and **6g**, obtained from 9-phenyl **3f** and 9-(β-phenylstyryl) derivatives **3g** are very stable and underwent no hydrolysis to the corresponding sulfoxides. The reaction of the thiaazaphenanthrenes with diethyl acetylenedicarboxylate (DEAD) as electrophile showed similar results, as shown in the case of thiaazaphenanthrene **3d** or **3f** in Table 1.

Structures of the Products.—The structures of the above compounds were determined on the basis of their spectroscopic data (see Experimental section), with that of compound **6f** being confirmed by X-ray analysis. The latter was carried out in order to try and explain the unusual upfield shifts of the benzene ring protons in its ^{1}H NMR spectrum relative to those of the analogous compounds **6a–c**, **g**. The molecular structure of compound **6f** is illustrated in Fig. 1. The phenyl ring on the sulfur atom is located very close to and parallel with the plane of one of the benzene rings of the dibenzothiazocine skeleton. This causes the unusual upfield shifts of the protons of benzene ring of dibenzothiazocine skeleton by the shielding effect of the phenyl group.

Mechanism of the Reaction.—We propose the mechanism shown in Scheme 3 for the ring transformation of 9-substituted 9-thia-10-azaphenanthrenes in their reaction with DMAD. Nucleophilic attack of **3** on the electron-deficient acetylene (DMAD) forms the zwitterionic intermediate **A**, which leads to the sulfonium ylide intermediate **B** by an intramolecular proton abstraction from the proximate S-alkyl group. Intramolecular attack of the carbanion of the ylide intermediate **B** on the double bond accompanied by cleavage of the N–S bond gives the products **4d**, **e**. The products **5a–c** are formed by a 1,3-hydrogen shift in the corresponding ring-opened precursors **4a–c**. On the other hand, the intermediate **A** gives rise to the thiazate intermediate **C**, which collapses to the product **6** by heterolytic cleavage of the N–S bond. The unstable ylides **6** are easily hydrolysed during purification to give the ring-opened sulfoxides **7** *via* the intermediates **D** and **E** as shown in Scheme 3. The carbanion of the intermediate **A** is protonated by water present in the reaction medium to give the aminosulfonium ion intermediate **F** which is next attacked by a second molecule of **3** to afford the product **8** *via* intermediate **G** after the loss of a proton.

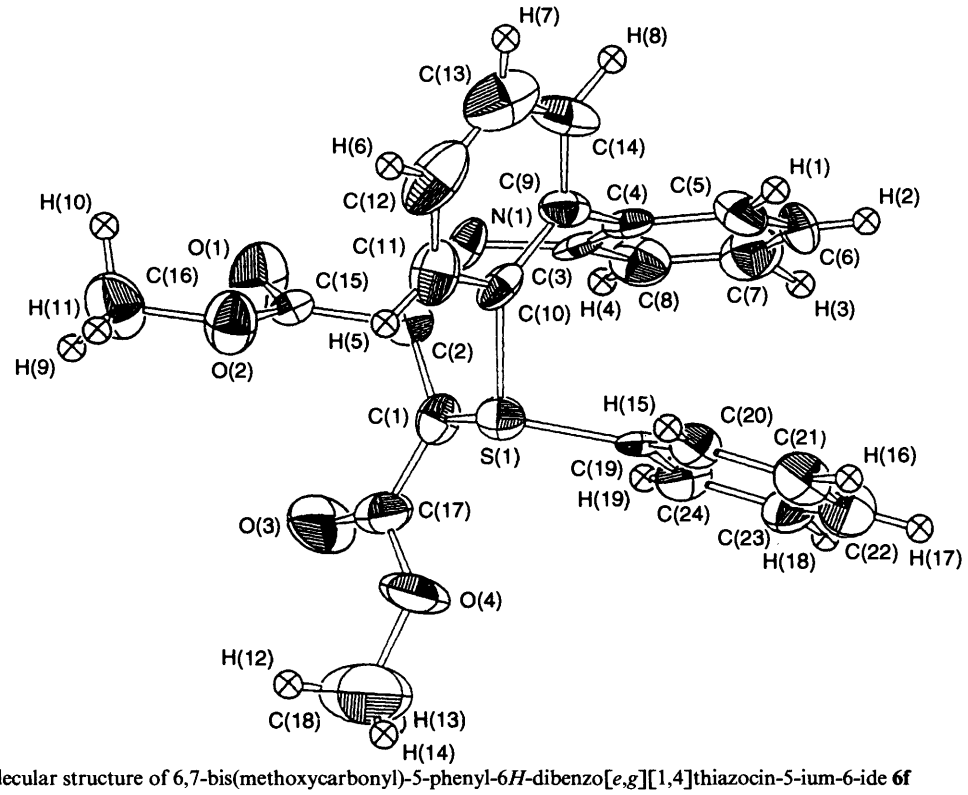
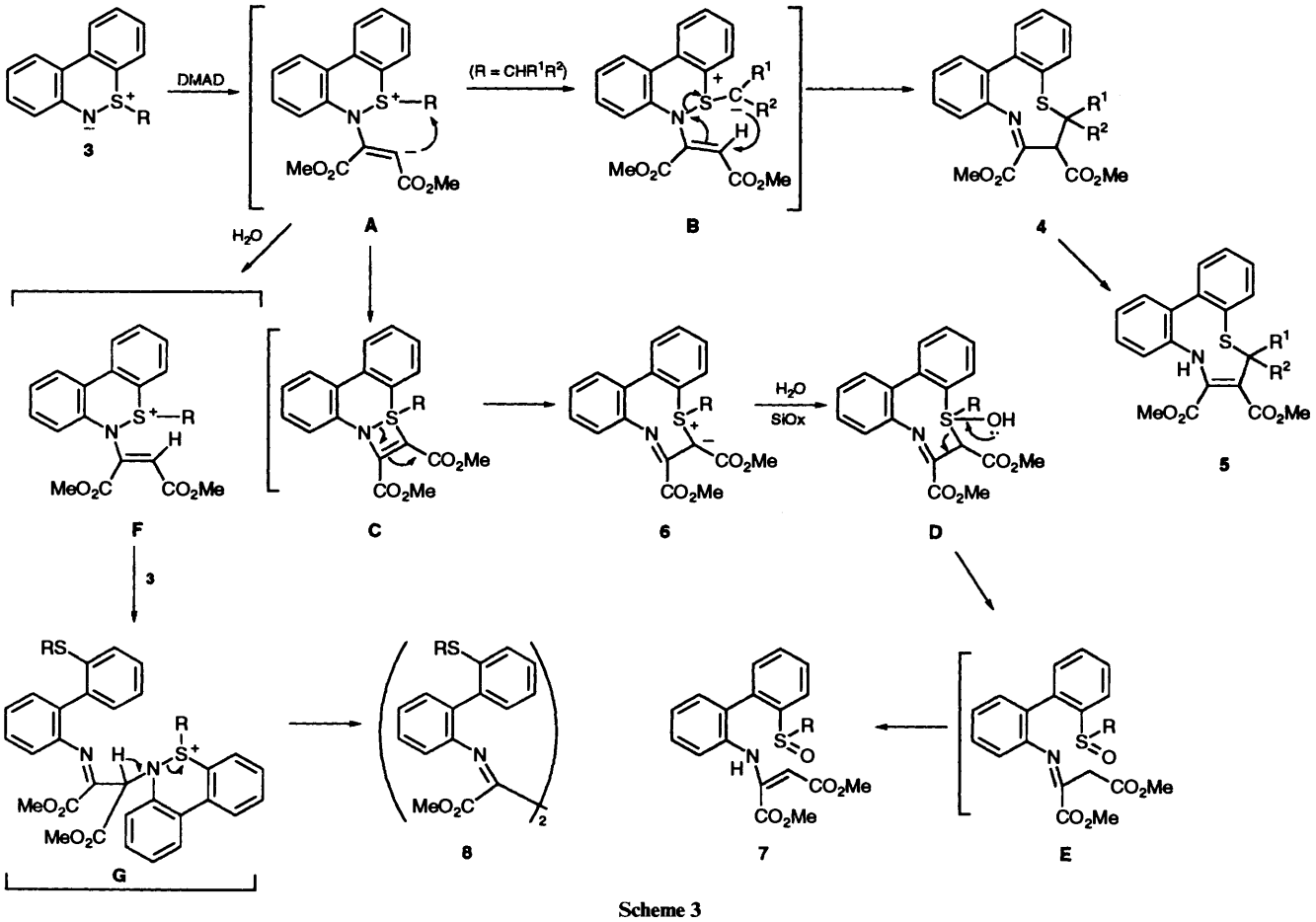
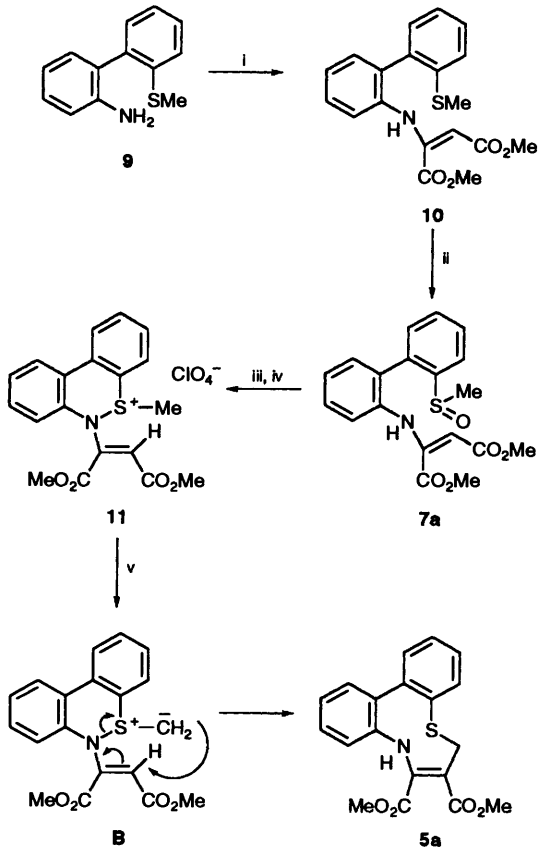


Fig. 1 X-Ray molecular structure of 6,7-bis(methoxycarbonyl)-5-phenyl-6*H*-dibenzo[*e*,*g*][1,4]thiazocin-5-ium-6-ide **6f**

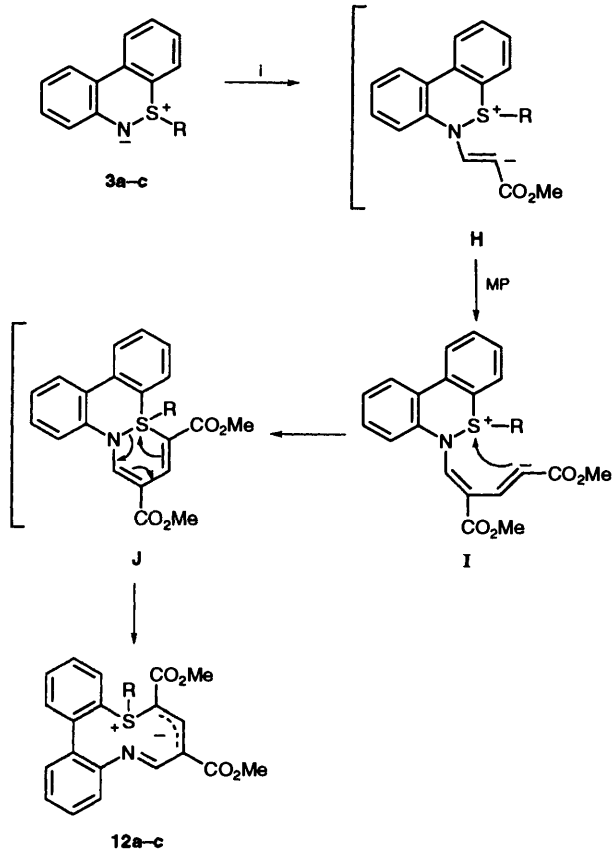


Scheme 3

In order to obtain more exact information concerning the mechanism, especially for the formation of the dibenzothiazonine skeleton **4** or **5**, we carried out the generation of the exocyclic intermediate **B** corresponding to that derived from **3a**. 6-[1,2-Bis(methoxycarbonyl)vinyl]-5-methyl-6*H*-dibenzo[*c*,*e*][1,2]thiazin-5-ium perchlorate **11**, a precursor of the inter-



Scheme 4 *Reagents and conditions:* i, DMAD, EtOH; ii, MCPBA, CH_2Cl_2; iii, $(CF_3CO)_2O$; iv, 70% $HClO_4$; v, NaH, THF

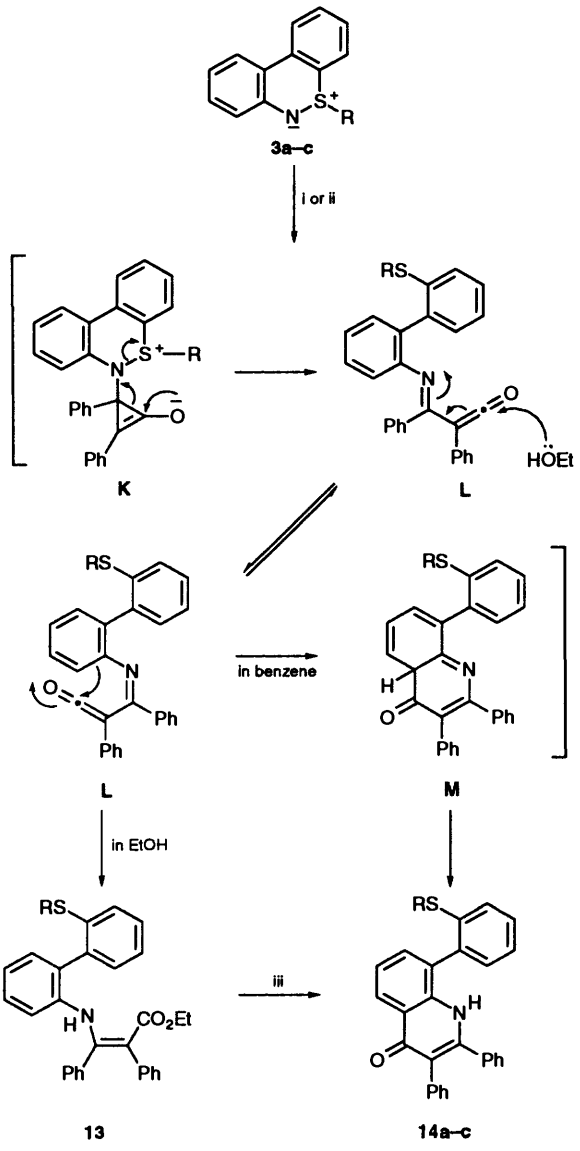


Scheme 5 *Reagents and conditions:* i, MP, benzene, room temp.

mediate **B**, was prepared as shown in Scheme 4. Michael addition of the 2-amino-2'-methylsulfanylbiphenyl **9**[4c] to DMAD afforded adduct **10** in 70% yield. Adduct **10** was oxidized with *m*-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 to give the sulfoxide **7a** in 87% yield. Treatment of sulfoxide **7a** with trifluoroacetic anhydride, followed by addition of 70% perchloric acid gave the thiazinium perchlorate **11** (71%), which was then treated with NaH in tetrahydrofuran (THF) at room temperature to generate the methylide intermediate **B**. This intermediate then spontaneously underwent intramolecular cyclization to afford the expected ring-expansion product **5a** (65%) *via* a 1,3-hydrogen shift.

We next carried out the reaction of thiaazaphenanthrenes **3a–c** with methyl propiolate (MP). Treatment of the 9-methyl derivative **3a** with MP in benzene at room temperature for 160 h yielded no 1:1 adduct, but the ring-expanded product **12a**, a 1:2-adduct of the ylide and MP, was formed in 14% yield as orange prisms (see Scheme 5). Similarly, the 9-ethyl **3b** and the 9-propyl derivatives **3c** also afforded the 1:2 adducts **12b** and **12c** as orange prisms in 5 and 10% yields, respectively. Their structures were determined on the basis of spectral results, final confirmation being achieved by an X-ray crystal structure determination of **12a**, the details of which have already been published.[5] The formation of compound **12** can be rationalized by the mechanism depicted in Scheme 5. Nucleophilic attack of the nitrogen anion of thiaazaphenanthrene **3** on methyl propiolate (MP) forms the zwitterionic intermediate **H**, whose carbanion attacks a further MP molecule to afford the second zwitterionic intermediate **I**. The intermediate **I** then cyclizes to give the final product **12** *via* the thiazine intermediate **J**, with fission of the S–N bond.

We also examined the reaction of the thiaazaphenanthrenes with an active olefinic electrophile (see Scheme 6). Treatment of **3a** with diphenylcyclopropenone in ethanol at room temperature afforded the ring-opened ethyl ester **13a** (16%). Similar ring-opening reactions were also observed in the case of the 9-ethyl **3b** and the 9-propyl derivatives **3c** to afford the corresponding adducts **13b** (20%) and **13c** (34%). The stilbene group in adducts **13a–c** is assumed to be in a *Z*-configuration based on the IR absorption of the NH group at 3160 cm^{-1}, shifted to lower wavenumber as a result of hydrogen bonding with the ester carbonyl oxygen. In contrast, the same reactions performed in benzene as an aprotic solvent gave 4-quinolone derivatives **14**, the structures of which were elucidated on the basis of spectral results (see Experimental section). These were also confirmed by an alternative synthesis; Reynolds *et al.* have reported an elegant synthesis of 2-methyl-4-quinolone from ethyl β-anilino-(*Z*)-but-2-enoate on heating in Dowtherm (diphenyl ether–biphenyl, 3:1).[6] We applied this thermal cyclization method to the preparation of **14** from the ethyl ester **13** obtained above. The ester **13** was heated in Dowtherm at 250 °C for 1 h, to afford the expected quinolone derivatives **14** in moderate yields in all cases. Thus, the structures of derivatives **14** were completely confirmed. We propose a mechanism for the formation of compounds **13** or **14** as follows. Nucleophilic attack by the nitrogen anion of thiaazaphenanthrene **3** on cyclopropenone forms the zwitterionic intermediate **K**, which collapses to the ketene intermediate **L** with fission of the S–N bond. In ethanolic reaction media, the intermediate **L** is attacked by ethanol to give the compounds **13**, while in benzene, the ketene intermediate **L** cyclizes at the *ortho*-position by electrophilic substitution at the benzene ring to give the intermediate **M** which undergoes a 1,3-hydrogen shift to produce compounds **14**.



Scheme 6 *Reagents and conditions:* i, diphenylcyclopropenone, EtOH, room temp.; ii, diphenylcyclopropenone, benzene, room temp.; iii, Dowtherm, 250 °C

Experimental

M.p.s were measured on a Yanagimoto micromelting point apparatus, and are uncorrected. IR spectra were measured on a JASCO A-1 spectrophotometer. ^{1}H NMR spectra were recorded on a Hitachi R-20B (60 MHz) or a JEOL GX-270 (270 Mz) spectrometer using tetramethylsilane as internal standard. The chemical shifts are in δ units (ppm) with coupling constants J 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. High-resolution mass determination was conducted on a JMA 2000 on-line system. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. Analytical and preparative TLC (PLC) were performed on Merck silica gel 60PF-254 plates.

9-(β-Phenylstyryl)-9-thia-10-azaphenanthrene **3g**.—TMEDA (5.24 cm^3, 3.47 mmol) was added to a hexane solution of butyllithium (1.6 mol dm^{-3}; 4.4 cm^3, 7.04 mmol) at 0 °C under nitrogen, and the mixture was stirred for 30 min. To this solution was added a solution of 2-amino-2′-trimethylsilylmethylsulfanylbiphenyl[4c] **1** (1 g, 3.48 mmol) in dry tetrahydrofuran (THF; 6 cm^3), and the mixture was stirred for 2 h. A solution of benzophenone (760 mg, 4.18 mmol) in dry THF (4 cm^3) was added to the mixture, which was stirred for a further 3 h before being poured into ice–water and extracted with CH_2Cl_2. The extract was washed with water, dried ($MgSO_4$) and evaporated. The residual oil was subjected to column chromatography on silica gel with hexane–ethyl acetate (5:1) as solvent to afford 2-amino-2′-(β-phenylstyrylsulfanyl)biphenyl **2** (1.29 g, 97.2%) as a yellow oil; ν_{max}/cm^{-1} 3450 and 3350 (NH_2); δ_H($CDCl_3$) 2.75–3.75 (2 H, br, NH_2), 6.70 (1 H, s, –CH=) and 6.73–7.70 (18 H, m, ArH); m/z 379 (M$^+$, base) (Found: M$^+$, 379.1368. $C_{26}H_{21}NS$ requires M, 379.1394). The biphenyl **2** (1 g, 2.63 mmol) was dissolved in dry CH_2Cl_2 (30 cm^3) and the solution was cooled to −78 °C and stirred while a solution of Bu^{t}OCl (320 mg, 2.94 mmol) in dry CH_2Cl_2 (20 cm^3) was added dropwise to it during 30 min. The mixture was stirred for a further 16 h during which time the temperature was gradually raised to 0 °C. Aq. NaOH (117 mg, 2.92 mmol) in water (2 cm^3) was added to the reaction mixture which was then vigorously 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 (2:1) to give *title compound* **3g** (850 mg, 84.7%) as orange prisms, after recrystallization from CH_2Cl_2–hexane, m.p. 150–152 °C; ν_{max}/cm^{-1} 1600, 1230 and 925; δ_H($CDCl_3$) 6.75–7.75 (11 H, m, ArH and =CH–) and 7.80–8.08 (2 H, m, ArH); m/z 377 (M$^+$) and 198 (base) (Found: C, 82.7; H, 5.0; N, 3.3. $C_{26}H_{19}NS$ requires C, 82.7; H, 5.1; N, 3.7%) (Found: M$^+$, 377.1218. $C_{26}H_{19}NS$ requires M, 377.1237).

Reactions of 9-Thia-10-azaphenanthrenes **3** *with Dimethyl Acetylenedicarboxylate (DMAD)*

9-Methyl-9-thia-10-azaphenanthrene **3a**.—A solution of DMAD (302 mg, 2.13 mmol) in dry benzene (10 cm^3) was added to a stirred solution of the thiaazaphenanthrene **3a**[4c] (412 mg, 1.93 mmol) in dry benzene (20 cm^3) under nitrogen, and the mixture was stirred for 20 h at room temperature. It was then evaporated under reduced pressure at room temperature to give an oil which was separated by PLC on silica gel with hexane–ethyl acetate (3:1) into three fractions. The upper fraction afforded dimethyl 1,2-bis(2′-methylsulfanylbiphenyl-2-ylimino)ethane-1,2-dicarboxylate **8a** (52 mg, 9.5%) as yellow needles. The middle fraction gave 7,8-bis(methoxycarbonyl)-6*H*,9*H*-dibenzo[*f*,*h*][1,5]thiazonine **5a** (278 mg, 40.5%) as colourless needles. These two products were isolated in our preliminary report.[1b] The fraction from the origin of the PLC plate was still a mixture, and was further separated by PLC on silica gel with hexane–ethyl acetate (1:2) to afford 5-methyl-6,7-bis(methoxycarbonyl)-6*H*-dibenzo[*e*,*g*][1,4]thiazocin-5-ium-6-ide **6a** (109 mg, 16%) and 2-[(*E*)-1,2-bis(methoxycarbonyl)vinylamino]-2′-methylsulfinylbiphenyl **7a** (109 mg, 15%). Compound **6a**, dark yellow prisms, m.p. 164–165 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1740 and 1650 (ester); δ_H($CDCl_3$) 1.97 (3 H, s, SMe), 3.67 (3 H, s, OMe), 3.74 (3 H, s, OMe) and 6.97–7.77 (8 H, m, ArH); δ_C($CDCl_3$) 33.1 (q), 51.0 (q), 52.6 (q), 121.1 (d), 123.5 (d), 126.1 (s), 129.2 (s), 129.2 (d), 129.6 (d), 130.9 (d), 131.6 (d), 132.2 (d), 133.9 (d), 143.6 (s), 151.7 (s), 159.1 (s), 166.8 (s) and 167.3 (s); m/z 355 (M$^+$) and 255 (base) (Found: C, 64.1; H, 4.8; N, 3.9. $C_{19}H_{17}NO_4S$ requires C, 64.2; H, 4.8; N, 3.9%). Compound **7a**, yellow prisms, m.p. 135–136 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 3270 (NH), 1730 (ester) and 1030 (SO); δ_H($CDCl_3$) 2.51 (3 H, s, SMe), 3.64 (3 H, s, OMe), 3.75 (3 H, s, OMe), 5.47 (1 H, s, –CH=), 6.75–6.88 (1 H, m, ArH), 7.14–7.66 (6 H, m, ArH), 8.15–8.20 (1 H, m, ArH) and 9.29 (1 H, br s, NH); δ_C($CDCl_3$) 41.7 (q), 51.3 (q), 52.9 (q), 97.1 (d), 120.0 (d), 123.7 (d), 124.2 (d), 128.6 (s), 129.3 (d), 129.5 (d), 130.5 (d),

130.8 (d), 131.0 (d), 135.2 (s), 138.4 (s), 144.9 (s), 146.3 (s), 164.4 (s) and 169.2 (s); *m/z* 373 (M^+) and 250 (base) (Found: C, 61.0; H, 5.1; N, 3.6. $C_{19}H_{19}NO_5S$ requires C, 61.1; H, 5.1; N, 3.75%).

9-Ethyl-9-thia-10-azaphenanthrene **3b**.—A mixture of DMAD (275 mg, 1.94 mmol) and thiaazaphenanthrene **3b**[4c] (400 mg, 1.76 mmol) in dry benzene (30 cm^3) was stirred at room temperature for 20 h under nitrogen, and worked up as above. The residual oil was submitted to PLC on silica gel with hexane–ethyl acetate (1:1) to afford the following products: dimethyl 1,2-bis(2′-ethylsulfanylbiphenyl-2-ylimino)ethane-1,2-dicarboxylate **8b** (25 mg, 2.4%), yellow prisms, m.p. 155–156 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1740 (ester), 1640 (C=N) and 1270; $\delta_H(CDCl_3)$ 1.15 (6 H, t, *J* 7, 2 × CH_2Me), 2.69 (4 H, q, *J* 7, 2 × CH_2Me), 3.35 (6 H, s, 2 × Me) and 6.92–7.41 (16 H, m, ArH); $\delta_C(CDCl_3)$ 14.1 (q), 27.7 (t), 51.8 (q), 117.9 (d), 125.2 (d), 126.7 (d), 127.6 (d), 128.3 (d), 128.9 (d), 131.0 (d), 131.2 (d), 135.6 (d), 139.9 (s), 145.4 (s), 156.7 (s), 163.1 (s) and 194.1 (s); *m/z* 596 (M^+) and 238 (base) (Found: C, 68.2; H, 5.3; N, 4.7. $C_{34}H_{32}N_2O_4S_2$ requires C, 68.4; H, 5.4; N, 4.7%); 2-[(*E*)-1,2-bis(methoxycarbonyl)vinylamino]-2′-ethylsulfinylbiphenyl **7b** (179 mg, 26%), yellow prisms, m.p. 118–120 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1730 and 1665 (ester) and 1030 (SO); $\delta_H(CDCl_3)$ 1.05 (3 H, t, *J* 7, CH_2Me), 2.20–2.90 (2 H, m, CH_2Me), 3.60 (3 H, s, OMe), 3.75 (3 H, s, OMe), 5.45 (1 H, s, –CH=), 6.75–6.88 (1 H, m, ArH), 7.14–7.66 (6 H, m, ArH), 8.04–8.12 (1 H, m, ArH) and 9.30 (1 H, br s, NH); $\delta_C(CDCl_3)$ 5.8 (q), 47.0 (t), 51.3 (q), 52.9 (q), 96.8 (d), 120.0 (d), 123.0 (d), 125.5 (d), 128.5 (s), 129.0 (d), 129.2 (d), 130.6 (d), 131.0 (d), 131.1 (d), 135.4 (s), 138.3 (s), 142.1 (s), 146.4 (s), 164.5 (s) and 169.2 (s); *m/z* 387 (M^+) and 198 (base) (Found: C, 61.9; H, 5.5; N, 3.6. $C_{20}H_{21}NO_5S$ requires C, 62.0; H, 5.5; N, 3.6%); 5-ethyl-6,7-bis(methoxycarbonyl)-6*H*-dibenzo[*e,g*][1,4]thiazocin-5-ium-6-ide **6b** (178 mg, 27%), pale yellow prisms, m.p. 140–141 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1740 and 1650 (ester); $\delta_H(CDCl_3)$ 0.91 (3 H, t, *J* 7, CH_2Me), 1.99–2.23 (2 H, m, CH_2Me), 3.67 (3 H, s, OMe), 3.75 (3 H, s, OMe), 6.91–7.78 (8 H, m, ArH); $\delta_C(CDCl_3)$ 9.7 (q), 43.0 (t), 51.0 (q), 52.6 (q), 59.9 (s), 121.0 (d), 123.3 (d), 123.9 (s), 129.0 (s), 129.4 (2 × d), 130.7 (d), 131.4 (d) 133.4 (d) 133.9 (d), 143.9 (s), 151.4 (s), 159.0 (s) and 167.4 (2 × s); *m/z* 369 (M^+) and 255 (base) (Found: C, 64.8; H, 5.2; N, 3.8. $C_{20}H_{19}NO_4S$ requires C, 65.02; H, 5.2; N, 3.8%).

9-Propyl-9-thia-10-azaphenanthrene **3c**.—A mixture of DMAD (324 mg, 2.28 mmol) and thiaazaphenanthrene **3c**[4c] (500 mg, 2.07 mmol) in dry benzene (35 cm^3) was stirred for 20 h at room temperature under nitrogen and worked up as above. The residue was separated by PLC on silica gel with hexane–ethyl acetate (1:1) to give the following products: dimethyl 1,2-bis(2′-propylsulfanyl-2′-biphenyl-2-ylimino)ethane-1,2-dicarboxylate **8c** (24 mg, 2%), yellow columns, m.p. 135–136 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1740 (ester), 1645 (C=N) and 1260; $\delta_H(CDCl_3)$ 0.87 (6 H, t, *J* 7.3, 2 × C_2H_4Me), 1.49 (4 H, h, *J* 7.3, 2 × CH_2CH_2Me), 2.63 (4 H, t, *J* 7.3, 2 × CH_2CH_2Me), 3.35 (6 H, s, 2 × OMe) and 6.93–7.44 (16 H, m, ArH); $\delta_C(CDCl_3)$ 13.4 (q), 22.3 (t), 35.9 (t), 51.8 (q), 117.9 (d), 125.2 (d), 126.6 (s), 127.6 (d), 128.2 (d), 129.2 (d), 131.1 (d), 131.3 (d), 135.8 (s), 140.0 (s), 145.5 (s), 156.7 (s) and 163.2 (s); *m/z* 624 (M^+) and 252 (base) (Found: C, 69.0; H, 5.7; N, 4.6. $C_{36}H_{36}N_2O_4S_2$ requires C, 69.2; H, 5.8; N, 4.5%); 6-ethyl-7,8-bis(methoxycarbonyl)-6*H*,9*H*-dibenzo[*f,h*][1,5]thiazonine **5c** (123 mg, 16%), a yellow oil; ν_{max}/cm^{-1} 3310 (NH) and 1720 (ester); $\delta_H(CDCl_3)$ 0.78 (3 H, t, *J* 7, CH_2Me), 1.25–1.82 (2 H, m, CH_2Me), 3.57 (3 H, s, OMe), 3.63 (3 H, s, OMe), 3.92 (1 H, t, *J* 6, CH), 6.01 (1 H, br s, NH) and 6.98–7.49 (8 H, m, ArH); $\delta_C(CDCl_3)$ 12.8 (q), 13.0 (t), 46.3 (d) 51.2 (q), 52.9 (1), 111.7 (s), 122.4 (d), 125.1 (d), 127.5 (d), 127.8 (d), 128.8 (d), 129.3 (d), 131.3 (d), 133.6 (s), 135.2 (d), 135.5 (s), 138.2 (s), 138.4 (s), 142.5 (s), 165.9 (s) and 167.2 (s); *m/z* 383 (M^+) and 184 (base) (Found: M^+, 383.1179. $C_{21}H_{21}NO_4S$ requires *M*, 383.1192); 2-[(*E*)-1,2-bis(methoxycarbonyl)vinylamino]-2′-propylsulfinylbiphenyl **7c** (222 mg, 27%), a yellow oil; ν_{max}/cm^{-1} 1750 and 1675 (ester) and 1030 (SO); $\delta_H(CDCl_3)$ 0.79 (3 H, t, *J* 7, CH_2CH_2Me), 1.45–1.73 (2 H, m, CH_2CH_2Me), 2.50–2.62 (2 H, m, CH_2CH_2Me), 3.64 (3 H, s, OMe), 3.76 (3 H, s, OMe), 5.46 (1 H, s, =CH–), 6.62–6.88 (1 H, m, ArH), 7.10–7.68 (6 H, m, ArH), 8.06–8.13 (1 H, m, ArH) and 9.35 (1 H, br s, NH); $\delta_C(CDCl_3)$ 12.5 (q), 15.4 (t), 51.1 (q), 52.7 (q), 55.8 (t), 96.6 (d), 119.8 (d), 121.3 (d), 123.5 (d), 124.1 (d), 124.9 (d), 128.2 (s), 129.1 (d), 130.5 (d), 131.0 (d), 135.1 (s), 138.2 (s), 142.7 (s), 146.2 (s), 164.3 (s) and 169.1 (s); *m/z* 401 (M^+) and 181 (base) (Found: M^+, 401.1324. $C_{21}H_{23}NO_5S$ requires *M*, 401.1297); 6,7-bis(methoxycarbonyl)-5-propyl-6*H*-dibenzo[*e,g*][1,4]thiazocin-5-ium-6-ide **6c** (293 mg, 3.7%), yellow prisms, m.p. 140–141.5 °C (decomp.) (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1745 and 1650 (ester); $\delta_H(CDCl_3)$ 0.75 (3 H, t, *J* 6, CH_2CH_2Me), 1.00–1.65 (2 H, m, CH_2CH_2Me), 1.75–2.25 (2 H, m, CH_2CH_2Me), 3.65 (3 H, s, OMe), 3.73 (3 H, s, OMe) and 6.85–7.90 (8 H, m, ArH); $\delta_C(CDCl_3)$ 12.4 (q), 18.4 (t), 50.3 (t), 51.0 (q), 52.6 (q), 59.5 (s), 121.0 (d), 123.2 (d), 124.2 (s), 129.1 (s), 129.4 (d), 129.5 (d), 130.7 (d), 131.4 (d), 133.1 (d), 133.8 (d), 143.8 (s), 151.5 (s), 159.0 (s), 167.3 (s) and 167.5 (s); *m/z* 383 (M^+) and 255 (base) (Found: C, 65.8; H, 5.55; N, 3.4. $C_{21}H_{21}NO_4S$ requires C, 65.8; H, 5.5; N, 3.65%).

9-Isopropyl-9-thia-10-azaphenanthrene **3d**.—A mixture of DMAD (353 mg, 2.48 mmol) and thiaazaphenanthrene **3d**[4c] (500 mg, 2.07 mmol) in dry benzene (30 cm^3) was stirred for 27 h at room temperature under nitrogen and worked up as above. The residual oil was separated by PLC on silica gel with hexane–ethyl acetate (2:1) to give the following products: 7,8-bis(methoxycarbonyl)-6,6-dimethyl-6,7-dihydrodibenzo[*f,h*]thiazonine **4d** (334 mg, 42%), yellow prisms, m.p. 143–145 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1760 and 1735 (ester) and 1662 (C=N); $\delta_H(CDCl_3)$ 1.55 (3 H, s, Me), 1.60 (3 H, s, Me), 3.63 (3 H, s, OMe), 3.72 (3 H, s, OMe), 4.23 (1 H, s, CH) and 6.66–7.70 (8 H, m, ArH); $\delta_C(CDCl_3)$ 24.5 (q), 28.0 (q), 47.5 (s), 52.2 (q), 53.1 (q), 57.5 (d), 114.8 (d), 124.3 (d), 127.9 (d), 128.3 (d), 128.3 (d), 128.8 (d), 130.1 (d), 131.2 (s), 132.1 (s), 139.3 (d), 146.0 (s), 147.0 (s), 156.6 (s), 164.1 (s) and 168.3 (s); *m/z* 383 (M^+) and 184 (base) (Found: C, 65.5; H, 5.5; N, 3.7. $C_{21}H_{21}NO_4S$ requires C, 65.8; H, 5.5; N, 3.7%); 2-[(*E*)-1,2-bis(methoxycarbonyl)vinylamino]-2′-isopropylsulfinylbiphenyl **7d** (76 mg, 9.1%), pale yellow prisms, m.p. 119–120.5 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1722 and 1661 (ester) and 1020 (SO); $\delta_H(CDCl_3)$ 0.88 (3 H, d, *J* 7, Me), 1.12 (3 H, d, *J* 7, Me), 2.40 (1 H, m, CH), 3.60 (3 H, s, OMe), 3.74 (3 H, s, OMe), 5.38 (1 H, s, –CH=), 6.60–8.15 (8 H, m, ArH), 9.28 (1 H, s, NH); *m/z* 401 (M^+) and 327 (base) (Found: C, 62.6; H, 5.65; N, 3.5. $C_{21}H_{23}NO_5S$ requires C, 62.8; H, 5.8; N, 3.5%).

In a similar manner, diethyl acetylenedicarboxylate (DEAD), instead of DMAD, reacted with the compound **3d** to give the corresponding ethyl esters: 7,8-bis(ethoxycarbonyl)-6,6-dimethyl-6,7-dihydrodibenzo[*f,h*][1,5]thiazonine (35.6%), a yellow oil; ν_{max}/cm^{-1} 1748 and 1722 (ester) and 1662 (C=N); $\delta_H(CDCl_3)$ 1.13 (3 H, t, *J* 7, OCH_2Me), 1.25 (3 H, t, *J* 7, OCH_2Me), 1.52 (3 H, s, Me), 1.61 (3 H, s, Me), 3.95–4.48 (5 H, m, CH and 2 × OCH_2Me) and 7.20–7.70 (8 H, m, ArH); $\delta_C(CDCl_3)$ 13.5 (q), 13.8 (q), 24.4 (q), 27.8 (q), 47.2 (s), 57.7 (d), 60.9 (t), 61.8 (t), 114.7 (d), 124.0 (d), 127.6 (d), 128.0 (d), 128.1 (d), 128.6 (d), 129.8 (d), 131.1 (s), 132.0 (s), 139.0 (d), 146.0 (s), 147.0 (s), 156.9 (s), 163.4 (s) and 167.5 (s); *m/z* 411 (M^+) and 184 (base) (Found: M^+, 411.1537. $C_{23}H_{25}NO_4S$ requires *M*, 411.1504); 2-[(*E*)-1,2-bis(ethoxycarbonyl)vinylamino]-2′-isopropylsulfinylbiphenyl (11.2%), yellow plates, m.p. 112–114 °C (from CH_2Cl_2–hexane); $\delta_H(CDCl_3)$ 0.93 (3 H, t, *J* 7, OCH_2Me),

1.18 (3 H, t, *J* 7, OCH_2Me), 1.11 (6 H, d, *J* 7, 2 × Me), 2.32 (1 H, m, CH), 4.05 (2 H, q, *J* 7, OCH_2Me), 4.19 (2 H, q, *J* 7, OCH_2Me), 5.38 (1 H, s, –CH=), 6.65–8.15 (8 H, m, ArH) and 9.25 (1 H, s, NH); *m/z* 429 (M^+) and 198 (base) (Found: C, 63.9; H, 6.2; N, 3.2; M^+, 429.1584. $C_{23}H_{27}NO_5S$ requires C, 64.3; H, 6.3; N, 3.3%; *M*, 429.1609).

9-*Cyclohexyl*-9-*thia*-10-*azaphenanthrene* **3e**.—A mixture of DMAD (166 mg, 1.17 mmol) and thiaazaphenanthrene **3e**[4c] (300 mg, 1.07 mmol) in dry benzene (25 cm^3) was stirred for 52 h at room temperature under nitrogen and worked up as above. The residue was submitted to PLC on silica gel with hexane–ethyl acetate (3:1) to give the following products: spiro[cyclohexane-1,6′-(7,8-bis(methoxycarbonyl)-6,7-dihydrodibenzo-[*f*,*h*][1,5]thiazonine)] **4e** (79 mg, 17%), a yellow oil; ν_{max}/cm^{-1} 1775 and 1730 (ester) and 1663 (C=N); $\delta_H(CDCl_3)$ 1.21–2.67 (10 H, m, C_6H_{10}), 3.62 (3 H, s, Me), 3.72 (3 H, s, Me), 4.24 (1 H, s, CH), 6.78–6.81 (1 H, m, ArH) and 7.15–7.58 (7 H, m, ArH); $\delta_C(CDCl_3)$ 21.8 (t), 22.1 (t), 25.2 (t), 28.9 (t), 32.9 (t), 52.2 (q), 53.0 (q), 53.7 (s), 58.8 (d), 114.7 (d), 124.3 (d), 128.0 (d), 128.1 (d), 128.2 (d), 128.7 (d), 129.8 (d), 131.4 (s), 132.2 (s), 137.7 (d), 146.6 (s), 146.9 (s), 156.6 (s), 164.4 (s) and 168.3 (s); *m/z* 423 (M^+) and 184 (base) (Found: M^+, 423.1484. $C_{24}H_{25}NO_4S$ requires *M*, 423.1504). 2-[(*E*)-1,2-bis(methoxycarbonyl)vinylamino]-2′-cyclohexylsulfinylbiphenyl **7e** (294 mg, 62%), pale yellow prisms, m.p. 128–130 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1740 and 1662 (ester) and 1030 (SO); $\delta_H(CDCl_3)$ 1.10–1.67 (10 H, m, CH_2 of C_6H_{11}), 2.30–2.45 (1 H, m, CH of C_6H_{11}), 3.60 (3 H, s, OMe), 3.78 (3 H, s, OMe), 5.42 (1 H, s, –CH=), 6.76–7.64 (7 H, m, ArH), 7.97–8.05 (1 H, m, ArH) and 9.39 (1 H, br s, NH); $\delta_C(CDCl_3)$ 21.9 (t), 25.0 (t), 25.1 (t), 25.4 (t), 27.2 (t), 51.1 (q), 52.5 (q), 58.8 (d), 95.9 (d), 119.9 (d), 123.6 (d), 128.5 (s), 128.6 (d), 128.9 (d), 130.4 (d), 130.8 (d), 131.3 (d), 135.8 (s), 138.1 (s), 140.6 (s), 146.5 (s), 164.4 (s) and 169.1 (s); *m/z* 441 (M^+) and 327 (base) (Found: C, 65.5; H, 6.3; N, 3.3. $C_{24}H_{27}NO_5S$ requires C, 65.3; H, 6.2; N, 3.2%).

9-*Phenyl*-9-*thia*-10-*azaphenanthrene* **3f**.—A mixture of DMAD (310 mg, 2.18 mmol) and thiaazaphenanthrene **3f**[4c] (500 mg, 1.82 mmol) in dry benzene (40 cm^3) was stirred for 42 h at room temperature under nitrogen and worked up as above. The oil obtained was purified by PLC on silica gel with hexane–ethyl acetate–CH_2Cl_2 (1:1:2) to afford 6,7- bis(methoxycarbonyl)-5-phenyl-6*H*-dibenzo[*e*,*g*][1,4]thiazocin-5-ium-6-ide **6f** (555 mg, 73%), yellow columns, m.p. 236–238 °C (from $CHCl_3$–hexane); ν_{max}/cm^{-1} 1740 and 1655 (ester); $\delta_H(CDCl_3)$ 3.68 (3 H, s, OMe), 3.81 (3 H, s, OMe), 6.25 (1 H, d, *J* 6.3, ArH), 6.41 (1 H, t, *J* 6.3, ArH), 6.84 (3 H, d, *J* 7.8, ArH), 7.04–7.19 (4 H, m, ArH), 7.43 (1 H, d, *J* 7.8, ArH), 7.59 (1 H, t, *J* 6.3, ArH), 7.71 (1 H, t, *J* 6.3, ArH) and 8.05 (1 H, d, *J* 7.1, ArH); $\delta_C(CDCl_3)$ 51.0 (q), 52.6 (q), 120.2 (q), 123.1 (d), 124.5 (d), 128.0 (s), 128.6 (d), 128.8 (d), 129.0 (d), 129.1 (d), 129.5 (d), 131.8 (d), 133.2 (d), 134.0 (d), 134.2 (s), 143.8 (s), 150.6 (s), 158.8 (s), 167.2 (s) and 167.3 (s); *m/z* 417 (M^+, base) (Found: C, 68.9; H, 4.5; N, 3.35. $C_{24}H_{19}NO_4S$ requires C, 69.05; H, 4.6; N, 3.4%).

In a similar manner, DEAD, reacted with the compound **3f** to afford the corresponding ethyl ester derivative, 6,7-bis(ethoxycarbonyl)-5-phenyl-6*H*-dibenzo[*e*,*g*][1,4]thiazocin-5-ium-6-ide (675 mg, 83.4%), yellow prisms, m.p. 218–220 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1738 and 1660 (ester); $\delta_H(CDCl_3)$ 1.21 (3 H, t, *J* 7, CH_2Me), 1.32 (3 H, t, *J* 7, CH_2Me), 4.19 (4 H, m, 2 × OCH_2Me), 6.15 (1 H, d, *J* 6.3, ArH), 6.41 (1 H, t, *J* 6.3, ArH), 6.84 (3 H, t, *J* 7.3, ArH), 7.02–7.17 (4 H, m, ArH), 7.40 (1 H, d, *J* 7.1, ArH), 7.56 (1 H, t, *J* 6.3, ArH), 7.69 (1 H, t, *J* 6.3, ArH) and 8.02 (1 H, d, *J* 7.1, ArH); $\delta_C(CDCl_3)$ 13.9 (q), 14.5 (q), 59.7 (t), 61.5 (t), 120.2 (d), 123.1 (d), 124.6 (d), 128.2 (s), 128.8 (d), 128.9 (d), 129.1 (d), 129.5 (d), 131.8 (d), 133.2 (d), 133.9 (d), 134.4 (s), 144.0 (s), 150.8 (s), 159.2 (s), 166.9 (s) and 167.2 (s); *m/z* 445 (M^+, base) (Found: C, 70.2; H, 5.15; N, 3.1. $C_{26}H_{23}NO_4S$ requires C, 70.1; H, 5.2; N, 3.1%).

9-(β-*Phenylstyryl*)-9-*thia*-10-*azaphenanthrene* **3g**.—A mixture of DMAD (83 mg, 0.58 mmol) and thiaazaphenanthrene **3g** (200 mg, 0.53 mmol) in dry benzene (15 cm^3) was stirred for 5 h at room temperature under nitrogen, and worked up as above to afford 6,7-bis(methoxycarbonyl)-5-(β-phenylstyryl)-6*H*-dibenzo[*e*,*g*][1,4]thiazocin-5-ium-6-ide **6g** (212 mg, 77.1%) as yellow prisms, m.p. 217–219 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1720 and 1650 (ester); $\delta_H(CDCl_3)$ 3.63 (3 H, s, OMe), 3.75 (3 H, s, OMe) and 6.78–7.73 (19 H, m, ArH and =CH–); $\delta_C(CDCl_3)$ 50.91 (q), 52.6 (q), 121.5 (d), 121.9 (d), 123.7 (d), 127.6 (d), 128.2 (d), 128.5 (d), 128.9 (d), 129.0 (d), 129.1 (d), 129.9 (d), 130.4 (d), 130.5 (s), 130.6 (d), 131.1 (d), 131.4 (d), 133.2 (d), 135.7 (s), 137.1 (s), 143.1 (s), 151.3 (s), 152.4 (s), 159.5 (s), 167.0 (s) and 167.4 (s); *m/z* 519 (M^+) and 178 (base) (Found: C, 73.9; H, 4.85; N, 2.7. $C_{32}H_{25}NO_4S$ requires C, 73.97; H, 4.85; N, 2.70%).

2-[(E)-1,2-*Bis*(*methoxycarbonyl*)*vinylamino*]-2′-*methylsulfanylbiphenyl* **10**.—A solution of DMAD (660 mg, 4.64 mmol) in ethanol (5 cm^3) was added slowly to a stirred solution of 2-amino-2′-methylsulfanylbiphenyl **9**[4c] (1 g, 4.64 mmol) in ethanol (30 cm^3), and the mixture was stirred for 40 h. Evaporation of the solvent afforded *title compound* **10** (1.17 g, 70.4%) as pale yellow prisms after recrystallization from CH_2Cl_2–hexane, m.p. 87.5–88 °C; ν_{max}/cm^{-1} 1740 and 1670 (ester); $\delta_H(CDCl_3)$ 2.40 (3 H, s, SMe), 3.60 (3 H, s, OMe), 3.63 (3 H, s, OMe), 5.27 (1 H, s, =CH–), 6.75–7.44 (8 H, m, ArH) and 9.15–9.45 (1 H, br s, NH); *m/z* 357 (M^+) (Found: C, 64.95; H, 5.4; N, 3.9. $C_{19}H_{19}NO_4S$ requires C, 63.85; H, 5.4; N, 3.9%).

2-[(E)-1,2-*Bis*(*methoxycarbonyl*)*vinylamino*]-2′-*methylsulfinylbiphenyl* **7a**.—To a solution of the biphenyl **10** (1 g, 2.30 mmol) in dry CH_2Cl_2 (40 cm^3) was added *m*-chloroperbenzoic acid (M-CPBA) (483 mg, 2.80 mmol) at 0 °C and the mixture was stirred for 12 h. 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 residual solids were recrystallized from CH_2Cl_2–hexane to afford *title compound* **7a** (912 mg, 87.3%) as pale yellow prisms, m.p. 135–136 °C.

6-[(E)-1,2-*Bis*(*methoxycarbonyl*)*vinyl*]-5-*methyl*-6H-*dibenzo*[c,e][1,2]*thiazin*-5-*ium Perchlorate* **11**.—Trifluoroacetic anhydride (2.2 cm^3) was slowly added to a stirred solution of sulfoxide **7a** (300 mg, 0.80 mmol) in dry CH_2Cl_2 (40 cm^3) at −60 °C, and the mixture was stirred for 1 h at this temperature, and then for a further 10 h over which time the temperature was gradually raised to 0 °C. Silver perchlorate (166 mg, 0.80 mmol) was added to the reaction mixture, which was then stirred for 4 h. The precipitate was filtered off and washed with CH_2Cl_2. Dry diethyl ether was added to the filtrate to precipitate crystals, which were collected and recrystallized from CH_2Cl_2–diethyl ether to afford the *title thiazinium perchlorate* **11** (259 mg, 70.7%) as colourless prisms, m.p. 181–183 °C (decomp.); ν_{max}/cm^{-1} 1750 and 1730 (ester) and 1090 (ClO_4^-); $\delta_H(CF_3CO_2H$ and $CDCl_3)$ 3.28 (3 H, s, SMe), 3.75 (6 H, br s, 2 × OMe), 7.02 (1 H, s, =CH–) and 7.10–8.35 (8 H, m, ArH) (Found: C, 49.8; H, 3.9; N, 2.9. $C_{19}H_{18}ClNO_8S$ requires C, 50.1; H, 4.0; N, 3.1%).

Reaction of Compound **11** *with Sodium Hydride*.—Sodium hydride (60% dispersion in mineral oil; 40 mg, 1 mmol) was added to a stirred suspension of perchlorate **11** (450 mg, 0.99 mmol) in dry THF (40 cm^3) under an N_2 atmosphere, and the mixture was stirred for 30 min at room temperature. The reaction mixture was poured into ice–water and extracted with

CH_2Cl_2. The organic layer was separated and subjected to PLC on silica gel with hexane–ethyl acetate (1:1) to give the compound **5a** (228 mg, 65%).

Reactions of 9-Alkyl-9-thia-10-azaphenanthrenes **3a–c** *with Methyl Propiolate.*—A solution of methyl propiolate (1.33 g, 15.8 mmol) in dry benzene (5 cm^3) was added to a solution of thiaazaphenanthrene **3a** (1.12 g, 5.26 mmol) in dry benzene (45 cm^3), and the mixture was stirred continuously for 1 week at room temperature under nitrogen. Benzene was evaporated off under reduced pressure at room temperature to leave an oil which was subjected to PLC on silica gel with hexane–ethyl acetate (1:1) to afford 6,8-bis(methoxycarbonyl)-5-methyl-6*H*-dibenzo[*g*,*i*][1,6]thiazecin-5-ium-6-ide **12a** (288 mg, 14%) as orange prisms after recrystallization from CH_2Cl_2–hexane, m.p. 178–180 °C (decomp.); ν_{max}/cm^{-1} 1650 (ester); $\delta_H(CDCl_3)$ 3.08 (3 H, s, SMe), 3.80 (3 H, s, OMe), 3.84 (3 H, s, OMe), 7.00–7.95 (8 H, m, ArH), 8.80 (1 H, d, *J* 1.5, CH) and 9.17 (1 H, d, *J* 1.5, CH); $\delta_C(CDCl_3)$ 29.8 (q), 51.2 (q), 51.8 (q), 86.2 (s), 103.2 (s) 115.2 (d), 125.1 (d), 129.6 (d), 130.0 (d), 131.4 (d), 131.9 (d), 132.0 (d), 133.4 (s), 137.1 (s), 138.0 (s), 142.8 (s), 147.8 (d), 153.4 (d), 167.4 (s) and 169.0 (s); *m*/*z* 381 (M^+) (Found: C, 66.0; H, 5.3; N, 3.4. $C_{21}H_{19}NO_4S$ requires C, 66.1; H, 5.0; N, 3.7%).

Under similar conditions to the above, the following dibenzothiazecin-5-ium-6-ide derivatives were obtained from the reaction of the thiaazaphenanthrenes **3b** and **3c** with methyl propiolate: 5-ethyl-6,8-bis(methoxycarbonyl)-6*H*-dibenzo[*g*,*i*][1,6]thiazecin-5-ium-6-ide **12b** (from **3b**; 4.89%), orange prisms after PLC on silica gel with hexane–ethyl acetate (3:1), m.p. 168–170 °C (decomp.) (from benzene–hexane); ν_{max}/cm^{-1} 1655 (ester); $\delta_H(CDCl_3)$ 1.02 (3 H, t, *J* 7.5, CH_2Me), 3.46–3.90 (2 H, m, CH_2Me), 3.81 (3 H, s, OMe), 3.85 (3 H, s, OMe), 7.10–7.75 (8 H, m, ArH), 8.82 (1 H, d, *J* 1.5, CH) and 9.17 (1 H, d, *J* 1.5, CH); *m*/*z* 395 (M^+) and 262 (base) (Found: C, 66.6; H, 5.4; N, 3.5. $C_{22}H_{21}NO_4S$ requires C, 66.8; H, 5.35; N, 3.5%); 6,8-bis(methoxycarbonyl)-5-propyl-6*H*-dibenzo[*g*,*i*][1,6]thiazecin-5-ium-6-ide **12c** (from **3c**; 9.55%) orange prisms after PLC on silica gel with hexane–ethyl acetate (2:1), m.p. 161–162 °C (decomp.) (from benzene–hexane); ν_{max}/cm^{-1} 1690 and 1670 (ester); $\delta_H(CDCl_3)$ 0.80 (3 H, t, *J* 6, CH_2CH_2Me), 1.15–1.55 (2 H, m, CH_2CH_2Me), 3.53–3.90 (2 H, m, CH_2CH_2Me), 3.80 (3 H, s, OMe), 3.85 (3 H, s, OMe), 7.12–7.85 (8 H, m, ArH), 8.82 (1 H, d, *J* 1.5, CH) and 9.18 (1 H, d, *J* 1.5, CH); *m*/*z* 409 (M^+) and 262 (base) (Found: C, 67.5; H, 5.75; N, 3.3. $C_{23}H_{23}NO_4S$ requires C, 67.5; H, 5.7; N, 3.4%).

Reaction of the 9-Alkyl-9-thia-10-azaphenanthrenes **3a–c** *with Diphenylcyclopropenone.*—(*a*) *In ethanol.* A mixture of compound **3a** (300 mg, 1.41 mmol) and diphenylcyclopropenone (290 mg, 1.41 mmol) in absolute ethanol (20 cm^3) was stirred for 15 h after which time the solvent was removed under reduced pressure. The residual oil was submitted to PLC on silica gel with hexane–ethyl acetate (4:1) to give 2-[(*Z*)-2-(ethoxycarbonyl)-1,2-diphenylvinylamino]-2′-methylsulfanylbiphenyl **13a** (105 mg, 16.0%) as colourless prisms after recrystallization from CH_2Cl_2–hexane, m.p. 118–119 °C; ν_{max}/cm^{-1} 3160 (NH) and 1650 (ester); $\delta_H(CDCl_3)$ 1.08 (3 H, t, *J* 7, CH_2Me), 2.47 (3 H, s, SMe), 4.03 (2 H, q, *J* 7, CH_2Me), 6.25–7.40 (18 H, m, ArH) and 10.03 (1 H, br s, NH); *m*/*z* 465 (M^+) and 392 (base) (Found: C, 77.1; H, 5.9; N, 3.0. $C_{30}H_{27}NO_2S$ requires C, 77.4; H, 5.85; N, 3.0%).

Under similar conditions to the above, the following compounds were obtained from the reaction of the thiaazaphenanthrenes **3b** and **c** with diphenylcyclopropenone: 2-[(*E*)-2-(ethoxycarbonyl)-1,2-diphenylvinylamino]-2′-ethylsulfanylbiphenyl **13b** (20.5%) as colourless prisms after recrystallization from CH_2Cl_2–hexane, m.p. 100–101 °C; ν_{max}/cm^{-1} 3160 (NH) and 1645 (ester); $\delta_H(CDCl_3)$ 1.12 (3 H, t, *J* 7, SCH_2Me), 1.37 (3 H, t, *J* 7, OCH_2Me), 2.98 (2 H, q, *J* 7, SCH_2Me), 4.07 (2 H, q, *J* 7, OCH_2Me), 6.30–7.50 (18 H, m, ArH) and 10.73 (1 H, br s, NH); *m*/*z* 479 (M^+) and 406 (base) (Found: C, 77.4; H, 6.0; N, 2.9. $C_{31}H_{29}NO_2S$ requires C, 77.6; H, 6.1; N, 2.9%); 2-[(*Z*)-2-ethoxycarbonyl-1,2-diphenylvinylamino]-2′-propylsulfanylbiphenyl **13c** (34.4%) as colourless prisms after recrystallization from CH_2Cl_2–hexane, m.p. 122–123 °C; ν_{max}/cm^{-1} 3160 (NH) and 1655 (ester); $\delta_H(CDCl_3)$ 1.03 (3 H, t, *J* 7, CH_2CH_2Me), 1.13 (3 H, t, *J* 7, OCH_2Me), 1.45–1.93 (2 H, m, CH_2CH_2Me), 2.94 (2 H, t, *J* 7, SCH_2CH_2Me), 4.07 (2 H, q, *J* 7, OCH_2Me), 6.84–7.48 (18 H, m, ArH) and 10.70 (1 H, br s, NH); *m*/*z* 493 (M^+) and 420 (base) (Found: C, 77.7; H, 6.4; N, 2.8. $C_{32}H_{31}NO_2S$ requires C, 77.9; H, 6.3; N, 2.8%).

(*b*) *In benzene.* A mixture of compound **3a** (300 mg, 1.41 mmol) and diphenylcyclopropenone (435 mg, 2.11 mmol) in dry benzene (30 cm^3) was stirred for 17 h at room temperature. The reaction mixture was concentrated to dryness to give a crude oil, which was purified by PLC on silica gel with hexane–ethyl acetate (2:1) as solvent to afford 8-(2′-methylsulfanylphenyl)-2,3-diphenylquinolin-4-(1*H*)-one **14a** (37 mg, 6.27%) as colourless prisms after recrystallization from benzene–hexane, m.p. 184.5–185.5 °C; ν_{max}/cm^{-1} 3400 (NH) and 1610 (CO); $\delta_H(CDCl_3)$ 2.40 (3 H, s, Me), 7.15–8.00 (17 H, m, ArH and NH) and 8.52 (1 H, dd, *J* 7 and 3, C_5-H); *m*/*z* 419 (M^+) and 418 (base) (Found: C, 80.05; H, 5.0; N, 3.4. $C_{28}H_{21}NOS$ requires C, 80.2; H, 5.05; N, 3.3%).

Under similar conditions to the above, the following dihydroquinolinone derivatives were obtained from the reaction of the thiaazaphenanthrenes **3b** and **3c** with diphenylcyclopropenone, respectively: 8-(2′-ethylsulfanylphenyl)-2,3-diphenylquinolin-4(1*H*)-one **14b** (91 mg, 15.9%) as colourless prisms after PLC on silica gel with hexane–ethyl acetate (2:1), m.p. 59–62 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 3400 (NH) and 1615 (CO); $\delta_H(CDCl_3)$ 1.24 (3 H, t, *J* 7.5, CH_2Me), 2.86 (2 H, q, *J* 7.5, CH_2Me), 7.22–7.90 (17 H, m, ArH and NH) and 8.56 (1 H, dd, *J* 6 and 3, C_5-H); *m*/*z* 433 (M^+) and 432 (base) (Found: 80.2; H, 5.9; N, 2.9. $C_{29}H_{23}NOS$ requires C, 80.3; H, 5.35; N, 3.2%); 2,3-diphenyl-8-(2′-propylsulfanylphenyl)quinolin-4(1*H*)-one **14c** (56 mg, 7.55%) as colourless prisms after PLC on silica gel with hexane–ethyl acetate (1:1), m.p. 154–155 °C (from CH_2Cl_2–hexane); ν_{max}/cm^{-1} 3400 (NH) and 1610 (CO); $\delta_H(CDCl_3)$ 0.93 (3 H, t, *J* 7, CH_2CH_2Me), 1.20–1.92 (2 H, m, CH_2CH_2Me), 1.81 (2 H, t, *J* 7, CH_2CH_2Me), 7.10–7.90 (17 H, m, ArH and NH) and 8.57 (1 H, dd, *J* 6 and 3, C_5-H); *m*/*z* 447 (M^+) and 446 (base) (Found: C, 80.2; H, 5.7; N, 3.1. $C_{30}H_{25}NOS$ requires C, 80.5; H, 5.6; N, 3.1%).

Thermal Cyclization of Compound **13**.—A mixture of compound **13a** (170 mg) and Dowtherm (20 cm^3) was heated for 1 h at 250 °C. The reaction mixture was column chromatographed on silica gel with hexane–ethyl acetate (1:1) to remove the Dowtherm, and further purified by PLC on silica gel with hexane–ethyl acetate (1:1) to afford the dihydroquinolinone **14a** (90 mg, 58.8%). Similarly, compounds **13b** and **13c** were heated in Dowtherm at 250 °C for 1 h to give the corresponding dihydroquinolinones **14b** (77.9%) and **14c** (57.7%), respectively.

X-Ray Study of 6,7-Bis(methoxycarbonyl)-5-phenyl-6H-dibenzo[e,g][1,4]*thiazocin-5-ium-6-ide* **6f**.—*Crystal data.* $C_{24}H_{19}NO_4S$, M = 417.48. Monoclinic, a = 14.864(6), b = 9.137(6), c = 15.469(6) Å, β = 102.41(3)Å, V = 2052(2) $Å^3$, Z = 4, D_c = 1.351 g cm^{-3}, space group $P2_1/c$ (#14) from systematic absences, $F(000)$ = 872, Mo-Kα radiation, λ = 0.710 69 Å (Mo-Kα) = 1.79 cm^{-1}.

A yellow plate crystal of the title compound having approximate dimensions of 0.150 × 0.080 × 0.150 mm was mounted in a glass capillary. All measurements were made on a

Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation and a 12 kW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 19 carefully centred reflections in the range $6.89 < 2\theta < 12.21°$ corresponded to a monoclinic cell. The data were collected at a temperature of 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.32°, with a take-off angle of 6.0°. Scans of $(0.89 + 0.30 \tan\theta)°$ were made at a speed of 16.0° min^{-1} (in omega). The weak reflections [$I < 10.0\ \sigma(I)$] were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 25.8 cm.

Data reduction. Of the 5197 reflections which were collected, 5012 were unique ($R_{int} = 0.125$). The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo-Kα is 1.8 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement. The structure was solved by direct methods.[7] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 975 observed reflections [$I < 3.00\ \sigma(I)$] and 328 variable parameters, and converged (largest parameter shift was 0.36 times its e.s.d.) with unweighted and weighted agreement factors of: $R = \Sigma||F_o| - F_c||/\Sigma|F_o| = 0.050$. $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)]^{\frac{1}{2}} = 0.047$. The standard deviation of an observation of unit weight was 1.28. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.23 and −0.27 e $Å^{-3}$, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[8] Anomalous dispersion effects were included in F_{calc};[9] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[10] All calculations were performed using the TEXSAN[11] crystallographic software package of Molecular Structure Corporation.

Supplementary data. Lists of atomic coordinates and thermal parameters, and bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.*

* For details of the CCDC deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, issue 1.

References

1 (*a*) M. Hori, T. Kataoka, H. Shimizu and K. Matsuo, *Tetrahedron Lett.*, 1979, 3969; (*b*) H. Shimizu, K. Matsuo, T. Kataoka and M. Hori, *Chem. Pharm. Bull.*, 1984, **32**, 4360.

2 (*a*) C. J. Moody, C. W. Rees, S. C. Tsoi and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 927; (*b*) R. S. Gairns, R. D. Grant, C. J. Moody, C. W. Rees and S. C. Tsoi, *J. Chem. Soc., Perkin Trans. 1*, 1986, 483.

3 (*a*) R. D. Grant, C. J. Moody, C. W. Rees and S. C. Tsoi, *J. Chem. Soc., Chem. Commun.*, 1982, 884; (*b*) R. S. Gairns, R. D. Grant, C. J. Moody, C. W. Rees and S. C. Tsoi, *J. Chem. Soc., Perkin Trans. 1*, 1986, 491; (*c*) R. D. Grant, C. W. Rees and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 1060.

4 (*a*) H. Shimizu, K. Ikedo, K. Hamada, H. Matsumoto, M. Ozawa, T. Kataoka and M. Hori, *Tetrahedron Lett.*, 1990, **31**, 7021; (*b*) H. Shimizu, K. Hamada, M. Ozawa, T. Kataoka, M. Hori, K. Kobayashi and Y. Tada, *Tetrahedron Lett.*, 1991, **32**, 4359; (*c*) H. Shimizu, K. Ikedo, K. Hamada, M. Ozawa, H. Matsumoto, K. Kamata, H. Nakamura, M. Ji, T. Kataoka and M. Hori, *J. Chem. Soc., Perkin Trans. 1*, 1991, 1733.

5 M. Hori, T. Kataoka, H. Shimizu, K. Matsuo, A. Sugimoto, K. Ikedo, K. Hamada, H. Ogura and H. Takayanagi, *J. Chem. Soc., Chem. Commun.*, 1987, 385.

6 G. A. Reynolds and C. R. Hauser, *Org. Synth.*, 1955, coll. vol. 3, p. 593.

7 Structure solutions methods: PHASE (Patterson heavy atom solution extractor), J. C. Calbrese, Univ. of Wisconsin–Madison, Ph.D. Thesis, 1972; DIRDIF (direct methods for difference structures—an automatic procedure for phase extension and refinement of difference structure factors), P. T. Beurskens, Technical Report 1984/1, Crystallography Laboratory, Toernooiveld, 6525 Ed. Nijmegen, Netherlands.

8 D. T. Cromer and J. T. Waber, Table 2.2A in *International Tables for X-ray Crystallography*, vol. IV, Kynoch Press, Birmingham, UK, 1974.

9 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.

10 D. T. Cromer and J. T. Waber, Table 2.3.1 in *International Tables for X-ray Crystallography*, vol. IV, Kynoch Press, Birmingham, UK, 1974.

11 TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, 1985.

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