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New Reactions of 2-Thioxo-1,2,3,4-tetrahydropyrimidines with some Electron-Deficient Ethylenes and *p*-Quinones

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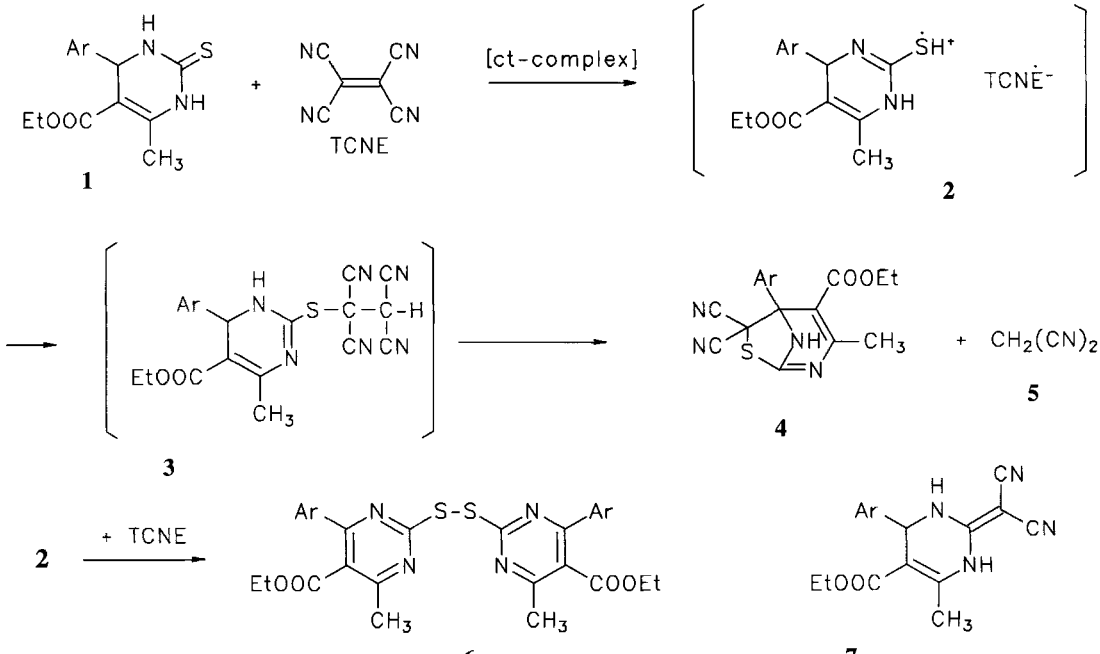
Molecular interactions involving charge-transfer complexes between aromatic and heterocyclic compounds as electron donors and electron π-acceptors have been the subject of several interesting investigations [1–11]. In several papers from our laboratory, we have described the interaction of 1,2,4-amino-triazolethioles [12] and thiosemicarbazides [13] as well as indolotriazinethiols [14] with π-acceptors.

In continuation of our studies of donor-acceptor interactions it was decided to synthesize a variety of new heterocyclic ring systems with expectation that they too might exihibt biological activity, using 2-thioxo-1,2,3,4-tetrahydro-pyidine **1** as the biologically active donor site and a selection of π-systems as acceptors.

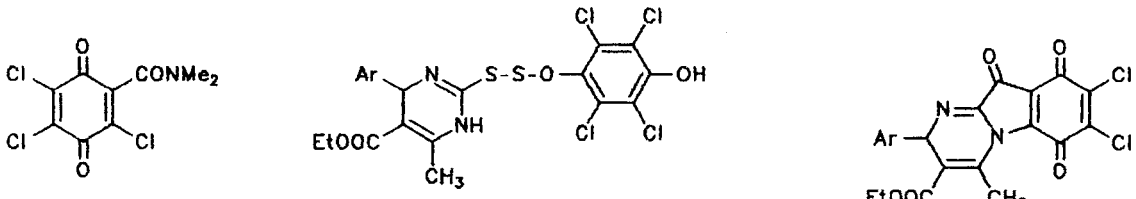
The results of the reaction of **1** with tetracyanoethylene (TCNE) are shown in Scheme 1. On mixing separate solutions of donors **1a–e** and TCNE in ethyl acetate new absorption maxima in the visible region (500–562 nm) arise which are attributed to CT-complex formation, since neither of the components absorbs in this region.

Addition of one mole of each pyrimidine thione **1a,b** to twofold molar amounts of TCNE in ethyl acetate at room temperature afforded 5-aryl-4-carbethoxy-6,6-dicyano-3-methyl-2,8-diaza-7-thiabicyclo[3.2.1]octa-1,3-dienes (**4**) and disulfide **6** as well as 2-dicyanopyrimidine **7** derivatives in



Scheme 1

a: Ar = Ph **b**: Ar = *p*-tolyl



8 **9** **10**

a: Ar = Ph **b:** Ar = *p*-tolyl

Scheme 2

38–40% yield. The formation of these products can be rationalized as follows: pyrimidinethione and TCNE form a CT-complex in the initial step. Subsequently the radical ion pair **2** is formed by complete electron transfer from **1** to TCNE. Transfer of a proton from the cation radical **2** to the TCNE anion radical generates the neutral radicals which may combine to give the adduct **3**. Elimination of malononitrile from **3** results in the formation of **4**. The disulfide **6** is suggested to be formed by dimerization of Ar-S· radicals and dehydrogenation of the dimerization product by TCNE radicals. **7** may be formed from **1** and malononitrile (set free on formation of **4**).

The IR spectra of 2,8-diaza-7-thiabicyclo[3.2.1]octa-1,3-dienes **4** show the presence of the ester carbonyl group by bands at 1695–1700 cm^{-1}, and sharp bands at 2200–2210 cm^{-1} for the cyano group. The ^{1}H-NMR spectra clearly indicate the absence of any signals due to pyrimidine H-4 but shows a triplet at δ=1.2–1.22 and a quartet at δ=4.18–4.20 (C_2H_5), and a singlet at δ=2.27–2.34 due to CH_3, as well as signals for phenyl and *p*-tolyl groups.

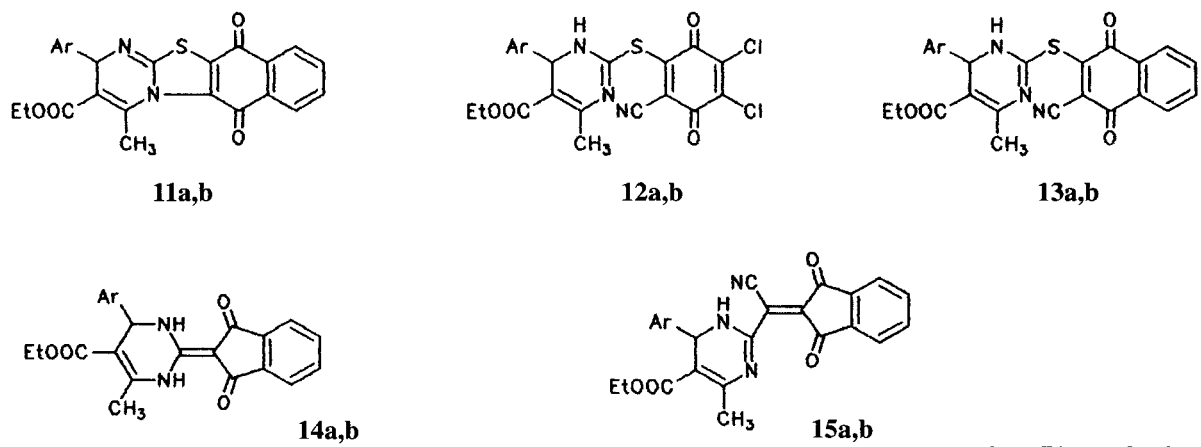
As summarized in Scheme 2, upon treatment of **1** with 2,3,5,6-*p*-benzoquinone (chloranil) the reaction products **6**, **9** and **10** could be isolated chromatographically. Interestingly, in addition to the products **6** and **9** [15], the formation of **10** confirms the participation of DMF in the course of the reaction as suggested in Scheme 3. Fortunately, intermediate **8** could be isolated from the reaction mixture, and can be prepared from both chloranil and DMF [14]. The ^{1}H-NMR spectra of compound **10** confirms the absence of any signals due to NH, but shows the presence of singlet at δ=5.26–5.30 due to pyrimidine H-4.

1a,b react with with 2,3-dichloro-1,4-napthoquinone by substitution of both chlorine atoms to form **11a,b**. In the reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and with 2,3-dicyano-1,4-naphthoquinone only one cyano group and no chlorine atom is substituted giving rise to **12a,b** and **13a,b**, respectively. 2-dicyanomethyleneindane-1,3-dione reacts with **1a,b** under desulfuration to give **14a,b** and **15ab**, resepctively, see Scheme3. The pathway of these reactions is unknown.

Experimental

Melting points: uncorrected. UV/VIS spectra: Perkin-Elmer Lambda 2 spectrophotometer equipped with a thermostatted cell. IR spectra: Shimadzu 470. ^{1}H-NMR spectra: Bruker AC 200 (200 MHz) and Bruker AM 400 (400 MHz); the spectra were recorded in $CDCl_3$ and DMSO-d_6, the chemical shifts are expressed in δ (values) with TMS as the internal standard. Mass spectroscopy: Finnigan MAT 8430 spectrometer operating at 70 eV. Elemental analysis were performed by the microanalytical unit of Cairo University.

1,2,3,4-Tetrahydro-6-methyl-4-aryl-2-thioxo-5-pyrimidine carboxylic acid ethyl esters (**1a–e**) were prepared as described



11a,b **12a,b** **13a,b**

14a,b **15a,b**

a: Ar = Ph **b:** Ar = *p*-tolyl

Scheme 3

in ref. [16]. The electron acceptors were prepared and purified as described in ref. [14].

2,8-Diaza-7-thiabiclo[3.2.1]octa-1,3-diene (**4a,b**), *2,2(4-Aryl-5-ethoxycarbonyl-6-methyl)dipyrimidinyldisulfide* (**6a,b**), and *2-Dicyanomethylene-1,2,3,4-tetrahydro-4-aryl-5-ethoxycarbonyl-6-methylpyrimidine* (**7a,b**)

To a stirred solution of 256 mg (0.002 mol) of TCNE in 10 ml dry ethyl acetate the pyrimidine thione **1a,b** (0.001 mol) in 25 ml dry ethyl acetate was added dropwise at room temperature. After standing for 72 hrs, the mixture was filtered, the precipitate was washed with cold ethyl acetate, and recrystallized to give compound **7**. The filtrate was concentrated and the residue then chromatographed on thin-layer plates using toluene/ethyl acetate (5 : 1) as eluent to give products **4** and **6**.

4a: Yield 26%, *m.p.* 240–242 °C, pale yellow crystals (Benzene). – ^{1}H-NMR ($CDCl_3$): δ= 1.20 (t, 3H, CH_3); 2.34 (s, 3H, CH_3); 4.20 (q, 2H, CH_2); 7.00–7.40 (m, 5H, Ar-H); 10.30 (br., 1H, N_3-H). – IR (KBr) : ν=3360 cm^{-1} (NH), 2200 (CN), 1695 (C=O). – MS (70 e V) : *m/z*(%) = 338 (M^+; 28), 312 (12), 293 (100), 267 (51). – $C_{17}H_{14}N_4SO_2$ (338.39); calcd. C 60.34, H 4.17, N 16.56, S 9.48; found C 60.51, H 4.28, N 16.39, S 9.31.

4b: Yield 29%, *m.p.* 218 °C, yellow crystals (Cyclohexane). – ^{1}H-NMR ($CDCl_3$) : δ = 1.22 (t, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 4.18 (q, 2H, CH_2), 6.95–7.38 (m, 4H, Ar-H), 10.28 (br., 1H, N_3-H). – IR(KBr): ν= 3340 cm^{-1} (NH), 2210 (CN), 1700 (C=O). – $C_{18}H_{16}N_4SO_2$ (352.42); calcd. C 61.35, H 4.58; N 15.90; S 9.10; found C 61.28, H 4.77, N 16.11, S 9.28.

6a: Yield 11%, *m.p.*260–262 °C, colourless crystals (Acetonitrile). – ^{1}H-NMR (D_6]DMSO): δ= 1.15 (t, 6H, $2CH_3$), 2.32 (s, 6H, $2CH_3$), 4.20 (q, 4H, $2CH_2$), 7.15–7.55 (m, 10H, Ar-H). – IR (KBr): ν=1710 cm^{-1} (C=O). – MS (70 e V): *m/z* (%)= 546 (M^+, 100), 274 (18), 273 (17), 245 (21), 230(28). – $C_{28}H_{26}N_4S_2O_4$ (546.67); calcd. C 61.52, H 4.79, N 10.25, S 11.73; found C 61.34; H 4.72; N 10.43; S 11.55.

6b: Yield 14%, *m.p.* 233–235 °C, colourless crystals (Acetonitrile). – ^{1}H-NMR ([D_6]DMSO): δ=1.20(t, 6H, CH_3), 2.28(s, 6H, $2CH_3$), 2.39 (s, 6H, $2CH_3$), 4.16 (q, 4H, $2CH_2$), 7.10–7.52 (m, 8H, Ar-H). – IR (KBr): ν = 3360 cm^{-1} (NH), 2220 (CN), 1690 (C=O). – $C_{30}H_{30}N_4S_2O_4$(574.72); calcd. C 62.70, H 5.26, N 9.75, S 11.16; found C 62.87; H 5.44, N 9.81, S 11.37.

7a: Yield 38%, *m.p.* 158–159 °C, colourless crystals (Ethanol). – ^{1}H-NMR ($CDCl_3$): δ= 1.18 (t, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.12 (q, 2H, CH_2), 5.24(s, 1H, pyrimidine H-4), 6.96–7.42 (m, 5H, Ar-H), 9.32 (br, 1H, N_1-H), 10.31 (br, 1H, N_3-H). – IR (KBr): ν=3320 cm^{-1} (NH), 2200 (CN), 1695 (C=O). – MS (70 eV): *m/z*(%) =308 (M^+, 81), 279 (100), 235(76), 231(79), 203(43), 199(44). – $C_{17}H_{16}N_4O_2$ (308.34): calcd. C 66.22, H 5.23, N 18.17; found C 66.36; H 5.11; N 17.95.

7b: Yield 41%, *m.p.* 108–110 °C, colourless crystals (Benzene). – ^{1}H-NMR ($CDCl_3$): δ = 1.15(t, 3H, CH_3), 2.28(s, 3H, CH_3), 2.34 (s., 3H, CH_3), 4.10(q, 2H, CH_2), 5.20 (s, 1H, pyrimidine H-4), 6.92–7.38 (m, 4H, Ar-H), 9.25 (br, 1H, N_1-H), 10.31(br, 1H, N_3-H). – IR (KBr): ν = 3310 cm^{-1} (NH), 2210(CN), 1700(C=O). – $C_{18}H_{18}N_4O_2$ (322.37); calcd. C 67.07, H 5.63, N 17.38; found C 66.83, H 5.77, N 17.12.

2-(N,N-Dimethylformamido)-3,5,6-trichloro-p-benzoquinone (**8**), *1-(2,3,5,6-Tetrachloro-4-hydroxyphenoxy-2(4-aryl-5-ethoxycarbonyl-6-methyl)-1,4-dihydro-pyrimidinyldisulfide* (**9**), and *Pyrimidinoindolotrione derivatives* (**10**)

To a stirred solution of 246 mg (0.001mol) of chloranil in 15 ml of DMF, the pyrimidine derivatives **1a** or **1b** (0.001 mol) in 10 ml of DMF were added dropwise at room temperature with stirring. Stirring was continued for 72 hrs. The reaction mixture was filtered, and the residue which contained compound **9** was washed several times with cold ethanol until the mother liquor became colourless. The filtrate was concentrated and the residue then chromatographed on thin layer plates using toluene/ethyl acetate (10:1) as eluent to give four zones, the fastest migrating one having a characteristic blue colour contained compound **8** [12] (5%), the second zone contained compound **9**, and the third 2,3,5,6-tetrachlorohydroquinone (11%), while the slowest zone contained compound **10**. Extraction of the zones and recrystallization from appropriate solvents afforded the pure compounds.

9a: Yield 28%, *m.p.* 196–198 °C, brown crystals (Ethanol). – ^{1}H-NMR ([D_6]DMSO): δ = 1.19 (t, 3H, CH_3), 2.26 (s, 3H, CH_3), 4.12 (q, 2H, CH_2), 5.28 (s, 1H, pyrimidine H-4), 7.11–7.54 (m, 5H, Ar-H), 9.12 (s, br, 1H, OH), 10.31 (s, br, 1H, N_3-H). – IR (KBr): ν= 3495–3280 cm^{-1} (OH, NH), 1690 (C=O), 1630 (Ar-C=C). – MS (70 eV): *m/z*(%)= 552/556 (M^+,100), 518 (22), 482 (24), 450 (41), 418 (28), 382 (36), 346 (38), 331(11), 315(10), 242(72). – $C_{20}H_{16}Cl_4N_2O_4S_2$ (554.30); calcd. C 43.34 H 2.91, N 5.05, S 11.57, Cl 25.58; found C 43.18, H 3.11, N 4.96, S 11.39, Cl 25.76.

9b: Yield 31%, *m.p.* 228–230 °C, buff crystals (Ethanol). – ^{1}H-NMR ([D_6]DMSO): δ= 1.16 (t, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.32(s, 3H, CH_3), 4.20 (q, 2H, CH_2), 5.25 (s, 1H, pyrimidine H-4), 7.00–7.41 (m, 4H, Ar-H), 9.16 (s, br, 1H, OH), 10.30 (s, br, 1H, N_3-H). – IR (KBr): ν= 3480–3300 cm^{-1} (OH, NH), 1700 (C=O), 1610 (Ar-C=C). – MS(70 e V): *m/z*(%)= 566/570 (M^+, 100), 532 (32), 496 (18), 432 (23), 328 (12), 257 (39), 154 (41). – $C_{21}H_{18}Cl_4N_2O_4S_2$ (568.32); calcd. C 44.38, H 3.19, N 4.93, S 11.28, Cl 24.95; found C 44.50, H 3.32, N 5.15, S 11.12, Cl 25.12.

10a: Yield 22%, *m.p.* 165–167 °C, reddish-brown crystals (Acetonitrile). – ^{1}H-NMR ([D_6]DMSO): δ= 1.17 (t, 3H, CH_3) 2.26 (s, 3H, CH_3), 4.18 (q, 2H, CH_2), 5.30 (s, 1H, pyrimidine H-4), 7.10–7.53 (m, 5H, Ar-H). – IR (KBr): ν= 1720, 1680 cm^{-1} (C=O), 1620 (Ar-C=C). – UV (Acetonitrile): λ_{max} = 528 nm, lg ε = 3.095. – MS(70 eV): *m/z*(%)=444/447 (M^+,100), 409 (33), 373 (41), 345 (61), 317 (14), 201(54). – $C_{21}H_{14}Cl_2N_2O_5$ (445.26); calcd. C 56.65, H 3.17, N 6.29, Cl 15.92; found C 56.82, H 3.34, N 6.19, Cl 16.21.

10b: Yield 26%, *m.p.* 183–185 °C, reddish-brown crystals (Ethanol) . – ^{1}H-NMR ([D_6]DMSO δ = 1.16 (t, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.31(s. 3H,CH_3), 4.12 (q, 2H, CH_2), 5.26 (s,1H, pyrimidine H-4), 7.00–7.49 (m, 4H,Ar-H). – IR (KBr): ν=1710, 1675 cm^{-1} (C=O), 1630 (Ar-C=C). – UV (Acetonitrile): λ_{max} = 540 nm, lgε = 3.180. – $C_{22}H_{16}Cl_2N_2O_5$ (459.29); calcd. C 57.53, H 3.51, N 6.10, Cl 15.43; found C 57.39, H 3.71, N 5.93, Cl 15.32.

Naphthoquinothiazolopyrimidine Derivatives (**11**)

To a solution of 227 mg 2,3-dichloro-1,4-naphthoquinone (0.001 mol) in 10 ml DMF, a solution of **1a** or **1b** (0.001 mol)

in 10 ml DMF was added and the reaction mixture stirred for 7 hrs. After 96 hrs at room temperature the solvent was evaporated, and the residue was purified chromatographically on TLC plates using toluene/ethyl acetate (10:1) as eluent. Recrystallization from the appropriate solvent gave the pure compounds **11a,b**.

11a: Yield 69%, *m.p.* 134–136 °C, reddish brown crystals (Ethanol). – ^{1}H-NMR ($CDCl_3$): δ = 1.22 (t, 3H, CH_3), 2.26 (s, 3H, CH_3), 4.20 (q, 2H, CH_2), 5.30 (s,1H, pyrimidine H-4), 7.20–8.10 (m, 9H,Ar-H). – IR (KBr): ν = 2960 cm^{-1} (aliph. CH), 1710, 1680 (C=O), 1620, 1580 (Ar-C=C). – UV (Acetonitrile): λ_{max} = 517 nm, lg ε = 3.125. – MS (70 eV) : *m/z*(%) = 430 (M^+, 42), 357 (39), 353 (100), 325 (43), 279 (10), 255 (11). – $C_{24}H_{18}N_2O_4S$ (430.28); calcd. C 66.99, H 4.22, N 6.51, S 7.45; found C 67.14, H 4.11, N 6.73, S 7.34.

11b: Yield 76%, *m.p.* 160–162 °C, reddish brown crystals (Ethanol) . – ^{1}H-NMR ($CDCl_3$): δ = 1.23 (t, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 4.16 (q, 2H, CH_2), 5.35 (s, 1H, pyrimidine H-4), 7.00–8.10 (m, 8H,Ar-H). – IR (KBr): ν = 1700, 1680 cm^{-1} (C=O), 1620 (Ar-C=C). – UV (Acetonitrile): λ_{max} = 525 nm, lg ε = 3.11. – MS (70 eV) : *m/z*(%) = 444 (M^+, 38), 429 (17), 416 (18), 371 (39), 353 (81), 325 (20), 289 (100), 261(90), 217(76), 199(91). – $C_{25}H_{20}N_2O_4S$ (444.51); calcd. C 67.55, H 4.53, N 6.30, S 7.21; found C 67.39, H 4.68, N 6.46, S 7.09.

2,3-Dichloro-5-cyano-6-thiopyrimidino-1,4-benzoquinone (**12**)

To a stirred solution of 227 mg 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.001 mol) in 15 ml of ethyl acetate a solution of **1a** or **1b** (0.001 mol) in 15 ml ethyl acetate was added, the mixture stirred for 48 hrs., filtered, and the precipitate was washed several times with cold ethyl acetate. Recrystallization from appropriate solvent afforded pure crystals of **12a,b**.

12a: Yield 63%, *m.p.* 287–289 °C, yellow crystals (Acetonitrile). – ^{1}H-NMR ([D_6]DMSO): δ = 1.20 (t, 3H, CH_3), 2.25 (s, 3H, CH_3), 4.18 (q, 2H, CH_2), 5.28 (s, 1H, pyrimidine H-4), 7.12–7.54 (m, 5H, Ar-H) 10.32 (br,1H, N_3-H). – IR (KBr): ν = 3380–3260 cm^{-1} (NH), 2940 (aliph. CH), 2210 (CN), 1720, 1670 (C=O), 1630 (Ar-C=C). – MS (70 eV) : *m/z*(%) = 475/478 (M^+, 100), 450 (46), 422 (19), 386 (33), 358 (29), 298 (41), 210 (35). $C_{21}H_{15}Cl_2N_3O_4S$ (476.33); calcd. C 52.95, H 3.17, N 8.82, S 6.73, Cl 14.89; found C 53.11, H3.26, N 8.63, S 6.86, Cl 15.07.

12b: Yield 66%, *m.p.* 301–303° °C, pale yellow crystals (Acetonitrile) . – ^{1}H-NMR ([D_6]DMSO): δ = 1.22(t,3H, CH_3), 2.28 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 4.16 (q, 2H, CH_2), 5.28 (s, 1H, pyrimidine H-4), 7.10–7.51 (m, 4H, Ar-H), 10.31(br, 1H, N_3-H). – IR (KBr): ν = 3410–3280 cm^{-1} (NH), 2920 (aliph. CH), 2220 (CN), 1710, 1675(C=O), 1620–1600 (Ar-C=C). – $C_{22}H_{17}Cl_2N_3O_4S$ (490.36); calcd. C 53.89, H 3.49, N 8.57, S 6.54, Cl 14.46; found C 54.12, H 3.33, N 8.77, S 6.69, Cl 14.29

2-Cyano-3-thiopyrimidino-1,4-naphthoquinone (**13**)

To a stirred solution of 208 mg 2,3-dicyano-1,4-naphthoquinone (0.001 mol) in 10 ml DMF, the pyrimidine thione **1a** or **1b** (0.001 mol) in 10 ml DMF was added at room temperature. The reaction mixture was left for 48 hrs., the solvent was evaporated and the residue purified chromatographically using toluene/ethyl acetate (5:1) as eluent. Recrystallization gave pure **13b,c**.

13b: Yield 69%, *m.p.* 315–317 °C, brown crystals (Ethanol). – ^{1}H-NMR ([D_6]DMSO): δ = 1.18 (t, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.34(s, 3H, CH_3), 4.18 (q, 2H, CH_2), 5.29 (s, 1H, pyrimidine H-4), 7.10–8.00 (m, 8H, Ar-H), 10.32 (br, 1H, N_3-H). – IR (KBr): ν = 3440–3220 cm^{-1} (NH), 2920(aliph. CH), 2210 (CN), 1710, 1680 (C=O), 1600 (Ar-C=C). – MS (70 eV): *m/z*(%) = 471 (M^+,49), 439 (100), 413 (21), 385 (16), 357 (27), 254 (41). – $C_{26}H_{21}N_3O_4S$ (471.54); calcd. C 66.23, H 4.49, N 8.91, S 6.80; found C 66.06, H 4.36, N 9.11, S 6.66.

13c: Yield 61%, *m.p.* 265–267 °C, reddish brown crystals (Ethanol). – ^{1}H-NMR[D_6]DMSO): δ = 1.16 (t, 3H, CH_3), 2.22 (s, 3H, CH_3), 3.86(s, 3H, OCH_3), 4.18 (q, 2H, CH_2), 5.30 (s, 1H, pyrimidine H-4), 7.00–7.96 (m, 8H, Ar-H), 10.30 (br, 1H, N_3-H). – IR (KBr): ν = 3430 cm^{-1} (NH), 2960 (aliph. CH), 2210 (CN), 1720, 1680 cm^{-1}(C=O), 1600, 1580 (Ar-C=C). – $C_{26}H_{21}N_3O_5S$ (487.54); calcd. C 64.05, H 4.34, N 8.62, S 6.58; found C 63.87, H 4.57, N 8.49, S 6.79.

2-Pyrimidino-1,3-indanedione (**14**) and *2-(Cyanopyrimidino)-1,3-indanedione* (**15**)

To a solution of 416 mg dicyanomethylenindane-1,3-dione (0.002 mol) in 15 ml DMF, pyrimidinethione **1a** or **1b** (0.001 mol) in 10 ml DMF was added dropwise at room temperature with stirring. The mixture was then left for another 72 hrs. On filtration of the reaction mixture a residue was obtained, which was recrystallized and proved to be compound **14a,b**. Concentration of the filtrate and chromatographic purification using toluene/ethyl acetate (5:1) followed by recrystallization from an appropriate solvent afforded **15a,b**.

14a: Yield 53%, *m.p.* 196–198 °C, pale yellow crystals (DMF). – ^{1}H-NMR ([D_6]DMSO): δ = 1.17 (t, 3H, CH_3), 2.26 (s, 3H, CH_3), 4.16 (q,2H, CH_2), 5.26 (s, 1H, pyrimidine H-4), 7.15–7.96 (m, 9H, Ar-H), 9.65 (br, 1H, N_1-H), 10.35 (br, 1H, N_3-H). – IR (KBr): ν = 3380–3230 cm^{-1} (NH), 1710, 1670 (C=O), 1620, 1580 (Ar-C=C). – UV (Acetonitrile): λ_{max} = 310 nm, lg ε = 3.323. – MS (70 eV): *m/z*(%) = 338 (M^+, 29), 360 (17), 345 (34), 317 (21), 243 (100), 170 (63). – $C_{23}H_{20}N_2O_4$ (388.42); calcd. C 71.12, H 5.19, N 7.21; found C 70.92, H 5.26, N 7.19.

14b: Yield 56%, *m.p.* 203–205 °C, pale yellow crystals (DMF). – ^{1}H-NMR ([D_6]DMSO): δ = 1.14 (t, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 4.12 (q, 2H, CH_2), 5.22(s, 1H, pyrimidine H-4), 7.10–7.86 (m, 8H, Ar-H), 9.60 (br, 1H, N_1-H), 10.35 (br, 1H, N_3-H). – IR (KBr): ν = 3360 cm^{-1} (NH), 1710, 1670 (C=O), 1630, 1600 (Ar-C=C). – UV (Acetonitrile): λ_{max} = 323 nm, lg ε = 3.341. – MS (70 eV): *m/z*(%) = 402 (M^+, 26), 374 (19), 257 (100), 184 (54). – $C_{24}H_{22}N_2O_4$ (402.45); calcd. C 71.63, H 5.51, N 6.96; found C 71.81, H 5.34, N 7.14.

15a: Yield 26%, *m.p.* 310–312 °C, yellow crystals (Ethanol). – ^{1}H-NMR ($CDCl_3$): δ = 1.18 (t, 3H, CH_3), 2.28 (s, 3H, CH_3), 4.18 (q, 2H, CH_2), 5.30 (s, 1H, pyrimidine H-4), 7.20–8.00 (m, 9H, Ar-H), 10.35(br, 1H, N_3-H). – IR(KBr): ν = 3440–3300 cm^{-1} (NH), 2220 (CN), 1720, 1670 (C=O), 1620, 1580 (Ar-C=C). – UV (Acetonitrile): λ_{max} = 400, 362 nm, lg ε = 3.147, 3.159. – MS (70 eV): *m/z*(%) = 425(M^+, 100), 371

(64), 353 (55), 325 (28). – $C_{25}H_{19}N_3O_4$ (425.44); calcd. C 70.58, H 4.50, N 9.88; found C 70.36, H 4.62, N 10.06.

15b: Yield 29%, *m.p.* 285–287 °C, yellow crystals (Ethanol). – ^{1}H-NMR ($CDCl_3$): δ = 1.16 (t, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 4.16 (q, 2H, CH_2), 5.28 (s, 1H, pyrimidine H-4), 7.10–8.00 (m, 8H, Ar-H), 10.33 (br, 1H, N_3-H). – IR (KBr): ν = 3410–3360 cm^{-1} (NH), 2950(aliph. CH), 2210 (CN), 1720, 1670 (C=O), 1630, 1600(Ar-C=C). – UV (Acetonitrile): λ_{max} = 405, 365 nm, lg ε = 3.186, 3.211. – $C_{26}H_{21}N_3O_4$ (439.47); calcd. C 71.06, H 4.82, N 9.56; found C 70.88, H 4.66, N 9.44

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