[4 + 2]-Cycloadditions of 3-Amino-4-imino-4*H*-thieno[3,4-*c*][1]benzopyran with some Selected Dienophiles

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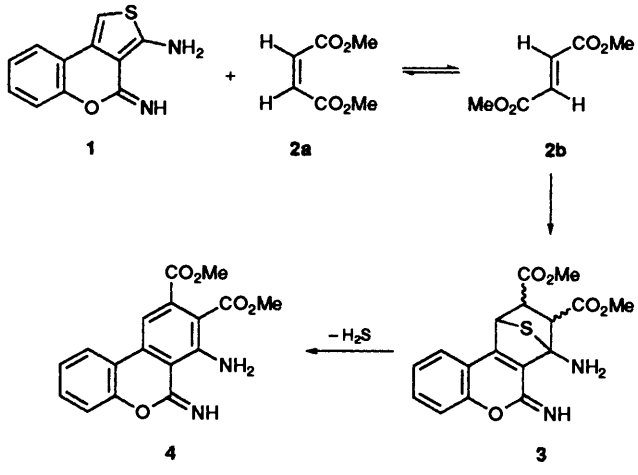
3-Amino-4-imino-4*H*-thieno[3,4-*c*][1]benzopyran **1** adds dimethyl maleate **2** and dimethyl acetylenedicarboxylate **6** in a [4 + 2] mode across the thiophene ring and reacts with 2,3-dichloro-1,4-naphthoquinone **12** by substitution of both chlorine atoms. All primary adducts, **3**, **7** and **13**, however, are unstable under the reaction conditions. The structures of the final products **4**, **10** and **15** have been assigned from their spectral data and their formation has been rationalized in terms of transformations available to the assumed primary products.

Synthesis of the title compound **1** has been described earlier[1,2] and in a separate study[3] the scope and the limitations of its reactions with β-keto esters and β-dicarboxylic esters were established. Here we report on the [4 + 2] cycloadditions of **1** with two selected dienophiles and on a double substitution which it undergoes with 2,3-dichloro-1,4-naphthoquinone **12**, leading, ultimately to novel condensed heterocyclic systems.

It is well documented that thiophene and its derivatives are reluctant partners in [4 + 2]-cycloadditions with dienophiles containing a double bond in general and with dimethyl maleate in particular. For instance, Gaertner and Tonkyn[5] failed to add maleic anhydride to tetramethylthiophene even when the reaction was carried out in boiling nitrobenzene (b.p. 211 °C). A similar failure was also reported by Clapp,[6] who attempted to induce tetraphenylthiophene to react with maleic anhydride. Similarly, thiophene fails to undergo [4 + 2]-cycloaddition with dienophiles[7] such as dimethyl maleate, dimethyl fumarate, methyl acrylate, acrylonitrile or acrylaldehyde, even under high pressure. A Diels–Alder adduct was obtained, however, with maleic anhydride (100 °C, 15 kbar, 3 h).[7] However it should be noted that at atmospheric pressure diene reactivity towards compounds containing a double bond has been observed with 2,5-dimethoxythiophene,[8] 2,4-bis(*N*-isopropyl-*N*-phenylamino)thiophene,[9] and 2,3,4,5-di(naphthalene-1,8-diyl)thiophene.[6]

Results and Discussion

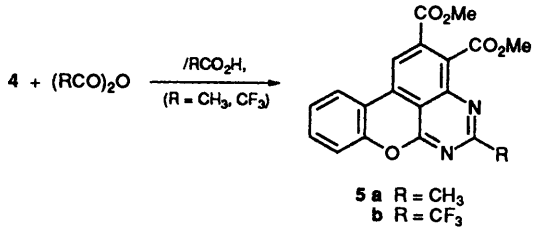
Treatment of compound **1** with neat dimethyl maleate **2a** gave a deep yellow precipitate (m.p. 165–166 °C) in 33% yield, to which structure **4** (Scheme 1) has been assigned on the basis of the results of combustion analysis, spectral data, and chemical evidence. The elemental analysis showed no evidence of sulfur being present and the gross formula $C_{17}H_{14}N_2O_5$ was deduced from results. This was confirmed by the mass spectrum which exhibited a molecular ion at *m/z* 326 (100%). The IR spectrum showed absorptions at 3370, 3290 and 1730, 1700 cm^{-1} (NH, NH_2 and CO respectively). The ^1H NMR ($CDCl_3$, 300 MHz) spectrum had broad singlet signals at δ_H 9.00 and 7.73 (NH_2 and NH respectively) exchangeable with D_2O; 1-H resonated at δ 7.12 (s). The $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 MHz) spectrum consisted of 17 lines as expected. These results suggested that compound **4** was formed as a result of Diels–Alder addition of dimethyl maleate or dimethyl fumarate (dienophile) to the thiophene ring of compound **1** (diene) according to a suprafacial-suprafacial mode (see Scheme 1). Although the intermediate adduct **3** was not isolated, this is not surprising in view of the high reaction temperature employed. Loss of hydrogen sulfide from **3** results in aromatization of the [*d*]-anellated ring and finally leads to compound **4**. Dimethyl fumarate **2b** formation in this reaction is the result of dimethyl maleate isomerization under the extreme reaction conditions, a phenomenon recently reported by Kotsuki and co-workers.[7]



1 **2a** **2b** **4** **3**

Scheme 1

Treatment of **4** with acetic anhydride in glacial acetic acid afforded a yellow powder, the analytical and spectral data of which were in full agreement with the proposed structure **5a**. Similarly, trifluoroacetylation of **4** gave compound **5b** (Scheme 2).



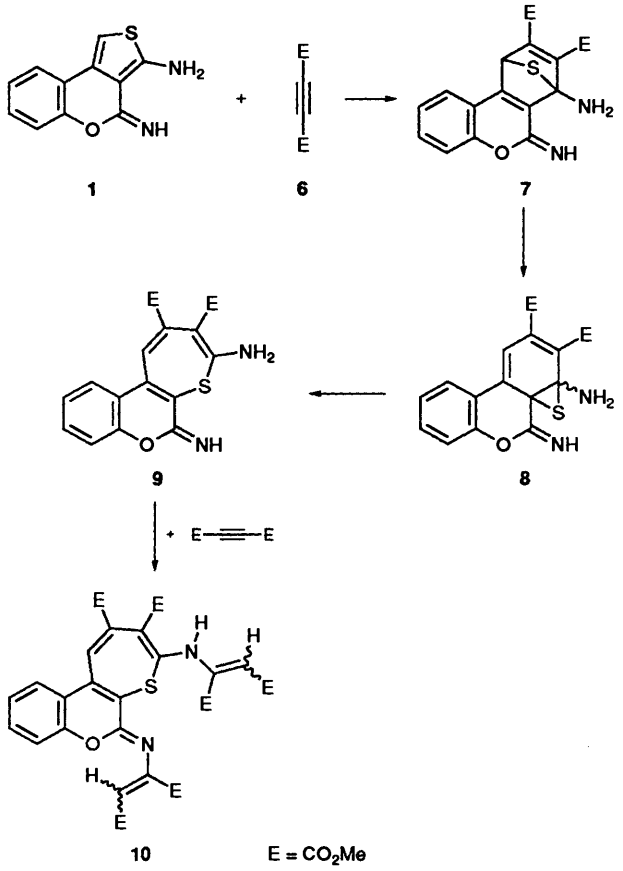
5a R = CH_3
b R = CF_3

Scheme 2

In order to provide further support for the validity of the reaction pathway illustrated in Scheme 1, we treated compound **1** with dimethyl acetylenedicarboxylate (DMAD). Generally, treatment of thiophene and its alkyl- and phenyl-substituted derivatives with acetylenes give benzene derivatives,[10–13] reactions explained in terms of [4 + 2]-cyclo-

addition as the initial step. Subsequently, sulfur extrusion follows probably *via* an unstable thiepine intermediate in equilibrium with its thianorcaradiene tautomer.[14]

In refluxing methanol or ethanol, compound **1** reacted with dimethyl acetylenedicarboxylate to give, not the expected dibenzopyran derivative of type **4**, but an inseparable mixture of the thiepines **10**. At room temperature the ratio of stereoisomers in the mixture was shown by ^{1}H NMR (300 MHz, $CDCl_3$) to be *ca.* 80:20. Attempts to separate the two compounds by plate chromatography or by sublimation (150 °C/0.2 mbar) were unsuccessful. The $^{13}C(^1H)$ NMR spectrum of the mixture, however, exhibited 58 lines consistent with the presence of 2 stereoisomers. A plausible reaction mechanism is one comprising: (i) cycloaddition of **1** to DMAD; (ii) isomerization of the 1:1 cycloadduct **7** to the thianocaradiene **8**; (iii) rearrangement of the latter to the unisolated thiepine **9** which might then undergo two consecutive additions of a Michael type to DMAD to yield **10** (Scheme 3). In principle, **7** could



Scheme 3

also rearrange into three other (constitutional) isomers of **9**, which, however, would have in common imino and amino groups in quasi-*peri* positions and thus would (i) render the corresponding bis-adducts of DMAD highly sterically hindered and (ii) in two of three cases show unfavourable [*c*]-anellation of the thiepine ring.

The thermal stability of the thiepines **10** also agrees with the main stability criterion: substitution with bulky substituents at their **2** and **7** positions. In fact, the failure of most attempts to isolate thiepines is known to be due to the rapid extrusion of sulfur from the incipiently formed thiepines. This phenomenon, observed even under mild conditions[15] has been ascribed to the predicted[16] antiaromatic character (E_R = −1.45 kcal/mol) of the thiepine system. From recent reports on some annulated thiepine derivatives,[17–21] it was inferred that the stability of the thiepine ring can be enhanced in two ways: (a) by delocalization of the π-electrons of the thiepine into other π-electron systems. For instance, in benzo[*d*]-[16] and benzo[*b*]-thiepines[18–20] and especially in thieno[3,4-*d*]- and furano[3,4-*d*]-thiepines,[21] delocalization gives rise to azulene-like charge-separated structures, contributing significantly to the ground state; (b) by introduction of two bulky groups at C-2 and C-7 of the thiepine. Such groups cause steric hindrance in the intermediate thianorcaradiene.[22]

On treating compound **1** with 2,3-dichloro-1,4-naphthoquinone **12** in the presence of triethylamine, our initial aim was to synthesize a [1,4]diazepine derivative of type **16** (Scheme 4). To our great surprise, however, we isolated a blue powder, (m.p. > 350 °C), the analytical and spectroscopic data for which supported its identification as compound **15**. The rationale for the formation of such a compound is illustrated in Scheme 4 (route a). This mechanistic pathway involves formation of the (unisolated) intermediate cyclized adduct **13** from the isomer **11** (generated *in situ* from **1**) and 2,3-dichloro-1,4-naphthoquinone **12**. Subsequent loss of two molecules of HCl (captured by NEt_3) by **13** should lead to the highly unstable arene oxide **14** which rapidly rearranged to its oxepine counterpart **15**.

The alternative structure **18** which could reasonably arise from route b, was ruled out on the basis of the following considerations. There was only one 2H exchangeable signal at δ 8.15 in the ^{1}H NMR ($[^2H_6]$DMSO, 300 MHz) spectrum. Acetylation and trifluoroacetylation of the above reaction product yielded only monoacetylated derivatives **19a** and **19b** instead of the diacetylated ones expected from **18**. However, the Michael adduct **19c** (Scheme 5) and diphenylurea **20** were the only products isolated when **15** was treated with phenyl isocyanate.

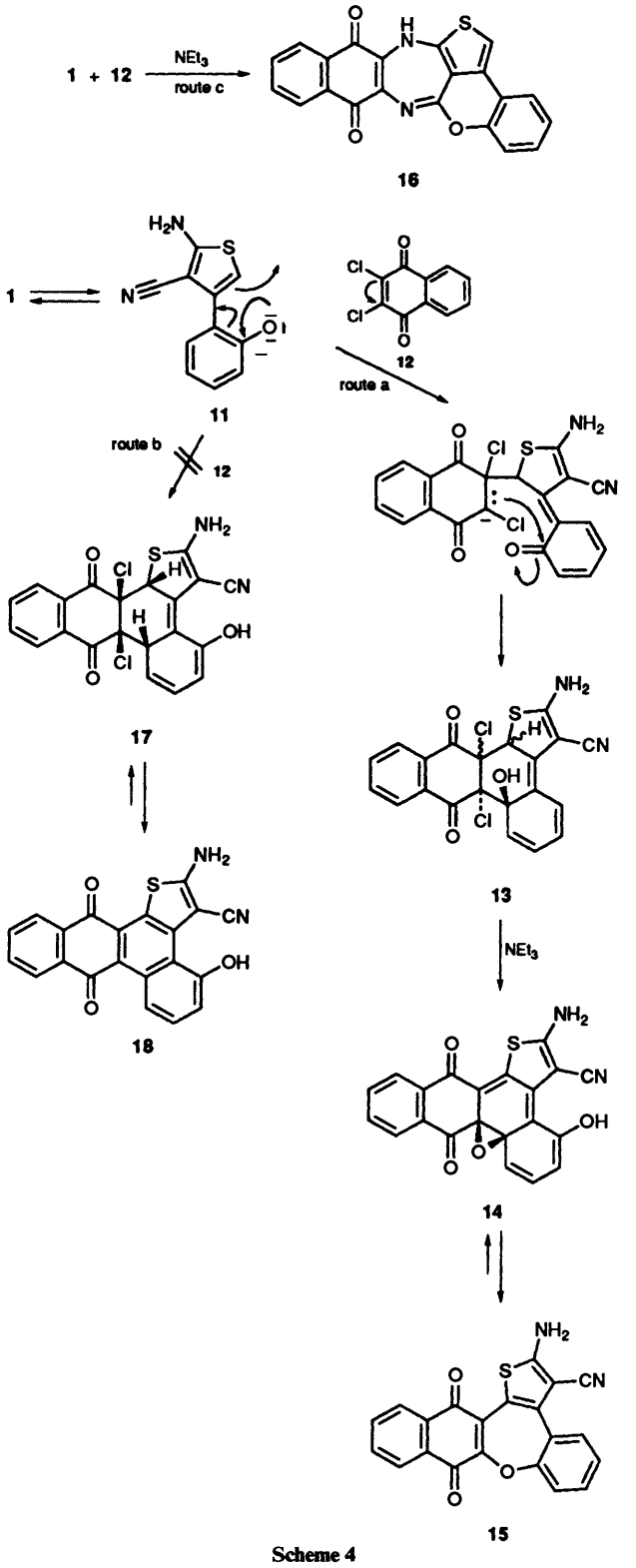
This study suggests that compound **1** could be used as a suitable precursor for the synthesis of new fused benzene derivatives (such as **4**), new fused thiepines (such as **10**) and new fused oxepines (such as **15**) with appropriate dienophiles and reaction conditions.

Experimental

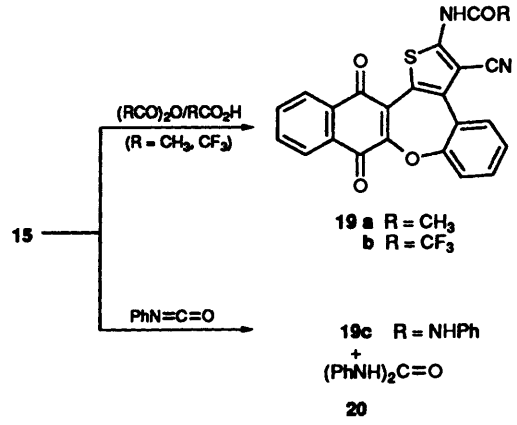
Elemental and spectroscopic analyses were performed in the Chemistry Department Analytical Center of Universität Duisburg-Gesamthochschule, Duisburg (FRG). All the melting points were determined with Reichert Thermovar microscope and are uncorrected. The IR and the UV spectra were measured with Perkin-Elmer 283 and 554 spectrophotometer, respectively. ^{1}H and $^{13}C(^1H)$-NMR spectra were recorded on Bruker WM 300 with TMS as internal reference. Coupling constants in brackets are reported in Hz. Mass spectra were obtained on Varian MAT 311A instrument by EI at 70 ev on direct injection. Combustion analyses were carried out with CHN + O/S elemental analyser 'CARLO ERBA' MOD.1106.

*3-Amino-4-imino-*4H*-thieno*[3,4-c][1]*benzopyran* **1**.—Compound **1** was prepared as previously described[1,2] and in the yield reported.[3] Analytical and spectroscopic results were also reported for the compound.

*Dimethyl 4-Amino-5-imino-*5H*-benzo*[3,4-c][1]*benzopyran-2,3-dicarboxylate* **4**.—A mixture of compound **1** (0.22 g, *ca.* 1 mmol) and dimethyl maleate **2** (5 cm^3) was heated to reflux at 170 °C for 3 h after which it was cooled to room temperature and diluted with carbon tetrachloride (100 cm^3). The resulting precipitate was filtered off and recrystallized from hexane to afford dimethyl fumarate **2a** in quantitative yield. The filtrate was evaporated to dryness and treatment of the resulting semicrystalline residue with diethyl ether precipitated a yellow compound which was filtered off, washed with ether and recrystallized from cyclohexane to yield an analytical sample of



Scheme 4



Scheme 5

4 (0.11 g, 33%), m.p. 165–166 °C; ν_{max}(KBr)/cm^{-1} 3370 and 3290 (NH_2, =NH), 3160 (arom. CH), 1730 and 1700 (ester C=O), 1640 (C=N) and 1610, 1590 and 1580 (arom. C=C); λ_{max}(THF)/nm 236 (log ε/dm^3 mol^{-1} cm^{-1} 3.82), 258 (3.80), 266 (3.84), 280 (3.71), 326 (3.34) and 400 (3.55); δ_H(300 MHz; $CDCl_3$; Me_4Si) 9.00 (2 H, br s, NH_2), 7.77–7.74 (1 H, dd, *J* 8.11 and 1.49, 10-H), 7.73 (1 H, br s, =NH), 7.31–7.26 (1 H, ddd, *J* 8.16, 7.75 and 1.47, 8-H), 7.10–7.05 (1 H, ddd, *J* 7.91, 7.65 and 1.18, 9-H), 7.12 (1 H, s, 1-H), 6.99–6.96 (1 H, dd, *J* 8.19 and 1.15, 7-H), 3.84 (3 H, s, CO_2Me), 3.78 (3 H, s, CO_2Me); δ_C(300 MHz; $CDCl_3$) 169.33 (C=O), 167.38 (C=O), 158.04 (C-5), 151.79 (C-6a), 151.45 (C-4), 139.24 (C-2), 136.83 (C-3), 131.09 (C-1), 123.85 (C-10), 123.62 (C-8), 117.57 (C-10a), 116.17 (C-9), 108.79 (C-10b), 107.38 (C-4a), 106.89 (C-7), 52.63 (OCH_3) and 52.17 (OCH_3); *m*/*z* (EI) 326 (M^+, 100%), 295 (18.9), 267 (4.3), 236 (85.1), 208 (20.4) and 181 (2.5) (Found: C, 62.5; H, 4.3; N, 8.4. $C_{17}H_{14}N_2O_5$ requires C, 62.58; H, 4.29; N, 8.59%).

Dimethyl 5-Methylbenzopyrano[2,3,4-de]*quinazoline-2,3-dicarboxylate* **5a**.—A mixture of compound **4** (0.20 g, *ca.* 0.6 mmol) and acetic anhydride (5 cm^3) in glacial acetic acid (10 cm^3) was stirred under reflux for 48 h and then cooled to room temperature and poured onto ice to give a yellow precipitate. This was filtered off and successively recrystallized from cyclohexane and ethyl acetate to give **5a** as a yellow powder (0.12 g, 56%) m.p. 222–224 °C; ν_{max}(KBr)/cm^{-1} 3060 and 3010 (arom. C–H), 2990 and 2940 (aliph. C–H), 1735 and 1710 (ester C=O), 1620 (C=N) and 1610, 1590, 1520 and 1510 (C=C/C–N); λ_{max}(EtOH)/nm 250 (log ε/dm^3 mol^{-1} cm^{-1} 2.78), 290 (2.70), 310 (2.78), 322 (2.85), 350 (2.89) and 390 (2.73); δ_H(300 MHz; $CDCl_3$) 8.34 (1 H, s, 1-H), 8.06–8.03 (1 H, dd, *J* 7.96 and 1.50, 11-H), 7.55–7.49 (1 H, ddd, *J* 8.36, 7.09 and 1.45, 9-H), 7.43–7.40 (1 H, dd, *J* 8.37 and 1.27, 10-H), 7.38–7.33 (1 H, ddd, *J* 7.47, 7.24 and 1.31, 8-H), 4.09 (3 H, s, OCH_3), 4.02 (3 H, s, OCH_3) and 2.77 (3 H, s, 5-CH_3); δ_C(300 MHz; $CDCl_3$) 167.85 (C=O), 167.52 (C=O), 165.02 (C-6a), 163.99 (C-5), 151.04 (C-7a), 149.92 (C-3a), 132.83 (C-2), 131.92 (C-1), 131.16 (C-3), 130.26 (C-11b), 125.57 (C-11), 123.55 (C-9), 118.99 (C-11c), 118.64 (C-10), 115.20 (C-8), 11.99 (C-11a), 53.25 (OCH_3), 53.01 (OCH_3), 26.83 (CH_3-5); *m*/*z* (EI) 350.1 (M^+, 66.3), 319 (65.5), 291 (15.9), 260 (3.9), 234.1 (100), 220 (4.8), 193 (1.7), 116.6 (10.4), 88.1 (1.6), 59.1 (1.5) and 44.1 (3.0) (Found: C, 65.0; H, 4.1; N, 8.0. $C_{19}H_{14}N_2O_5$ requires C, 65.14; H, 4.13; N, 8.00%).

Dimethyl 5-Trifluoromethylbenzopyrano[2,3,4-de]*quinazoline-2,3-dicarboxylate* **5b**.—A magnetically stirred mixture of compound **4** (0.16 g, 0.49 mmol) and trifluoroacetic anhydride (5 cm^3) in trifluoroacetic acid (5 cm^3) was heated to reflux for 48 h after which it was cooled to room temperature and worked up as above to afford crude material (0.17 g) which was recrystallized from cyclohexane to yield **5b** as yellow needles (0.15 g, 87%), m.p. 198–200 °C; ν_{max}(KBr)/cm^{-1} 3070 and 3000 (arom. CH), 2950 (aliph. CH), 1730 (ester C=O) and 1620 (C=N), 1610, 1590 and 1570 (C=C/C–N); λ_{max}(EtOH)/nm 250 (log ε/dm^3 mol^{-1} cm^{-1} 2.78), 292 (2.71), 328 (2.88), 360 (2.92) and 380 (2.81); δ_H(300 MHz; $CDCl_3$) 8.50 (1 H, s, 1-H), 8.07–8.04 (1 H, dd, *J* 7.97 and 1.47, 11-H), 7.60–7.54 (1 H, ddd, *J* 8.37, 7.11 and 1.44, 9-H), 7.47–7.43 (1 H, dd, *J* 8.57 and 1.39, 10-H), 7.43–7.38 (1 H, ddd, *J* 6.92, 7.64 and 1.44, 8-H), 4.09 (3

H, s, OCH_3) and 4.04 (3 H, s, OCH_3); δ_C(300 MHz; $CDCl_3$) 166.30 (CF_3), 165.48 (C=O), 164.42 (C=O), 154.75 (C-5), 150.70 (C-6a), 148.99 (C-7a), 133.99 (C-3a), 132.64 (C-1), 132.25 (C-3), 130.56 (C-2), 126.38 (C-11), 123.60 (C-9), 120.79 (C-11b), 118.79 (C-10), 118.49 (C-11c), 117.82 (C-8), 113.90 (C-11a), 53.53 (OCH_3), 53.17 (OCH_3); *m/z* (EI) 404.1 (M^+, 71.0), 385.1 (4.1), 373.1 (100), 359.1 (4.6), 345.1 (5.5), 314.1 (4.3), 316.1 (2.2), 286.1 (15.4), 217 (2.6), 191.1 (2.4) and 44.1 (3.6) (Found: C, 56.4; H, 2.8; N, 6.8. $C_{19}H_{11}F_3N_2O_5$ requires C, 56.44; H, 2.72; N, 6.93%).

Dimethyl 4-[1,2-*Di*(*methoxycarbonyl*)*vinyl*]*amino*-6-[1,2-*di*-(*methoxycarbonyl*)*vinyl*]*imino*-6H-*thiepino*[3,4-c][1]*benzo*-*pyran*-2,3-*dicarboxylate* **10**.—To a boiling and stirred solution of compound **1** (0.27 g, 1.25 mmol) in methanol or ethanol (20 cm^3), was gradually added dimethyl acetylenedicarboxylate (DMAD) (1.2 cm^3). The resulting mixture was stirred and heated to reflux for 3 h after which it was evaporated to half its volume and stored at room temperature for 24 h. The resulting orange precipitate was filtered off and recrystallized from methanol (or ethanol) to afford **10** (0.39 g), mixed m.p. 172–174 °C; all attempts to separate the two compounds by plate chromatography or by sublimation (150 °C/0.2 mbar) were fruitless; ν_{max}(KBr)/cm^{-1} 3090 and 3000 (arom. CH), 2950 (aliph. CH), 1750–1690 (esters C=O) and 1660, 1630, 1610, 1580, 1550 and 1525 (C=N, C=C and C–N); λ_{max}(THF)/nm 252 (log ε/dm^3 mol^{-1} cm^{-1} 3.28), 292 (3.19), 322 (3.11), 368 (3.06) and 400 (3.01); δ_H(300 MHz; $CDCl_3$) 12.16 (1 H, br s, NH), 11.81 (1 H, br s, NH), 7.47–7.04 (arom. and thiepine H), 6.44–5.66 (ethylenic H) and 3.95–3.65 (OCH_3 and H); δ_C(300 MHz; $CDCl_3$) 166.69–163.77 (12 lines, 12 esters C=O); 151.73, 150.50, 150.44, 150.35, 150.14, 148.89, 144.94, 144.61, 143.33, 142.27, 136.39, 136.29, 128.12, 127.67, 117.94, 117.63, 112.40, 111.74, 107.94, 107.79 (quaternary C-atoms); 134.16, 133.64, 129.72, 129.33, 124.70, 124.59, 124.46, 124.18, 116.87, 116.79, 112.77, 112.07, 101.81, 97.16 (sp^2 carbons bearing one hydrogen atom each); 53.60–51.44 (12 lines, 12 OCH_3 groups C-atoms); *m/z* (EI) 642.2 ($M^{+\bullet}$, 4.1), 611 (0.4), 583 (11.8), 551 (4.9), 523 (1.7), 491 (1.4), 185 (28.5), 154 (100), 126 (50.2), 59.1 (67.9) and 44 (15.8) (Found: C, 54.15; H, 4.7; N, 4.4; S, 4.8. $C_{29}H_{26}N_2O_{13}S$ requires C, 54.21; H, 4.05; N, 4.36; S, 4.98%).

2-*Amino*-9,14-*dihydro*-9,14-*dioxonaphtho*[2,3-b]*thieno*[2,3-d][1]*benzoxepine*-3-*carbonitrile* **15**.—To a stirred solution of compound **1** (0.88 g, 4.1 mmol) and triethylamine (0.404 g, 4 mmol) in anhydrous tetrahydrofuran (10 cm^3), was gradually added a THF solution of 2,3-dichloro-1,4-naphthoquinone **12** (0.91 g, 4 mmol). The mixture was heated under reflux for 3 h after which it was cooled to room temperature and stored for 48 h. The precipitate which formed was filtered off and washed several times with 50% aqueous methanol to yield a blue powder (0.105 g, 70%). Two recrystallizations of the latter from 85% aqueous dimethylformamide provided an analytical sample of the title compound **15**, m.p. > 350 °C; ν_{max}(KBr)/cm^{-1} 3390 and 3320 (NH_2), 2200 (C≡N), 1650 and 1630 (quinones C=O) and 1600, 1590, 1580, 1550 and 1515 (C=C); λ_{max}-(THF)/nm 250 (log ε/dm^3 mol^{-1} cm^{-1} 3.13), 292 (3.01), 336 (2.95) and 550 (2.76); δ_H[300 MHz; $(CD_3)_2SO$] 8.15 (1 H, br s, NH_2); 7.99–7.97 (1 H, dd, *J* 7.88 and 1.81, 13-H), 7.97–7.94 (1 H, dd, *J* 7.57 and 1.95, 10-H), 7.85–7.80 (1 H, ddd, *J* 7.05, 6.90 and 1.46, 12-H), 7.80–7.75 (1 H, ddd, *J* 7.04, 6.92 and 1.39, 11-H), 7.71–7.68 (1 H, dd, *J* 7.04 and 1.45, 4-H), 7.60–7.54 (1 H, ddd, *J* 7.68, 7.74 and 1.53, 6-H), 7.39–7.37 (1 H, dd, *J* 8.09 and 1.10, 7-H), 7.37–7.34 (1 H, ddd, *J* 12.19, 8.12 and 1.15, 5-H); δ_C[300 MHz; $(CD_3)_2SO$] 184.32 (C-9), 177.21 (C-14), 170.76 (C-8a), 154.22 (C-2), 148.45 (C-7a), 141.55 (C-14a), 134.52 (C-12), 133.94 (C-11), 132.22 (C-13), 130.94 (C-13a), 130.84 (C-9a), 129.27 (C-14b), 128.12 (C-10), 126.39 (C-4), 126.24 (C-3b), 126.01 (C-6), 125.77 (C-5), 121.85 (C-7), 115.89 (CN), 110.64 (C-3a) and 84.38 (C-3); *m/z* (EI) 370.1 ($M^{+\bullet}$, 100), 342.1 (25.6), 314.1 (10.1), 214.1 (5.4) and 76.1 (6.3) (Found: C, 68.0; H, 2.75; N, 7.4; S, 8.6. $C_{21}H_{10}N_2O_3S$ requires C, 68.11; H, 2.70; N, 7.57; S, 8.65%).

2-*Acetamido*-9,14-*dihydro*-9,14-*dioxonaphtho*[2,3-b]*thieno*-[2,3-d][1]*benzoxepine*-3-*carbonitrile* **19a**.—A stirred suspension of compound **15** (0.100 g, 0.27 mmol) and acetic anhydride (3 cm^3) in glacial acetic acid (3 cm^3) was heated to reflux in an oil-bath for 12 h and then cooled to room temperature. The orange precipitate which formed was filtered off, washed well with methanol and air-dried to afford the title compound **19a** (0.11 g, 99%), m.p. > 350 °C; ν_{max}(KBr)/cm^{-1} 3270 and 3220 (NH), 3090, 3060 (arom. CH), 2990 (aliph. CH), 2210 (C≡N), 1700 (acetamide C=O), 1670, 1660 (quinones C=O) and 1590, 1580, 1570, 1550 and 1500 (C=C); λ_{max}(THF)/nm 250 (log ε/dm^3 mol^{-1} cm^{-1} 3.19), 292 (3.09), 322 (2.99) and 484 (2.67); δ_H[300 MHz; $(CD_3)_2SO$] 8.04–8.00 (1 H, ddd, *J* 5.18, 5.45 and 1.67, 12-H), 8.03–8.01 (1 H, dd, *J* 6.11 and 1.64, 13-H), 7.87–7.84 (1 H, ddd, *J* 5.41, 5.38 and 1.71, 11-H), 7.86–7.84 (1 H, dd, *J* 7.89 and 1.72, 10-H), 7.78–7.75 (1 H, dd, *J* 7.67 and 1.24, 7-H), 7.61–7.56 (1 H, ddd, *J* 8.29, 7.76 and 1.45, 6-H), 7.43–7.40 (1 H, dd, *J* 7.87 and 1.32, 5-H), 7.43–7.37 (1 H, ddd, *J* 8.33, 7.87 and 1.30, 4-H), 2.32 (3 H, s, $COCH_3$) and 1.97 (1 H, br s, CONH); δ_C[300 MHz; $(CD_3)_2SO$] 206.75 (acetamide C=O), 183.90 (C-9), 177.98 (C-14), 169.93 (C-8a), 155.65 (C-2), 152.04 (C-7a), 138.25 (C-14a), 134.73 (C-12), 134.49 (C-11), 132.23 (C-13), 131.32 (C-13a), 130.89 (C-9a), 128.70 (C-10), 126.69 (C-4), 126.37 (C-5), 126.08 (C-6), 125.99 (C-3b), 122.09 (C-7), 120.21 (C-3a), 114.69 (C≡N), 91.83 (C-3), 30.85 (CH_3); *m/z* (EI) 412.1 ($M^{+\bullet}$, 25.7), 370 (100), 342.1 (25.0), 314.1 (9.5) and 43 (24.2) (Found: C, 66.85; H, 3.0; N, 6.8; S, 7.9. $C_{23}H_{12}N_2O_4S$ requires C, 66.99; H, 2.91; N, 6.80; S, 7.77%).

9,14-*Dihydro*-9,14-*dioxo*-2-(*trifluoroacetamido*)*naphtho*[2,3-b]*thieno*[2,3-d][1]*benzoxepine*-3-*carbonitrile* **19b**.—A stirred suspension of compound **15** (0.02 g, 0.05 mmol) and trifluoroacetic anhydride (4 cm^3) in trifluoroacetic acid (5 cm^3) was treated in a similar way to compound **19a**. Work-up of the resulting yellow precipitate yielded compound **19b** (0.025 g, 99%), m.p. 335–337 °C; ν_{max}(KBr)/cm^{-1} 3200 (NH), 3090–3000 (arom. CH), 2210 (C≡N), 1730 (trifluoroacetamide C=O), 1670 and 1660 (quinones C=O) and 1600–1550 (C=C/C–N); λ_{max}-(EtOH)/nm 252 (log ε/dm^3 mol^{-1} cm^{-1} 3.23), 284 (3.11), 322 (3.18), 460 (2.64) and 580 (2.28); *m/z* (EI) 466.1 ($M^{+\bullet}$, 100), 438.1 (2.5), 369.1 (36.4), 341 (18.3) and 313.1 (6.25) (Found: C, 59.3; H, 1.95; N, 5.9; S, 6.5. $C_{23}H_9N_2O_4SF_3$ requires C, 59.23; H, 1.93; N, 6.01; S, 6.87%).

9,14-*Dihydro*-9,14-*dioxo*-2-(*phenylureido*)*naphtho*[2,3-b]-*thieno*[2,3-d][1]*benzoxepine*-3-*carbonitrile* **19c**.—A stirred suspension of compound **15** (0.11 g, *ca.* 0.3 mmol) in neat phenyl isocyanate (5 cm^3) was heated under reflux for 6 h in an oil-bath and then cooled to room temperature. The resulting purple suspension was filtered off, washed with methanol and air-dried, to give the title compound **19c** (0.112 g, 77%), m.p. > 350 °C; ν_{max}(KBr)/cm^{-1} 3360, 3290 and 3240 (NH), 3060 (arom. CH), 2210 (C≡N), 1720 (C=O, urea), 1660 and 1650 (quinones C=O) and 1590, 1570 and 1540 (C=C/C–N); λ_{max}(THF)/nm 250 (log ε/dm^3 mol^{-1} cm^{-1} 3.20), 300 (2.99) and 500 (2.44); *m/z* (EI) 397 [(M – PhNH)$^+$, 26.3], 396 [M – $PhNH_2)^{+\bullet}$, 100], 370.1 (78.8), 369.1 (6.8), 368.1 (9.3), 340 (14.2), 314 (15.6), 120.1 (6.5), 119.1 (46.9), 93.1 (96.3) and 92.1 (12.1) (Found: C, 68.65; H, 3.1; N, 8.6; S, 6.5. $C_{28}H_{15}N_2O_4S$ requires C, 68.71; H, 3.07; N, 8.59; S, 6.54%).

After storage for several hours at room temperature the above mother liquor afforded a copious white precipitate.

Recrystallization of this from methanol gave white needles of diphenylurea **20**, m.p. 255–257 °C.

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