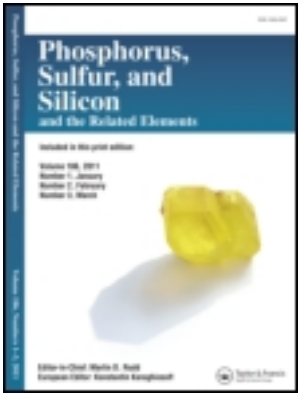

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Rhodanine in Fused-Heterocycles Syntheses

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Rhodanine in Fused-Heterocycles Syntheses

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*The reaction of 3-aminothiazolidine-2-thione-4-one (3-aminorhodanine, **1**) with some π-deficient compounds afforded three types of products: bicyclic noncondensed derivatives such as bis(3-aminothiazole-2-thione-4-one), the condensation product 2-(3-amino-2-thioxothiazolo)-1,3-indanedione, as well as the fused heterocyclic compounds thioxothiazolo[3,4-c]oxadiazine, furo[2,3-b]thiazole, thiazolo[3,4-c]benzoxadiazine, and naphthoquinothiazolo[3,4-c]oxadiazine.*

Keywords 3-Aminorhodanine; π-deficients; oxadiazine and thiazole derivatives

INTRODUCTION

Considerable attention has been drawn to the condensation reaction between 3-aminothiazolidine-2-thione-4-one (3-aminorhodanine, **1**) and both aldehydes and ketones to give 3-alkylidene and/or arylidene rhodanines.[1–4] The reaction could be regioselectively controlled to involve either the 3-amino or 5-methylene groups in condensation.[1,3] The main target of this synthesis is the investigation of biological activity of the condensation products formed.[5] On the other hand, bicyclic noncondensed derivatives of rhodanine containing amino acid groups[6] or two thiazole moieties[7] have been reported. Recently it has been reported that compounds containing two thiazole moieties linked to each other either directly or through different bridges display biological activities, especially antifungal, antimicrobial, antiviral, sedative, and analgesic activity.[4,5,7–10] In light of the aforementioned findings and pursuing our research in the field of the synthesis of heterocyclic as well as

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Dedicated to Professor Henning Hopf on occasion of his 65th birthday.
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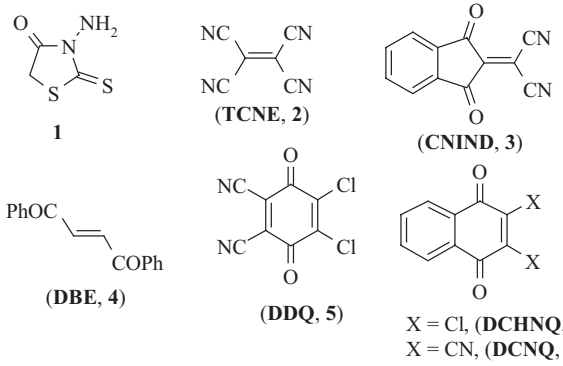


SCHEME 1

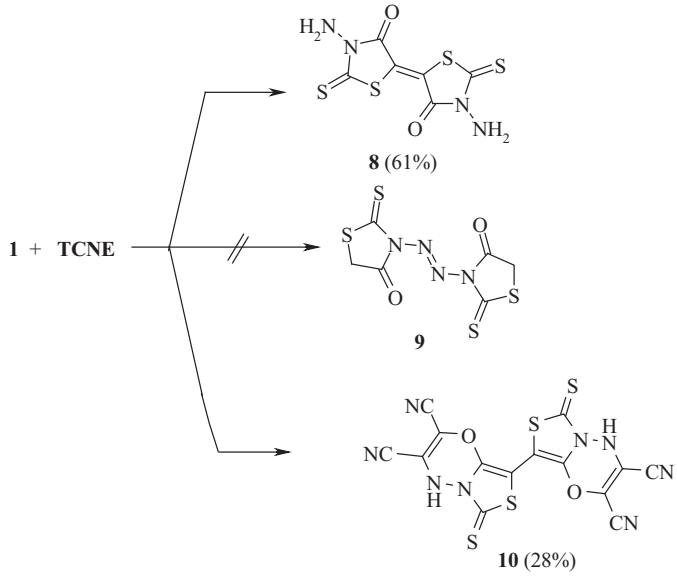
fused heterocyclic compounds via reaction of π-defficient compounds with electron-donor compounds,[11–23] we investigated the reactions of 3-aminorhodanine with some π-deficient compounds (Scheme 1).

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization

3-Aminorhodanine (**1**) reacted with 1,1,2,2-ethenetetracarbonitrile (**TCNE**, **2**) in acetonitrile at r.t. Chromatographic separation of the reaction mixture gave numerous colored zones, from which products **8** and **10** could be isolated (Scheme 2). Two possible structures were considered for the dimeric product (structures **8** and **9** in Scheme 2). Structural assignment of **8** was based on spectroscopic data and combustion analysis. The IR spectrum showed absorption bands at $\upsilon = 3300–3200$ (NH_2), 1700, and 1690 cm^{-1} (CO). The ^1H NMR spectrum displayed only one singlet at δ5.75 ppm indicating the presence of NH_2 and absence of the thiazole-CH_2 group. Furthermore, the ^{13}C NMR spectrum of **8** showed two signals at $\delta = 167.0$ and 199.8 charactersitic of the *C*=O and *C*=S carbon atoms, respectively, in addition to the signal for *C*-5 of the thiazole ring at $\delta = 138.1$ ppm. According to semi-empirical calculations at the MM2 level of theory[24] for compound **8**, its *trans* form ($\Delta E = 235.74$ kcal/mol) was energetically more favorable compared with its *cis* form ($\Delta E = 479.39$ kcal/mol).

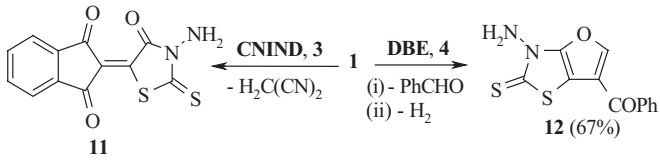
Compound **10** was another product isolated from the reaction of **1** with **2** in a low yield. The simplicity of the ^1H NMR spectrum by the appearance of only one singlet at $\delta = 7.3$ ppm, corresponding to an oxadiazine-NH proton, left no doubt about the symmetrical structure of **10**. This structure was also supported by correct elemental analysis



SCHEME 2

and by the mass spectrum, which exhibited a molecular ion peak at *m/z* 442 (100%). The IR spectrum showed a characteristic absorption band at $\upsilon = 3388$ cm^{-1} (oxadiazine-NH) and another at 2210 cm^{-1}, confirming the presence of cyano groups. Moreover, the ^{13}C NMR signals of compound **10** were assigned, and the appearance of only seven carbon signals indicated the symmetrical feature of the proposed structure. These signals appeared at $\delta = 117.2$, 117.4 (*C*N), 194.8 (*C*=S), 148.9 (thiazole-*C*-4), 115.0, 118.1 (oxadiazine-*C*-5 and -*C*-6), and $\delta = 91.2$ due to *C*-5 of the thiazole ring. Semi-empirical calculations for compound **10** using the MM2 level of theory indicated a larger stability of its *trans* form ($\Delta E = 237.41$ kcal/mol) compared with its *cis* form ($\Delta E = 807.58$ kcal/mol).

On the other hand, 2-dicyanomethyleneindane-1,3-dione (**CNIND**, **3**) interacted with **1** to give the condensation product **11** via a nucleophilic attack of the rhodanine methylene function on the dicyanomethylene carbon atom of **3**, followed by elimination of a molecule of malononitrile (Scheme 3). The IR spectrum of **11** indicated the presence of carbonyl and amino groups and excluded any cyano groups. The ^{1}H NMR spectrum showed a broad singlet for NH_2 at $\delta = 5.7$ ppm in addition to signals of aromatic protons. The ^{13}C NMR spectrum revealed resonances at $\delta = 186.4$ (*C*=O of indanedione), 167.4 (*C*=O of thiazole), and 199.8 (*C*=S), as well as signals for aromatic carbon atoms. The



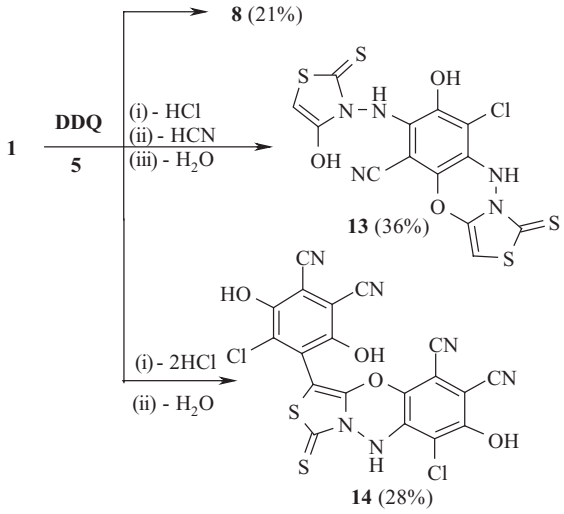
SCHEME 3

structure of compound **11** was also assigned on the basis of elemental analysis, supporting the sum formula $C_{12}H_6N_2S_2O_3$, and was confirmed also by the mass spectrum, which gave a correct molecular ion at $m/z =$ 290 (92%).

As an example for another π-deficient compound, we investigated of the reaction of **1** with *E*-1,2-dibenzoylethene (**DBE**, **4**). Equimolar amounts of **1** and **4** were refluxed in acetic acid and afforded the product **12** in 67% yield (Scheme 3). The formation of **12** may be explained in terms of the nucleophilic attack of the rhodanine methylene group to the -C=C- double bond in **4** followed by the elimination of a molecule of benzaldehyde and dehydrogenation. The structural proof of **12** was based on spectroscopic and analytical data. The ^{1}H NMR spectrum clearly indicated the absence of rhodanine-CH_2 protons. It showed a broad singlet at $\delta = 5.75$ ppm due to the exocyclic NH_2 group as well as signals for the furane ring proton and aromatic protons. The IR spectrum indicated the presence of an amino group ($\upsilon = 3338$ cm^{-1}) and a carbonyl group ($\upsilon = 1680$ cm^{-1}). Furthermore, the ^{13}C NMR spectrum gave strong evidence for the formation of compound **12**, and showed signals for *C*=O at $\delta = 181.6$; for *C*=S at $\delta = 194.5$, and for carbon atoms of the furane ring at $\delta = 153.4$, 143.6, 132.3, and 117.9.

Particularly interesting is the chemical behavior of **1** toward benzo- and naphthoquinones (Scheme 4). An addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (**5**) to **1** results in the formation of the dimeric product **8** in addition to products **13** and **14**. The molecular formulas of the products are evidenced by their elemental analyses as well as by mass spectra. The structure of **13** was confirmed on the basis of its spectroscopic properties. The IR spectrum of **13** indicated the presence of bands characteristic for the OH, NH, and CN groups.

The ^{1}H-NMR spectrum clearly revealed the absence of any signals due to rhodanine-CH_2 or exocyclic NH_2 groups. It confirmed the presence of a CH moiety in the thiazole ring ($\delta = 7.66$) as well as of oxadiazine-NH at $\delta = 7.24$ and exocyclic NH and OH protons. Moreover, a singlet appeared at $\delta = 4.50$, related to thiophene-H-3. The ^{13}C NMR spectrum of compound **13** showed signals at $\delta = 79.3$, 85.6 (thiazole-*C*H-5), 112.5 (Ar-*C*-Cl), 114.8 (CN), 116.8 (Ar-*C*-CN), 138.0,

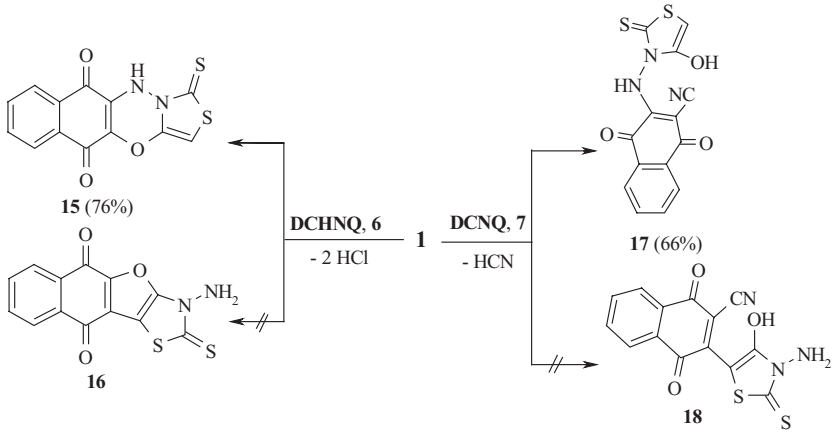


SCHEME 4

139.8 (Ar-*C*-NH), 152.8, 154.5, 156.6, and 160.9 (Ar-*C*-O, thiazole-*C*-O and oxadiazine-*C*-O) next signals for the C=S groups at $\delta = 192.8$ and 194.6. On the other hand, the assignment of signals in the ^{13}C NMR spectrum of **14** supported the structure shown in Scheme 4, with resonances at $\delta = 79.8$ (thiazol-*C*H-5), 111.8, 112.4 (Ar-*C*-Cl), 113.2, 113.8, 114.0, 114.8 (*C*N), 115.0, 115.2, 115.6, 115.8 (Ar-*C*-CN), 124.4 (thiazole-*C*-5), 137.7 (Ar-*C*-NH), 150.0, 154.2, 156.9, 158.0, and 161.6 (*C*-O) and at $\delta = 194.7$ for the *C*=S group. Several alternative structures for **13** and **14** were excluded based on elemental compositions and spectroscopic properties.

The addition of a pyridine solution of 2,3-dichloro-1,4-naphthoquinone (**6**) to a solution of **1** in pyridine afforded the naphthoquinothiazolooxadiazine derivative **15**, rather than naphthoquinofurothiazole **16** (Scheme 5). The ^{1}H NMR spectrum of **15** indicated the presence of oxadiazine-NH and thiazole-CH protons in addition to aromatic protons. No ^{1}H NMR resonance for an exocyclic NH_2 group was observed. The ^{13}C NMR spectrum displayed further evidence for the proposed structure and revealed resonances for *C*=O ($\delta = 186.7$), *C*=S ($\delta = 194.6$), thiazole-*C*H ($\delta = 73.9$), and oxadiazine-*C*-3 ($\delta = 154.9$), as well as signals for aromatic carbon atoms.

The reaction of 2,3-dicyano-1,4-naphthoquinone (**DCNQ**, **7**) as an electron acceptor with **1** as an electron donor yielded naphthoquinone derivative **17** as the only product, rather than compound **18** (Scheme 5). ^{1}H and ^{13}C NMR spectra of **17** confirmed the presence of the *CH*



SCHEME 5

function of the thiazole ring. At the same time, the ^{13}C NMR spectrum excluded the presence of a thiazolone carbonyl carbon atom, the signal of which usually appears at $\delta = 167.00$.[3]

In conclusion, the results described in this article demonstrate that the reaction of **1** with π-deficient compounds used afforded three types of products. These are bicyclic noncondensed derivatives, condensation products, as well as interesting fused-heterocyclic compounds, which were easily synthesized in one step and that cannot be easily prepared by conventional synthetic methods. Furthermore, to the best of our knowledge, there are no literature reports about rhodanine fused with heterocycles.

EXPERIMENTAL

Apparatus and Chemical Methods

Melting points are uncorrected. Combustion analyses were carried out at the microanalytical unit at Cairo University (Cairo, Egypt). IR spectra were recorded on a Nicolet 320 FTIR and Shimadzu 408 spectrophotometers using potassium bromide pellets. ^1H-NMR (400.13 MHz) and ^{13}C-NMR (100.6 MHz): Bruker AM 400 spectrometer; chemical shifts are given as δ (ppm) with TMS as an internal standard. Mass spectra (70 eV, electron impact mode) were obtained on a Finnigan MAT 8430 instrument. Preparative Layer Chromatography (PLC) was used with air-dried 1.0-mm thick layers of slurry-applied silica gel Merck PF_{254} (Merck, Darmstädt, Germany) on 48-cm wide and 20-cm high glass plates. Zones were detected by quenching indicator fluorescence upon exposure to 254-nm UV light and eluting with acetone.

Starting Materials

3-Aminothiazolidine-2-thione-4-one (3-aminorhodanine, **1**) and *E*-1,2-dibenzoylethene (**DBE**, **4**) were purchased from Aldrich (München, Germany). 1,1,2,2-Ethenetetracarbonitrile (**TCNE**, **2**, Merck, Darmstädt, Germany) was recrystallized from chlorobenzene and sublimed. 2-dicyanomethyleneindane-1,3-dione (**CNIND**, **3**) was prepared according to the procedure described by Chatterjee.[25] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (**DDQ**, **5**, Aldrich, München, Germany) was recrystallized from benzene/chloroform (2:3). 2,3-Dicyano-1,4-naphthoquinone (**DCNQ**, **7**) was prepared from 2,3-dichloro-1,4-naphthoquinone (**DCHNQ**, **6**, Merck, Darmstädt, Germany) according to Budni and Jayadevappa.[26]

Reaction of 1,1,2,2-Ethenetetracarbonitrile (TCNE, 2) with 1

A solution of **1** (148 mg, 1 mmol) in dry acetonitrile (20 mL) was added to a solution of **2** (256 mg, 2 mmol) in dry acetonitrile (15 mL), and the reaction mixture was stirred for 48 h at r.t. The solvent was evaporated in vacuo, and the obtained reddish-brown residue was dissolved in acetone, chromatographed (PLC), and eluted with toluene/ethyl acetate (2:1) to give only a reddish-brown zone containing compound **8**. The material confined to the start was rechromatographed using chloroform/methanol (5:1) to give compound **10**.

3,3′-Diamino-2,2′-dithioxo-[5,5′]bithiazolidinylidene-4,4′-dione (8)

Yield 178 mg (61%), reddish-brown crystals (ethanol), m.p. 270–272°C. IR (KBr): υ = 3270, 3200 (NH_2), 1710–1690 (CO) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 5.75 (br s, NH_2). ^{13}C NMR (DMSO-d_6): δ = 138.1 (thiazole-*C*-5), 167.0 (*C*=O), 199.8 (*C*=S). MS (70 eV), m/z (%): 292 [M^+] (100), 218 (15), 190 (72), 162 (24), 116 (25), 88 (63), 79 (32). $C_6H_4N_4S_4O_2$ (292.39): Calcd. C, 24.65; H, 1.38; N, 19.16; S, 43.87; Found: C, 24.81; H, 1.32; N, 19.22; S, 43.72.

3,3′-Dithioxo-4*H*,4′*H*-[1,1′]bis[7-oxa-2-thia-3*a*,4-diazaindenyl]-5,5′,6,6′-tetracarbonitrile (10)

Yield 125 mg (28%), brown crystals (methanol); m.p. 283–285°C. IR (KBr): υ = 3388 (NH), 2210 (CN), 1618 (C=C) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 7.30 (br s, 2H, 2 oxadiazine-NH). ^{13}C NMR (DMSO-d_6): δ = 115.0 (oxadiazine-*C*-5), 117.2 (CN), 117.4 (CN), 118.1 (oxadiazine-*C*-6), 91.2 (thiazole-*C*-5), 148.9 (oxadiazine-*C*-3), 194.8 (*C*=S). MS (70 eV),

m/z (%): 442 [M^+] (100), 410 (35), 394 (22), 362 (18), 221 (62), 205 (81), 162 (21), 77 (15). $C_{14}H_2N_8O_2S_4$ (442.49): Calcd.: C, 38.00; H, 0.46; N, 25.32; S, 28.99. Found: C, 37.89; H, 0.43; N, 25.49; S, 29.08.

Reaction of 2-Dicyanomethyleneindane-1,3-dione (CNIND, 3) with 1

To a stirred solution of 208 mg (1 mmol) of **3** in dry acetonitrile (20 mL), compound **1** (148 mg, 1 mmol) in dry acetonitrile (20 mL) was added dropwise at r. t. and the stirring was continued for 96 h when compound **11** had precipitated.

2-(3-Amino-4-oxo-2-thioxothiazolidin-5-ylidene)-1,3-indanedione (11)

Yield 206 mg (71%), red crystals (methanol), m.p. 263–265°C. IR (KBr): υ = 3379–3251 (NH_2), 1729, 1708, 1680 (CO), 1597 (Ar-C=C) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 5.70 (br s, NH_2), 7.22–7.58 (m, 4H, Ar-H). ^{13}C NMR (DMSO-d_6): δ = 128.7, 132.6, 137.7 (Ar-*C*), 140.4, 159.1 (indanedione-*C*-2 and thiazole-*C*-5), 167.4 (thiazolone-*C*=O), 186.4 (*C*=O of indanedione), 199.8 (C=S). MS (70 eV), m/z (%): 290 [M^+] (88), 217 (25), 189 (100), 161 (11), 104 (32), 76 (31). $C_{12}H_6N_2O_3S_2$ (290.32): Calcd.: C, 49.65; H, 2.08; N, 9.65; S, 22.09. Found: C, 49.53; H, 2.14; N, 9.59; S, 22.17.

Reaction of *E*-1,2-Dibenzoylethene (DBE, 4) with 1

A solution of *E*-1,2-dibenzoylethene (**DBE**, **4**) (236 mg, 1 mmol) in glacial acetic acid (15 mL) was added to a solution of **1** (148 mg, 1 mmol) in glacial acetic acid (10 mL). The reaction mixture was refluxed for 6 h when a brown precipitate of 6-amino-3-benzoyl-5-thioxofuro[2,3-*b*]thiazole (**12**) was formed.

3-Amino-6-benzoyl-2,3-dihydrofuro[2,3-*d*]thiazole-2-thione (12)

Yield 188 mg (68%), brown crystals (DMF/ethanol), m.p. 128–130°C. IR (KBr): υ = 3338 (NH_2), 2924 (Aliph-CH), 1680 (CO), 1596 (Ar-C=C) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 5.75 (br s, 2H, NH_2), 7.25–7.80 (m, 6H, furane-*C*H and Ar-H). ^{13}C NMR (DMSO-d_6): δ = 117.9 (furane-*C*H), 126.9 (C-*m*), 128.2 (C-*p*), 128.8 (C-*o*), 132.3 (furane-*C*-3), 133.0 (C-*i*), 143.6 (furane-*C*-3a), 153.4 (furane-*C*-3b), 181.6 (C=O), 194.5 (*C*=S). MS (70 eV), m/z (%): 276 [M^+] (12), 248 (31), 232 (34), 171 (41), 105 (100), 84 (62), 56 (60). $C_{12}H_8N_2S_2O_2$ (276.34): Calcd.: C, 52.16; H, 2.92; N, 10.14; S, 23.21. Found: C, 52.24; H, 3.05; N, 10.21; S, 23.14.

Reaction of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 5) with 1

To a solution of **5** (227 mg, 1 mmol) in dry acetonitrile (10 mL) was added a solution of **1** (148 mg, 1 mmol) in dry acetonitrile (20 mL), and the reaction mixture was stirred for 48 h at r. t. The color of the reaction mixture changed from dark green to reddish brown. The solvent was removed *in vacuo,* and the residue was subjected to preparative plates chromatography using toluene/ethyl acetate (2:1) to give only one zone containing compound **8** (21%). The material confined to the start was rechromatographed using toluene/ethyl acetate (1:1) as an eluent. The fastest migrating zone contained compound **13**, and the slowest migrating contained compound **14**. Extraction of the zones with acetone and recrystallization from the respective solvents (see the following section) to afford the pure compounds.

5-Chloro-6-hydroxy-7-(4′-hydroxy-2′-thioxo-2′,3′-dihydrothiophen-3′-ylamino)-3-thioxo-4*H*-9-oxa-2-thia-3a,4-diaza-cyclopenta[*b*]naphthalene-8-carbonitrile (13)

Yield 160 mg (36%), reddish-brown crystals (DMF/ethanol), m.p. 210–212°C. IR (KBr): υ = 3456–3228 (OH, NH), 2924 (aliphatic-CH), 2210 (CN), 1636 (Ar-C=C) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 4.50 (s, 1H, thiophene-H-3), 6.20 (br s, 1H, NH), 7.24 (br s, 1H, oxadiazine-NH), 7.34 (s, 1H, OH), 7.66 (s, 2H, thiazole-CH), 8.30 (s, 1H, OH). ^{13}C NMR (DMSO-d_6): δ = 79.3, 85.6 (thiazoles-*C*H-5), 112.5 (Ar-*C*-Cl), 114.8 (CN), 116.8 (Ar-*C*-CN), 138.0, 139.8 (Ar-*C*-NH), 152.8, 154.5, 156.6, 160.9 (Ar-*C*-O, thiazole-*C*-O and oxadiazine-*C*-O), 192.8, 194.6 (*C*=S). MS (70 eV), m/z (%): 446 [M+2] (52), 445 [M+1] (20), 444 [M^+] (100), 338 (62), 182 (100), 149 (39), 77 (21). $C_{13}H_7ClN_5O_3S_4$ (444.94): Calcd.: C, 35.09; H, 1.59; N, 15.74; S, 28.83. Found: C, 34.89; H, 1.59; N, 15.72; S, 28.87.

5-Chloro-1-(2′-chloro-4′,5′-dicyano-3′,6′-dihydroxyphenyl)-6-hydroxy-3-thioxo-4*H*-9-oxa-2-thia-3a,4-diazacyclopenta[*b*]naphthalene-7,8-dicarbonitrile (14)

Yield 145 mg (28%), brown crystals (DMF/ethanol), m.p. 283–284°C. IR (KBr): υ = 3355–3175 (OH, NH), 2208 (CN), 1630 (Ar-C=C) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 7.22 (br s, 1H, oxadiazine-NH). ^{13}C NMR (DMSO-d_6): δ = 79.8 (thiazole-*C*H-5), 111.8, 112.4 (Ar-*C*-Cl), 113.2, 113.8, 114.0, 114.8 (*C*N), 115.0, 115.2, 115.6, 115.8 (Ar-*C*-CN), 124.4 (thiazole-*C*-5), 137.7 (Ar-*C*-NH), 150.0, 154.2, 156.9, 158.0, 161.6 (*C*-O), 194.7 (*C*=S). MS (70 eV), m/z (%): 517 [M+3] (20), 516 [M+2] (74), 515 [M^+] (100),

513 (39), 511 (24), 475 (12), 346 (17), 292 (11), 256 (8), 105 (27), 79 (90), 60 (100). $C_{19}H_4Cl_2N_6O_4S_2$ (515.32): Calcd.: C, 44.29; H, 0.78; Cl, 13.76; N, 16.31; S, 12.45. Found: C, 44.17; H, 0.75; Cl, 13.83; N, 16.24; S, 12.56.

Reaction of 2,3-Dichloro-1,4-naphthoquinone (DCHNQ, 6) with 1

To a stirred solution of 227 mg (1 mmol) of **6** in dry pyridine (10 mL), compound **1** (148 mg, 1 mmol) in dry pyridine (10 mL) was added at r. t. The reaction mixture was stirred at r. t. for 72 h until the reaction was completed and blue crystals of **15** had precipitated.

3-Thioxo-4*H*-11-oxa-2-thia-3a,4-diazacyclopenta[*b*]anthracene-5,10-dione (15)

Yield 229 mg (76%), blue crystals (DMF), m.p. 186–188°C. IR (KBr): υ = 3310 (NH), 1680 (CO), 1620 (Ar-C=C) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 7.28 (br s, 1H, oxadiazine-NH), 7.54–8.28 (m, 5H, Ar-H and thiazole-CH). ^{13}C NMR (DMSO-d_6): δ = 73.9 (thiazole-*C*-5), 128.5, 132.8, 133.1, 137.5, 139.8 (Ar-*C*), 154.9 (thiazole-*C*-4), 186.7 (*C*=O), 194.6 (*C*=S). MS (70 eV), m/z (%): 302 [M^+] (16), 274 (100), 246 (90), 190 (52), 76 (55). $C_{13}H_6N_2O_3S_2$ (302.33): Calcd.: C, 51.65; H, 2.00; N, 9.27; S, 21.21. Found: C, 51.72; H, 1.93; N, 9.33; S, 21.33.

Reaction of 2,3-Dicyano-1,4-naphthoquinone (7) with 1

To a stirred solution of 208 mg (1 mmol) of **7** in dry acetonitirile (15 mL), compound **1** (148 mg, 1 mmol) in dry acetonitrile (20 mL) was added dropwise at r. t. and stirring was continued for 48 h. The color of the reaction mixture changed from dark green to bluish-violet. The solvent was removed *in vacuo,* and the residue was subjected to PLC using toluene/ethyl acetate (3:1) to give only 1 zone containing compound **17**.

1,4-Dioxo-3-(2-thioxothiazol-3-ylamino)-1,4-dihydronaphthalene-2-carbonitrile (17)

Yield 217 mg (66%), violet-blue crystals (methanol), m.p. 295–297°C IR (KBr): υ = 3422–3216 (OH, NH), 2220 (CN), 1685–1671 (CO), 1617 (Ar-C=C) cm^{-1}. ^1H NMR (DMSO-d_6): δ = 6.60 (br s, 1H, NH), 7.50–8.30 (m, 5H, Ar-H and thiazole-CH). ^{13}C NMR (DMSO-d_6): δ = 73.9 (thiazole-*C*-2), 97.2 (*C*-CN), 117.2 (*C*N), 128.5, 132.8 and 137.5 (Ar-*C*), 156.6, 177.5 (*C*-OH, *C*-NH), 187.0 (*C*=O), 199.8 (*C*=S) MS (70 eV), m/z (%): 329 [M^+] (36), 257 (17), 240 (16), 209 (12), 166 (10), 127 (21), 66 (28),

28 (100). $C_{14}H_7N_3O_3S_2$ (329.35): Calcd. C, 51.05; H, 2.14; N, 12.76; S, 19.47. Found: C, 51.14; H, 2.18; N, 12.72; S, 19.39.

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