Studies with condensed thiophenes: reactivity of condensed aminothiophenes toward carbon and nitrogen electrophiles

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The condensed aminothiophenes **5–7a,b** react with 1,4-naphthoquinone in refluxing ethanol to yield products of addition followed by hydrogen sulfide elimination in a Diels–Alder type reaction. When the reaction is carried out under microwave irradiation a dipolar addition occurred affording products of substitution at C-l. Compounds **5–7a,b** coupled with aromatic diazonium salts to yield arylazo derivatives **15** and **16** where coupling occurred at C-1. The condensed aminothiophenes **5–7a,b** reacted with dimethylformamide dimethylacetal to yield amidines **17–19**.

Keywords: aminothiophenes, Diels–Alder reactions, amidines, fused pyridazines, fused thiophenes, quinones

The reactivity of condensed aminothiophenes of type **1** toward electron poor olefins and acetylenes has been investigated during the last fifteen years.[1-5] It has been established that **1** react with electron-poor olefins to yield benzo-fused heterocycles **2**. Reaction with acetylenes in refluxing dioxane has been claimed to afford thiepins **3**, but later we were able to show, through ^{1}H NMR and X ray crystal determination, that the actual product was the C-l alkylation product **4**[6] (Scheme 1).

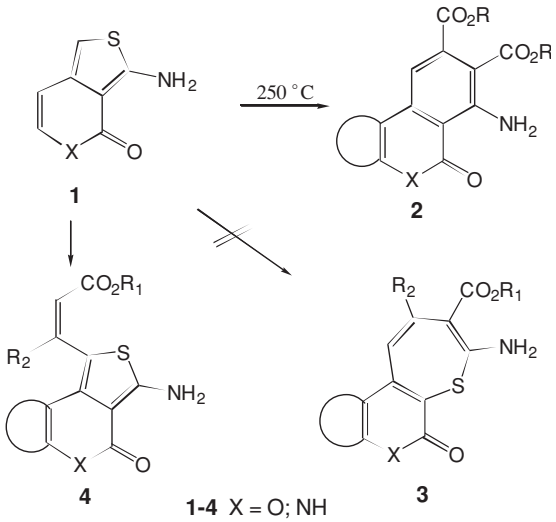
Results and discussion

In conjunction with our interest in developing efficient routes to polyfunctional heteroaromatics as dyes for D2T2 printing and/or hair and skin colouring, we report here results of our investigation into the reactivity of **5–7a,b** toward some electrophilic reagents by conventional heating and under microwave irradiation, the latter a technique that has found extensive utility recently as environmentally benign methodology.[7-10]

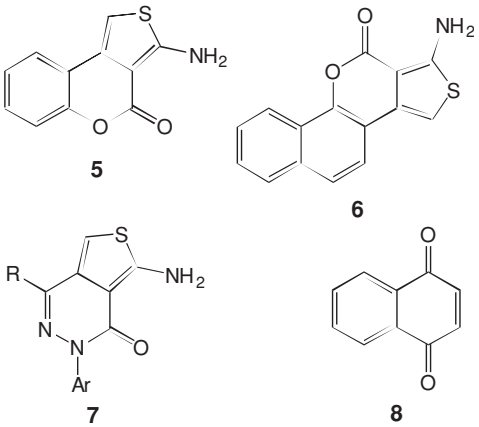
We have found that the products of reactions of **5–7a,b** with 1,4-naphthoquinone (**8**) depend on the applied reaction conditions. Compounds **5** and **7a,b** react with **8** in refluxing ethanol to yield products of cycloaddition and subsequent hydrogen sulfide elimination. These are formulated as **9** and **10a,b** and are assumed to be formed in intermolecular [4+2] cycloaddition reactions with elimination of hydrogen sulfide to yield the final products. This finds a parallel in the reported behaviour of **5–7a,b** toward electron-poor olefins.[3-6]

However, when the reactions of **5**, **6** and **7b** with 1,4-naphthoquinone is carried out under microwave irradiation in the presence of few drops of acetic acid, the C-l arylation products **11–13** were formed. Formation of the products **11–13** could be proposed to proceed through a dipolar adduct of the type suggested to account for the formation of C-l alkylation products upon reacting **5, 6** and **7a** with enaminones.[6]

The aminothienocoumarin **5** coupled with aryldiazonium chlorides to afford red products. These we formulate as the aminoarylazo derivatives **l5a-e**, most likely formed *via* intermediacy of **14**. Compounds **15a-e** were established based on IR spectra, which show absorption bands at ν *ca* 3370 and 3270 cm^{-1} for NH_2. ^{1}H NMR spectra displayed signals for aromatic protons along with a broad signal at δ_H *ca* 7 ppm (D_2O exchangeable) for the two amino protons. No signals for thiophene H-1 as singlet at δ_H *ca* 6.90 ppm was observed. Similarly compound **6** coupled with aryldiazonium chlorides affording **16a–c** (Scheme 2).



Scheme 1



7a, R = CO_2Et; Ar = C_6H_5
7b, R = benzotriazol-1-yl; Ar = 4-$CH_3C_6H_4$

Reaction of compounds **5–7a,b** with dimethylformamide dimethylacetal (DMFDMA) in a domestic microwave oven in the presence of a few drops of dimethylformamide afforded condensation products **17–19a,b**; no trace of C-1 alkylation products were observed. Compounds **19a,b** upon reflux in AcOH / c.HC1 mixture (3:1 by volume), afforded the pyridopyridazine derivatives **22a,b**, while compounds **17** and **18** when treated with the same reagent and same reaction condition, formed compounds **20** and **21** based on the

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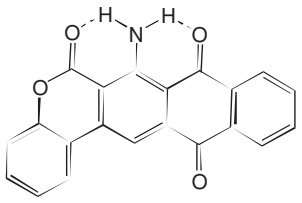

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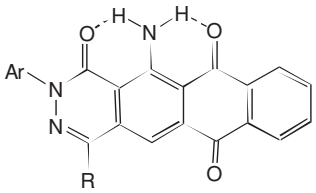
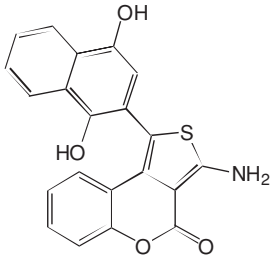


10a, R = CO_2Et; Ar = C_6H_5

10b, R = benzotriazol-1-yl;
Ar = 4-$CH_3C_6H_4$



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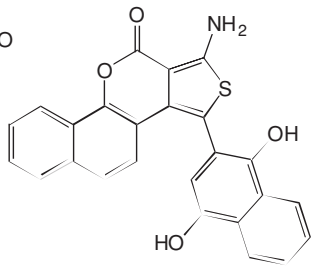

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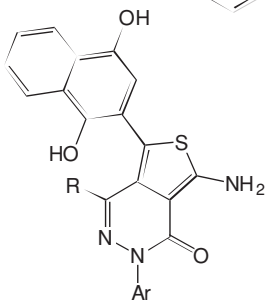


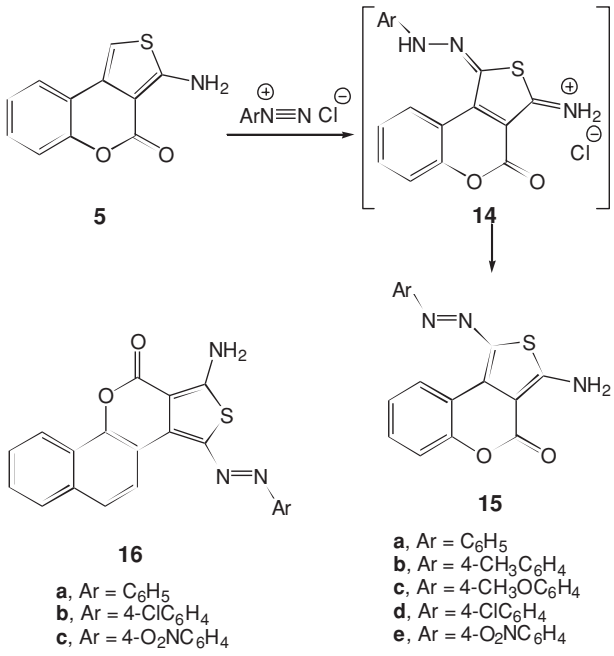
13, R = benzotriazol-1-yl; Ar = 4-$CH_3C_6H_4$

^{1}H NMR and ^{13}C NMR spectra, that reveal the presence of methylene protons at δ_H = *ca* 5.03,5.15 and δ_C = *ca* 33.79 and 25.75 ppm respectively (Scheme 3).

Experimental

IR spectra were recorded in KBr with a Pye Unicam SP 1100 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian EM-390-400 MHz spectrometer in $CDCl_3$ or [$^2H_6$] DMSO as solvent and TMS as internal standard; chemical shifts are reported in δ units (ppm). Mass spectra were measured on MS 30 and MS 9 (AEI), 70 eV. Microanalyses were performed on LECO CHNS-932. Microwave experiments were conducted in a microwave oven DAEWOO, edition II (KOR-8667). Compounds **5–7a,b** were prepared following published procedures.[3,5]

Reaction of compounds **5–7a,b** *with 1,4-naphthoquinone*:
Method A, thermal reaction: A mixture of each of **5** and **7a,b** (10 mmol) with 1,4-naphthoquinone (1.58 g, 10 mmol) in ethanol (20 ml) was refluxed for 10 h. The solvent was removed and the residue cooled to deposit a solid, which was crystallised from ethanol/dioxane (1:3).



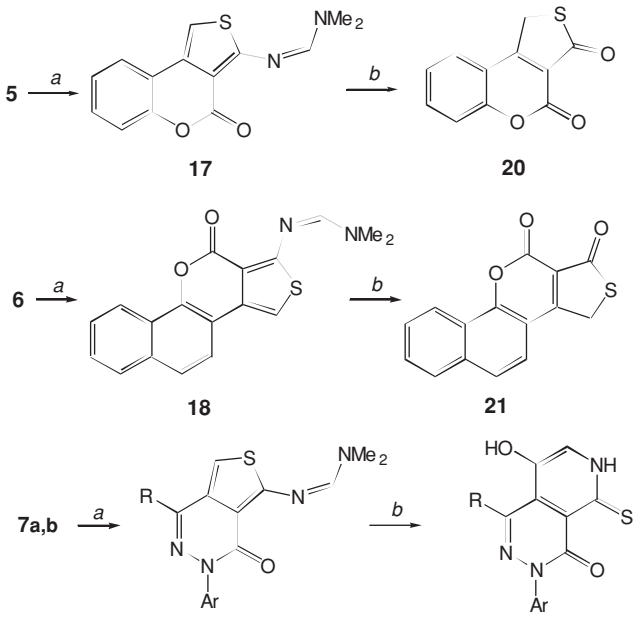
16

a, Ar = C_6H_5
b, Ar = 4-ClC_6H_4
c, Ar = 4-$O_2NC_6H_4$

15

a, Ar = C_6H_5
b, Ar = 4-$CH_3C_6H_4$
c, Ar = 4-$CH_3OC_6H_4$
d, Ar = 4-ClC_6H_4
e, Ar = 4-$O_2NC_6H_4$

Scheme 2



19,22: **a**, R = CO_2Et; Ar = C_6H_5
b, R = benztriazol-1-yl, Ar = 4-$CH_3C_6H_4$

reagents *a*: DMFDMA
b AcOH/HCl

Scheme 3

7-Amino-5-oxa-benzo[a]naphthacene-6,8,13-trione (**9**): Compound **9** was obtained as red crystals (2.16 g, 63%), m.p. 290–291 °C. IR: ν_{max}/cm^{-1} 3383 and 3286 (NH_2), 1708 (CO), 1689 (CO) and 1669 (CO). ^{1}H NMR ($CDCl_3$): δ_H 7.39–7.46 (m, 2H, arom-H), 7.62 (t, 1H, *J* = 7.6 Hz, arom-H), 7.76–7.87 (m, 2H, arom-H), 8.20 (s, 1H, H-14), 8.26 (t, 2H, *J* = 8.5 Hz, arom-H), 8.35 (d, 1H, *J* = 7.6 Hz, arom-H), 9.48(s, 1H, NH, D_2O exchangeable), 10.40 (s, 1H, NH, D_2O exchangeable). MS: *m/z* 341 (100%) [M$^+$]. Found C, 73.72; H, 3.39; N, 4.35. $C_{21}H_{11}NO_4$ (341.32) requires C, 73.89; H, 3.24; N, 4.10 %.

Ethyl 5-amino-4,6,11-trioxo-3-phenyl-3,4,6,11-tetrahydro-2,3-diazanaphthacene-1-carboxylate (**10a**): Compound **10a** was obtained as red crystals (2.64 g, 60%), m.p. 308–310 °C. IR: ν_{max}/cm^{-1}

3340 and 3230 (NH_2), 1718 (ester CO), 1657 (br) (CO); ^{1}H NMR ($CDCl_3$): δ_H 1.50 (t, 3H, J = 7 Hz, CH_3), 4.55 (q, 2H, J = 7 Hz, OCH_2), 7.49 (d, 1H, J = 7.2 Hz, arom-H), 7.50–7.58 (m, 2H, arom-H), 7.64–7.66 (m, 2H, arom-H), 7.78–7.86 (m, 2H, arom-H), 8.31 (d, 1H, J = 7.5 Hz, arom-H), 8.36–8.37 (m, 2H, arom-H), 9.98 (br, 1H, NH, D_2O exchangeable), 10.29 (br, 1H, NH, D_2O exchangeable.); ^{13}C NMR (DMSO-d_6): δ_C 184.8, 168.4, 163.2, 157.2, 154.9, 143.2, 140.2, 138.9, 135.8, 135.0, 134.1, 133.2, 130.4. 129.6, 129.4, 127.7, 127.6, 126.5, 114.6, 113.4, 111.3, 63.3, 14.8. MS: *m/z* 439 (58%) [M$^+$]. Found C, 68.00; H, 4.00; N, 9.65. $C_{25}H_{17}N_3O_5$ (439.42) requires C, 68.33; H, 3.89; N, 9.56

12-Amino-4-benzotriazol-1-yl-2-p-tolyl-2H-2,3-diazanaphthacene-1,6,11-trione (**10b**): Compound **10b** was obtained as red crystals (2.78 g, 56%), m.p. 280–282 °C. IR: ν_{max}/cm^{-1} 3375 and 3267 (NH_2), 1665 and 1568 (br) (CO), ^{1}H NMR (DMSO-d_6): δ_H 2.39 (s, 3H, CH_3), 7.35–7.37 (m, 3H, arom-H), 7.59–7.61 (m, 3H, arom-H), 7.72 (t, 1H, J = 7.4 Hz, arom-H), 7.86 (t, 1H, J = 7.4 Hz, arom-H), 7.93–7.99 (m, 2H, arom-H), 8.09 (d, 1H, J = 7.4 Hz, arom-H), 8.24 (d, 1H, J = 7.6 Hz, arom-H), 8.30 (d, 1H, J = 7.6 Hz, arom-H), 9.92 (s, 1H, NH, D_2O-exchangeable), 10.09 (s, 1H, D_2O-exchangeable). MS: *m/z* 498 (100%) [M$^+$]. Found C, 69.73; H, 3.92; N, 17.14. $C_{29}H_{18}N_6O_3$ (498.49) requires C, 69.87; H, 3.63; N, 16.85 %.

Method B, microwave heating: A mixture of each of **5, 6** and **7b** (10 mmol) and 1,4-naphthoquinone (1.58 g, 10 mmol) in the presence of few drops of acetic acid was irradiated in a microwave oven at full power for 60 s. The solid products obtained were crystallised from acetic acid.

3-Amino-1-(1,4-dihydroxynaphthalen-2-yl)thieno[3,4-c][1]benzopyran-4-one (**11**). Compound **11** was obtained as grey crystals (2.92 g, 78%), m.p. 280–281 °C. IR: ν_{max}/cm^{-1} 3430 (OH), 1672 (CO). ^{1}H NMR (DMSO-d_6): δ_H 6.70 (s, 1H, naphthyl-H-3), 6.92 (t, 1H, J = 7.6 Hz, naphthyl-H), 7.20–7.29 (m, 3H, naphthyl-H), 7.52–7.54 (m, 2H, coumarinyl-H), 7.89 (s, 2H, NH_2, D_2O exchangeable), 8.11 (dd, 1H, J = 6.8 Hz, coumarinyl-H), 8.17 (dd, 1H, J = 6.8 Hz, coumarinyl-H), 8.82 (s, 1H, OH, D_2O exchangeable), 9.72 (s, 1H, OH, D_2O exchangeable). MS: *m/z* 375 (28%) [M$^+$]. Found C, 66.90; H, 3.58; N, 4.03; S, 8.14. $C_{21}H_{13}NO_4S$ (375.39) requires C, 67.19; H, 3.49; N, 3.73; S, 8.54 %.

1-Amino-3-(1,4-dihydroxynaphthalen-2-yl)naphtho[1,2-b]thieno[3,4-d]pyran-4-one (**12**): Compound **12** was obtained as grey crystals, yield: 3.48 g (82%), m.p. > 300 ºC; IR: ν_{max}/cm^{-1} 3401 (OH), 3277 and 3177 (NH_2), 1699 (CO); ^{1}H NMR (DMSO-d_6): δ_H 7.22 (s, 1H, naphthyl-H), 7.57 (d, 1H, J = 8.9 Hz, arom-H), 7.61–7.67 (m, 2H, arom-H), 7.87 (s, 2H, NH_2, D_2O exchangeable), 7.89–7.94 (m, 3H, arom-H), 8.02–8.07 (m, 2H, arom-H), 8.30–8.33 (m, 2H, arom-H), 8.63 (s, 1H, OH, D_2O exchangeable), 9.80 (s, 1H, OH, D_2O exchangeable); ^{13}C NMR (DMSO-d_6): δ_C 184.7, 169.3, 159.4, 148.1, 143.0, 135.4, 135.2, 134.9, 134.4, 133.8, 133.1, 132.9, 128.8, 128.7, 128.2, 127.6, 127.1, 126.5, 124.2, 123.9, 122.8, 122.5, 113.8, 106.8, 101.4. MS: *m/z* 425 (100%) [M$^+$]. Found C, 70.77; H, 3.54; N, 3.59; S, 7.28. $C_{25}H_{15}NO_4S$ (425.45) requires C, 70.57; H, 3.55; N, 3.29; S, 7.53

7-Amino-4-benzotriazol-1-yl-5-(1,4-dihydroxynaphthalen-2-yl)-2-p-tolylthieno[3,4-d]pyridazin-1(2H)-one (**13**): Compound **13** was obtained as brown crystals (4.00 g, 75%), m.p. >300 °C. IR: ν_{max}/cm^{-1} 3460 (OH), 2909 and 2882 (NH_2), 1654 br (CO). ^{1}H NMR (DMSO-d_6): δ_H 2.50 (s, 3H, CH_3), 6.75 (s, 1H, naphthyl-H), 7.28–7.39 (m, 5H, arom-H), 7.59–7.65 (m, 3H, arom-H), 7.72 (s, 2H, NH_2, D_2O exchangeable), 7.79–7.84 (m, 3H, arom-H), 7.90 (d, 1H, J = 8.4 Hz, arom-H), 8.62 (s, 1H, OH, D_2O exchangeable), 9.40 (s, 1H, OH, D_2O exchangeable). ^{13}C NMR (DMSO-d_6): δ_C 184.0, 182.4, 170.2, 158.2, 148.9, 145.7, 141.6, 138.6, 136.1, 135.4, 134.9, 133.4, 132.1, 131.9, 130.4, 130.2, 129.8, 126.9, 126.7, 126.5, 126.2, 123.8, 120.6, 120.2, 114.5, 113.6, 22.10. MS: *m/z* 532 (100%) [M$^+$]. Found C, 65.64; H, 3.75; N, 15.44; S, 5.80. $C_{29}H_{20}N_6O_3S$ (532.57) requires C, 65.40; H, 3.78; N, 15.78; S, 6.02 %.

Reaction of compounds **5,6** *and* **7b** *with aromatic diazonium salts*: A solution of aryldiazonium chloride (prepared as described earlier)[5] (10 mmol) at 0 °C was added to a solution of each of **5,6** and **7b** (10 mmol) in acetic acid (50 ml) containing sodium acetate (0.60 g). The reaction mixture was stirred at room temperature for 1 hr and the solid product was collected by filtration and crystallised from DMF/ethanol (3:1).

3-Amino-1-phenylazothieno[3,4-c][1]benzopyran-4-one (**15a**). Compound **15a** was obtained as red crystals (2.45 g, 77%), m.p. 232–234 °C. IR: ν_{max}/cm^{-1} 3375 and 3368 (NH_2), 1706 (CO). ^{1}H NMR (DMSO-d_6): δ_H 7.02 (br s, 2H, NH_2), 7.31–7.38 (m, 2H, arom-H), 7.41–7.45 (m, 1H, arom-H), 7.51–7.54 (m, 2H, arom-H), 7.61 (d, 1H, J = 8 Hz, arom-H), 7.73 (d, 2H, J = 8.2 Hz, arom-H), 8.85 (d, 1H, J = 8 Hz, arom-H). ^{13}C NMR (DMSO-d_6): δ_C 169.3 (CO), 159.3, 153.6, 153.0, 136.0, 134.0, 132.6, 130.5, 130.0, 129.8, 126.2, 122.7, 118.2, 118.1, 101.4. MS: *m/z* 321 (100%) [M$^+$]. Found C, 63.22; H, 3.51; N, 12.86; S, 10.04. $C_{17}H_{11}N_3O_2S$ (321.35) requires C, 63.53; H, 3.45; N, 13.07; S, 9.97 %.

3-Amino-1-p-tolylazothieno[3,4-c][1]benzopyran-4-one (**15b**): Compound **15b** was obtained as wine-red crystals (2.37 g, 71%), m.p. 290–292 °C. IR: ν_{max}/cm^{-1} 3386 and 3261 (NH_2), 1683 (CO); ^{1}H NMR (DMSO-d_6): δ_H 2.38 (s, 3H, CH_3), 6.96 (brs, 2H, NH_2), 7.29–7.33 (m, 3H, arom-H), 7.40 (t, 1H, J = 8 Hz, arom-H), 7.55 (t, 1H, J = 8 Hz, arom-H), 7.59 (d, 2H, J = 8.6 Hz, *p*-tolyl-H), 8.76 (d, 1H, J = 8 Hz, arom-H). ^{13}C NMR (DMSO-d_6): δ_C 169.0 (CO), 159.4, 153.5, 151.0, 140.2, 135.0, 132.5, 131.1, 129.7, 128.0, 126.2, 122.7, 118.3, 118.1, 101.1, 21.9 (CH_3). MS: *m/z* 335 (100%) [M$^+$]. Found C, 64.76; H, 3.99; N, 12.60; S, 9.32. $C_{18}H_{13}N_3O_2S$ (335.37) requires C, 64.46; H, 3.90; N, 12.52; S, 9.56 %.

3-Amino-1-(4-methoxyphenylazo)thieno[3,4-c][1]benzopyran-4-one (**15c**): Compound **15c** was obtained as wine-red crystals (2.42 g, 69%), m.p. 280–281 °C. IR: ν_{max}/cm^{-1} 3376 and 3261 (NH_2), 1687 (CO). ^{1}H NMR (DMSO-d_6): δ_H 3.84 (s, 3H, OCH_3), 6.96 (br s, 2H, NH_2), 7.08 (d, 2H, J = 9 Hz, *p*-methoxyphenyl-H), 7.33 (d, 1H, J = 8 Hz, arom-H), 7.41 (t, 1H, J = 7.6 Hz, arom-H), 7.55 (t, 1H, J = 7.6 Hz, arom-H), 7.72 (d, 2H, J = 9 Hz, *p*-methoxyphenyl-H), 8.79 (d, 1H, J = 8 Hz, arom-H). MS: *m/z* 351(100%) [M$^+$]. Found C, 61.25; H, 3.73; N, 11.88; S, 8.79. $C_{18}H_{13}N_3O_3S$ (351.38) requires C, 61.52; H, 3.72; N, 11.95; S, 9.12 %.

3-Amino-1-(4-chlorophenylazo)thieno[3,4-c][1]benzopyran-4-one (**15d**): Compound **15d** was obtained as red crystals (2.61 g, 74%), m.p. 300–302 °C. IR: ν_{max}/cm^{-1} 3377 and 3270 (NH_2), 1689 (CO). ^{1}H NMR ($CDCl_3$): δ_H 7.07 (br s, 2H, NH_2), 7.38 (d, 1H, J = 8.4 Hz, arom-H), 7.43 (t, 1H, J = 8 Hz, arom-H), 7.57 (d, 2H, J = 8.4 Hz, arom-H), 7.61–7.63 (m, 1H, arom-H), 7.73 (d, 2H, J = 8.7 Hz, 4-chlorophenyl-H), 8.80 (d, 1H, J = 8.7 Hz, 4-chlorophenyl-H). ^{13}C NMR (DMSO-d_6): δ_C 169.6 (CO), 159.2, 153.7, 151.7, 136.8, 134.0, 133.9, 131.3, 130.5, 130.0, 129.3, 127.9, 122.7, 121.7, 101.8. MS: *m/z* 355 (100%) [M$^+$]. Found C, 57.48; H, 3.01; N, 11.77; S, 8.77. $C_{17}H_{10}ClN_3O_2S$ (355.79) requires C, 57.38; H, 2.83; N, 11.81; S, 9.01 %.

3-Amino-1-(4-nitrophenylazo)thieno[3,4-c][1]benzopyran-4-one (**15e**): Compound **15e** was obtained as wine-red crystals (2.62 g, 72%), m.p. 302–304 °C. IR: ν_{max}/cm^{-1} 3374 and 3269 (NH_2), 1689 (CO); ^{1}H NMR (DMSO-d_6): δ_H = 7.03 (br s, 2H, NH_2), 7.42 (d, 1H, J = 8 Hz, arom-H), 7.48 (t, 1H, J = 7.2 Hz, arom-H), 7.67 (t, 1H, J = 7.2 Hz, arom-H). 7.84 (d, 2H, J = 8.8 Hz, 4-nitrophenyl-H), 8.32 (d, 2H, J = 8.8 Hz, 4-nitrophenyl-H), 8.88 (d, 1H, J = 8 Hz, arom-H). MS: *m/z* 366(100%) [M$^+$]. Found C, 55.87; H, 2.91; N, 15.29; S, 8.41. $C_{17}H_{10}N_4O_4S$ (366.34) requires C, 55.73; H, 2.75; N, 15.29; S, 8.75 %.

3-Amino-1-phenylazo)thieno[3,4-c][1]benzopyran-4-one (**16a**): Compound **16a** was obtained as wine-red crystals (2.96 g, 80%), m.p. > 300 °C. IR: ν_{max}/cm^{-1} 3391 and 3274 (NH_2), 1699 (CO); ^{1}H NMR (DMSO-d_6): δ_H 7.07 (br s, 2H, NH_2), 7.40 (t, 1H, J = 7.4 Hz, phenyl-H), 7.55 (t, 2H, J = 7.6 Hz, phenyl-H), 7.71 (t, 2H, J = 7.2 Hz, arom-H), 7.76 (d, 2H, J = 8.8 Hz, phenyl-H). 7.95 (d, 1H, J = 8.9 Hz, arom-H), 8.04 (t, 1H, J = 7.2 Hz, arom-H). 8.37 (t, 1H, J = 7.2 Hz, arom-H), 8.93 (d, 1H, J = 8.8 Hz, arom-H). ^{13}C NMR (DMSO-d_6): δ_C 169.55 (CO), 157.4, 153.2, 149.8, 147.4, 137.6, 135.1, 131.6, 130.5, 129.9, 129.0, 128.4, 125.3, 123.8, 123.0, 122.7, 113.7, 104.8, 102.3. MS: *m/z* 371 (100%) [M$^+$]. Found C, 67.96; H, 3.23; N, 11.06; S, 8.50. $C_{21}H_{13}N_3O_2S$ (371.41) requires C, 67.91; H, 3.52, N, 11.31; S, 8.63 %.

3-Amino-1-(4-chlorophenylazo)thieno[3,4-c][1]benzopyran-4-one (**16b**): Compound **16b** was obtained as wine-red crystals (3.10 g, 77%), m.p. > 300 °C. IR: ν_{max}/cm^{-1} 3395 and 3280 (NH_2), 1699 (CO). ^{1}H NMR ($CDCl_3$): δH 7.58 (d, 2H, J = 8.4 Hz, 4-chlorophenyl-H), 7.70–7.76 (m, 4H, arom-H and 4-chlorophenyl-H), 7.93 (d, 1H, J = 8.8 Hz, arom-H), 8.03–8.05 (m, 1H, arom-H), 8.32 (br s, 2H, NH_2, D_2O exchangeable), 8.36–8.38 (m, 1H, arom-H). 8.88 (d, 1H, J = 8.8 Hz, arom-H). MS: *m/z* 405 (100%) [M$^+$]. Found C, 62.21; H, 3.17; N, 10.46; S, 7.67. $C_{21}H_{12}ClN_3O_2S$ (405.85) requires C, 62.14; H, 2.98; N, 10.35; S, 7.90.

3-Amino-1-(4-nitrophenylazo)thieno[3,4-c][1]benzopyran-4-one (**16c**): Compound **16c** was obtained as wine-red crystals (3.04 g, 73%), m.p. > 300 °C. IR: ν_{max}/cm^{-1} 3387 and 3270 (NH_2), 1703 (CO); ^{1}H NMR (DMSO-d_6): δ_H 7.12 (br s, 2H, NH_2, D_2O exchangeable), 7.72–7.73 (m, 2H, arom-H), 7.84 (d, 2H, J = 9 Hz, 4-nitrophenyl-H), 7.94 (d, 1H, J = 8.8 Hz, arom-H), 8.06 (m, 1H, arom-H), 8.32 (d, 2H, J = 9 Hz, 4-nitrophenyl-H), 8.38 (d, 1H, J = 7 Hz arom-H), 8.90 (d, 1H, J = 8.8 Hz, arom-H). MS: *m/z* 416 (100%) [M$^+$]. Found C, 60.22;

H, 3.14; N, 13.18; S, 7.27. $C_{21}H_{12}N_4O_4S$ (416.40) requires C, 60.57; H, 2.90; N, 13.15; S, 7.70 %.

Reaction of compounds **5–7a,b** *with dimethylformamide dimethylacetal*: A solution of each of **5–7a,b** (10 mmol) and DMFDMA (1.19 g, 10 mmol) in the presence of a few drops of dimethylformamide was irradiated in a microwave oven at full power for 30 sec. The solid products obtained were crystallised from dioxane.

N,N-Dimethyl-N′-(4-oxo-4H-thieno[3,4-c][1]benzopyran-3-yl)formamidine (**17**): Compound **17** was obtained as brown crystals (2.18 g, 80%), m.p.158–160 °C. IR: ν_{max}/cm^{-1} 1732 (ring CO). ^{1}H NMR (DMSO-d_6): δ_H 3.05 (s, 3H, N–CH$_3$), 3.13 (s, 3H, N–CH$_3$), 7.22–7.26 (m, 2H, coumarinyl-H), 7.36–7.40 (m, 1H, coumarinyl-H), 7.47 (s, 1H, H-1), 7.97 (d, 1H, *J* = 8 Hz, coumarinyl-H), 8.02 (s, 1H, amidine-H). ^{13}C NMR (DMSO-d_6): δ_C 170.9 (ring CO), 157.7, 157.2, 151.2, 133.7, 130.1, 125.1, 124.4, 118.6, 117.6, 107.5, 105.6, 41.1 (N–CH$_3$), 35.7 (N–CH$_3$). MS: *m/z* 272 (100%) [M$^+$]. Found C, 61.42; H, 4.47; N, 10.18; S, 11.87. $C_{14}H_{12}N_2O_2S$ (272.32) requires C, 61.74; H, 4.44; N, 10.28; S, 11.77 %.

N,N-Dimethyl-N′-(11-oxo-11H-naphtho[1,2-b]thieno[3,4-d]pyran-1-yl)formamidine (**18**): Compound **18** was obtained as buff crystals (2.28 g, 71%), m.p. 178–180 °C. IR: ν_{max}/cm^{-1} 1720 (CO). ^{1}H NMR (DMSO-d_6): δ_H 3.08 (s, 3H, N–CH$_3$), 3.15 (s, 3H, N–CH$_3$), 7.55 (s, 1H, H-1), 7.58–7.66 (m, 2H, arom-H), 7.79 (d, 1H, *J* = 8.5 Hz, arom-H), 7.97 (d, 1H, *J* = 8.5 Hz, arom-H), 8.04 (d, 1H, *J* = 8.5 Hz, arom-H). 8.07 (s, 1H, amidine-H), 8.26 (d, 1H, *J* = 8 Hz, arom-H). ^{13}C NMR (DMSO-d_6): δ_C 171.1 (CO), 157.9, 157.0, 146.0, 134.4, 134.2, 128.9, 128.1, 127.8, 124.8, 124.0, 122.2, 121.8, 113.9, 107.5, 105.8, 41.1 (N–CH$_3$), 35.6 (N–CH$_3$). MS: *m/z* 322 (100%) [M$^+$]. Found C, 67.03; H, 4.61; N, 8.61; S, 9.80.$C_{18}H_{14}N_2O_2S$ (322.38) requires C, 67.06; H, 4.37; N, 8.68; S, 9.94 %.

Ethyl 5-(dimethylaminomethyleneamino)-4-oxo-3-phenyl-3,4-dihydrothieno[3,4-d]pyridazine-1-carboxylate (**19a**): Compound **19a** was obtained as brown crystals, yield: 3.10 g (84%), m.p.155–157 °C. IR: ν_{max}/cm^{-1} 1723 ester (CO), 1661 ring (CO). ^{1}H NMR (CDCl$_3$): δ_H 1.43 (t, 3H, *J* = 8 Hz, CH$_3$), 3.14 (s, 3H, N–CH$_3$), 3.18 (s, 3H, N–CH$_3$), 4.56 (q, 2H, *J* = 8 Hz, OCH$_2$), 7.36 (t, 1H, *J* = 7.2 Hz, phenyl-H), 7.46 (t, 2H, *J* = 7.2 Hz, phenyl-H), 7.57 (d, 2H, *J* = 7.6 Hz, phenyl-H), 7.82 (s, 1H, H-7), 7.95 (s, 1H, amidine-H). ^{13}C NMR (CDCl$_3$): δ_C 163.9 (ester CO), 158.3 (ring CO), 157.0 (amidine-C), 141.9, 133.8, 129.4, 129.2, 128.8, 128.1, 127.1, 126.5, 112.9, 62.9 (OCH$_2$), 41.35 (N–CH$_3$), 35.49 (N–CH$_3$), 14.86 (CH$_3$). MS: *m/z* 370 (100%) [M$^+$]. Found C, 58.62; H, 4.88; N, 15.13; S, 8.48. $C_{18}H_{18}N_4O_3S$ (370.42) requires C, 58.36; H, 4.89; N, 15.12; S, 8.65 %.

N′-(1-Benzotriazol-1-yl-4-oxo-3-p-tolyl-3,4-dihydrothieno[3,4-d]pyridazin-5-yl)-N,N-dimethylformamidine (**19b**): Compound **19b** was obtained as yellow crystals (3.20 g, 75%), m.p. 228–230 °C. IR: ν_{max}/cm^{-1} 1652 (ring CO). ^{1}H NMR (DMSO-d_6): δ_H 2.37 (s, 3H, CH$_3$), 3.02 (s, 3H, N–CH$_3$), 3.11 (s, 3H, N–CH$_3$), 7.30 (d, 2H, *J* = 8 Hz, tolyl-H), 7.51 (d, 2H, *J* = 8 Hz, tolyl-H), 7.56 (d, 1H, *J* = 7.6 Hz, benzotriazolyl-H), 7.68 (t, 1H, *J* = 7.6 Hz, benzotriazolyl-H), 7.87 (s, 1H, H-7), 8.06 (d, 1H, *J* = 7.6 Hz benzotriazolyl-H), 8.09 (s, 1H, amidine-H), 8.23 (d, 1H, *J* = 7.6 Hz, benzotriazolyl-H). ^{13}C NMR (DMSO-d_6): δ_C 158.5 (ring CO), 157.6 (amidine-C), 145.6, 139.8, 137.7, 136.4, 132.6, 131.4, 130.4, 130.1, 127.3, 126.6, 125.8, 120.7, 114.3, 113.9, 112.8, 41.1 (N–CH$_3$), 35.3 (N–CH$_3$), 21.7 (CH$_3$). MS: *m/z* 429 (100%) [M$^+$]. Found C, 61.44; H, 4.46; N, 22.61; S, 7.13. $C_{22}H_{19}N_7OS$ (429.49) requires C, 61.52; H, 4.45; N, 22.82; S, 7.46 %.

Reaction of compounds **17–19a,b** *with AcOH/HCl mixture*: A solution of each of **17–19a,b** (10 mmol) in AcOH/HCl (10 ml, 3:1 by volume) was refluxed for 3 h, then allowed to cool to room temperature. The solid product so formed was collected by filtration and crystallised from acetic acid.

3H-Thieno[3,4-c][1]benzopyran-3,4(1H)-one (**20**): Compound **20** was obtained as light brown crystals (1.90 g, 87%), m.p. 264–265 °C. IR: ν_{max}/cm^{-1} 1754 and 1678 (CO). ^{1}H NMR (DMSO-d_6): δ_H 5.03 (s, 2H, CH$_2$), 7.49–7.54 (m, 2H, arom-H), 7.84 (t, 1H, *J* = 7.8 Hz, arom H), 8.01 (d, 1H, *J* = 7.8 Hz, arom H). MS: *m/z* 218 (100%) [M$^+$]. Found C, 60.87; H, 2.90; S, 15.09. $C_{11}H_6O_3S$ (218.22): C, 60.54; H, 2.77; S, 14.69 %.

1H-Naphtho[1,2-b]thieno[3,4-d]pyran-1,11(3H)-dione (**21**). Compound **21** was obtained as light brown crystals (1.84 g, 69%), m.p. 298–300 °C. IR: ν_{max}/cm^{-1} 1755 and 1667 (CO). ^{1}H NMR (DMSO-d_6): δ_H = 5.15 (s, 2H, CH$_2$), 7.17 (t, 1H, *J* = 8.20 Hz, arom-H), 7.82 (t, 1H, *J* = 8.20 Hz, arom-H), 7.91 (d, 1H, *J* = 8.6 Hz, arom-H), 7.98 (d, 1H, *J* = 8.6 Hz, arom-H), 8.10 (d, 1H, *J* = 8.20 Hz, arom-H), 8.43 (d, 1H, *J* = 8.20 Hz, arom-H). MS: *m/z* 268 (100%) [M$^+$]. Found C, 66.85; H, 3.27; S, 11.87. $C_{15}H_8O_3S$ (268.28): C, 67.15; H, 3.00; S, 11.95 %.

Ethyl 8-hydroxy-4-oxo-3-phenyl-5-thioxo-3,4,5,6-tetrahydropyrido[3,4-d]pyridazine-1-carboxylate (**22a**): Compound **22a** was obtained as brown crystals (2.22 g, 65%), m.p. 210–212 °C. IR: ν_{max}/cm^{-1} 3435 (OH), 3268 (NH), 1712 (ester CO), 1652 (ring CO). ^{1}H NMR (DMSO-d_6): δ_H 1.33 (t, 3H, *J* = 8 Hz, CH$_3$), 4.38 (q, 2H, *J* = 8 Hz, OCH$_2$), 7.40–7.47 (m, 1H, phenyl-H), 7.51–7.59 (m, 4H, phenyl-H), 8.03 (s, 1H, OH, D$_2$O exchangeable), 8.64 (s, 1H, H-7), 11.75 (br s, 1H, NH, D$_2$O exchangeable). MS: *m/z* 343 (20%) [M$^+$]. Found C,56.13 ; H, 4.03; N, 12.31, S, 8.94. $C_{16}H_{13}N_3O_4S$ (343.35) requires C, 55.97; H, 3.81; N, 12.23, S, 9.33 %.

4-Benzotriazol-1-yl-5-hydroxy-8-thioxo-2-p-tolyl-7,8-dihydropyrido[3,4-d]pyridazin-1(2H)-one (**22b**): Compound **22b** was obtained as green crystals (3.52 g, 88%), m.p. 310–312 °C. IR: ν_{max}/cm^{-1} 3441 (OH), 3269 (NH), 1682 (CO). ^{1}H NMR (CDCl$_3$): δ_H 2.49 (s, 3H, CH$_3$), 7.31 (d, 2H, *J* = 8.2 Hz, tolyl-H), 7.52 (t, 1H, *J* = 8 Hz, benzotriazolyl-H), 7.60–7.63 (m, 3H, benzotriazolyl-H and 2H tolyl-H), 8.20 (d, 1H, *J* = 8 Hz, benzotriazolyl-H), 8.27 (d, 1H, *J* = 8 Hz, benzotriazolyl-H), 8.50 (s, 1H, OH, D$_2$O exchangeable), 8.66 (s, 1H, H-7), 11.38 (s, 1H, NH). MS: *m/z* 402 (100%) [M$^+$]. Found C, 59.83; H, 3.58; N, 20.76; S, 7.67. $C_{20}H_{14}N_6O_2S$ (402.42) requires C, 59.69; H, 3.50; N, 20.88, S, 7.96 %.

The authors are grateful to University of Kuwait, Research Administration for financial support through project SC 02/02. Analytical facilities provided by SAF are greatly appreciated.

Received 24 June 2004; accepted 2 December 2004
Paper 04/2597

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