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RESEARCH ARTICLE

A convenient and efficient method for the synthesis of benzo- and naphthothiazolediones

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A series of benzo- and naphthothiazolediones have been synthesized by the reactions of *N*-substituted thioureas with π-deficient quinones. The products were obtained by the reaction of *N*-aroylphenylthioureas with 2,3,5,6-tetracholoro-1,4-benzoquinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone and 2,3-dichloro-1,4-naphthoquinone.

Keywords: Benzoquinones; Naphthoquinone; Aroylphenylthioureas; Benzo(naphtho)thiazolediones

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1. Introduction

Thioureas are important compounds as building blocks in the synthesis of heterocycles. For example, thioureas condense with α-halocarbonyl compounds to afford 2-amino-1,3-thiazoles [1, 2]. Besides, benzothiazoles can be prepared from arylthioureas in the presence of bromine [3]. The utility of thioureas in the synthesis of aminothiazolines [4], thiohydantoins [5, 6], 1,3,5-triazines [7], and 2-aminoxazolidines [8] was also described. Derivatives of aryl-disubstituted ureas and thioureas can also provide a rich source of candidates for development as agrochemical and pharmaceutical products [9].

The chemistry of quinones is of considerable interest, this class includes many natural products and numerous important synthetic products [10, 11]. A large variety of quinones, including many fused heterocyclic rings, have been used as synthetic intermediates in medicinal and industrial chemistry. Quinones are particularly important in dye chemistry [12], and many quinone dyes are commercially available. Quinone-type dyestuffs have received increasing attention because of the search for new infrared dyes for optical recording media [13, 14]. Moreover, organic molecules containing electron donor and acceptor moieties constitute a very interesting topic due to their optical and electronic properties [15].

Benzothiazoles are currently valued as a novel class of selective antitumor agents [16, 17]. Recently, some fused heterocyclic compounds such as benzoxazole, benzomidazole, benzothiazole, and oxazolopyridine derivatives are reported to have eukaryotic II inhibitor

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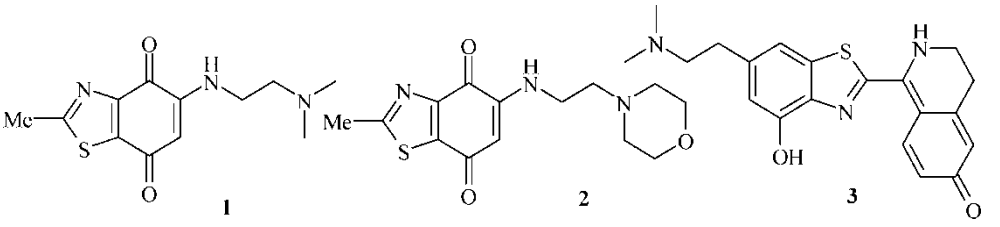

Figure 1. Some naturally occurring benzothiazoles.

activities [18]. It was also found that benzothiazoles **1** and **2** are thiazolequinone CDC25 inhibitors [19] (figure 1). In addition, the new alkaloid designated as violatinctamine (**3**) (figure 1) was shown to have a unique heterocyclic skeleton, which combines a benzothiazole unit and a dihydroisoquinoline unit [20].

In the last decade, we have worked on developing the chemistry of heterocycles having paracyclophane moieties (heterophanes), such as azoparacyclophane [21], [2.2]-(5,8)phthalazinophane [22] and many others, *via* cycloaddition of various selected dienophiles with alkenylparacyclophanes [23]. Moreover, we have synthesized pyridine, imidazol, isoxazole and pyrrole derivatives of [2.2]paracyclophane *via* the reaction of acetyl(aldehydic)paracyclophanyl nitrones with dipolarophiles [24–26]. Additionally, we have recently reported on a very convenient one step procedure to synthesize 1*H*,2,4-triazoles [27].

The interesting applications of benzo(naphtho)thiazoles prompted us to carry out the reactions of 2,3,5,6-tetracholoro-1,4-benzoquinone (**4a**), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (**4b**) and 2,3-dichloro-1,4-naphthoquinone (**4c**) with aroylphenylthioureas **5a–c**.

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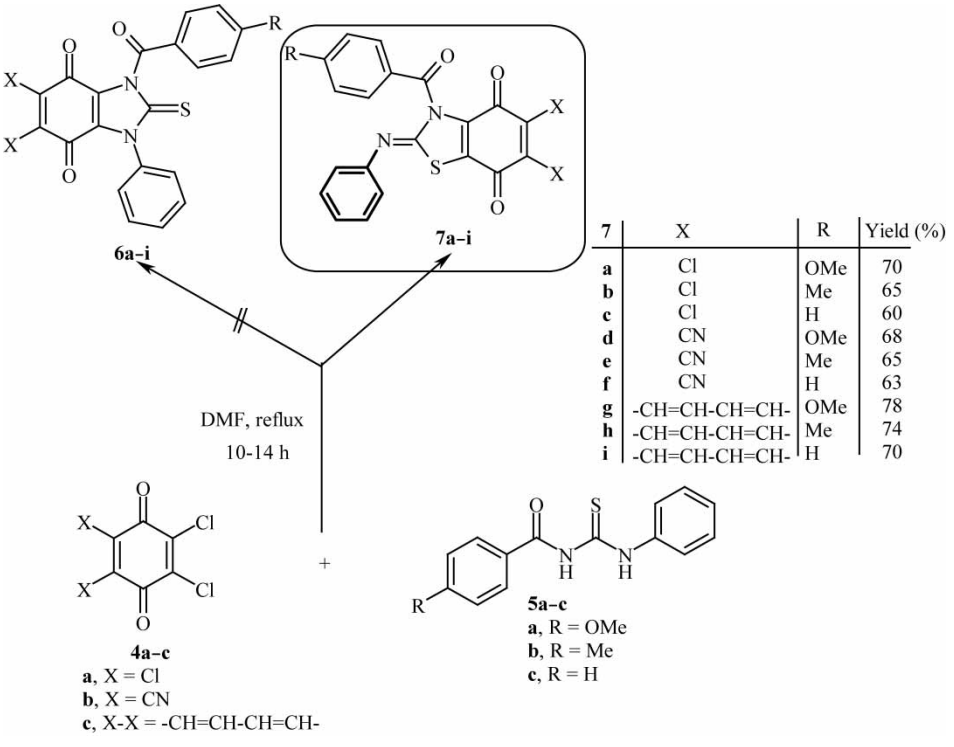
2. Results and discussion

Scheme 1 outlines the synthesis of benzo- and naphthothiazolediones **7a–i** by the reaction of 2,3,5,6-tetracholoro-1,4-benzoquinone (**4a**), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (**4b**) and 2,3-dichloro-1,4-naphthoquinone (**4c**) with aroylphenylthioureas **5a–c** under reflux in DMF (scheme 1). The reaction products were most likely stereochemically described to have diastereomer of *E*(*anti*)-form and therefore these products were identified as (E)-[3-aroyl-2-phenylamino-benzo(naphtho)thiazolediones **7a–i** (scheme 1).

In particular, it must be pointed out that the ^{1}H NMR spectra of **7a–i**, did not reveal any signals related to the −NH, −OH or −SH protons. In the ^{13}C NMR spectra, the C=S carbon signal were not noted, whereas the spectra revealed the appearance of three carbonyl signals where two were assigned for the quinone structure *C*-4 ($\delta = 173.9$–174.8) and *C*-7 or *C*-9 ($\delta = 175.0$–177.0) and the other for the amide group ($\delta = 160.4$–162.9). The structural proof of the obtained products was established by the NMR, mass and IR spectra in addition to elemental analyses. For example, the IR spectrum of **7a** reveals absorption bands at $\lambda_{max} =$ 1692–1685 (C=O), 1592 (C=N) and 1490 cm^{-1} (C=C). The ^{13}C NMR spectrum of **7a** showed carbonyl carbon signals at $\delta_C = 160.9$, 174.6 and 177.0 corresponding to N*C*O, *C*-4 and -7, respectively. Besides, five distinctive carbon signals were recognized at $\delta_C = 150.0$, 140.0, 139.0, 132.8 and 133.0 related to *C*-2, Ar−*C*−OCH_3, Ar−*C*−N, *C*-3′ and -7′, respectively.

Most indicative was in **7a** the appearance of aromatic protons as two doublets of doublets and four multiplets. The two doublets of doublets were assigned to the *para*-substituted aryl protons and they appeared at $\delta_H = 6.85$ (*J* 8.0, 1.2 Hz) and 8.20 (*J* 7.8, 1.3 Hz). In addition, the



7	X	R	Yield (%)
a	Cl	OMe	70
b	Cl	Me	65
c	Cl	H	60
d	CN	OMe	68
e	CN	Me	65
f	CN	H	63
g	-CH=CH-CH=CH-	OMe	78
h	-CH=CH-CH=CH-	Me	74
i	-CH=CH-CH=CH-	H	70

SCHEME 1 Synthesis of various (*E*)-[3-aroyl-2-phenylimino]-2,3-dihydrobenzo- and napthothiazolediones **7a–i**.

methoxy protons appeared at $\delta_H = 3.85$, whereas the corresponding carbon signal appeared at $\delta_C = 51.0$ (see the Experimental section). In **7d–f**, the IR spectra showed broad absorption bands at $\lambda_{max} = 2220–2210$ and 1694–1682 cm^{-1} corresponding to the cyano and carbonyl groups, respectively. The δ_H values of the aromatic protons in the ^1H NMR spectrum of **7d–f** were not considerably deshielded compared with those in **7a–c**. The ^{13}C NMR spectrum of **7d**, as an example, revealed two very close cyano carbon signals at $\delta_C = 113.2$ and 113.4. The spectroscopic data confirmed that we have in hand compounds **7a–i** and excluded any other suggestions such as the formation of compounds **6a–i** (scheme 1). According to semi-empirical calculations using the MM2 level of theory [28], compounds **7a–i** are found in *anti*-form which is more energtically stable. For example, the minimized calculated steric energy for the *syn*(*Z*) form of **7f** is 35.3 kcal/mol, whereas this energy for its *anti*(*E*) form is 32.9 kcal/mol.

The reactions of the quinone π-acceptors **4a–c** with **5a–c**, indeed, showed a type of tautomerism between the NH and the C=S into the N=C−SH groups in **5a–c**, under our reaction conditions. Thereafter, the SH group adds to the C-2 of the quinone accompanied by elimination of HCl to produce **9a–i** (scheme 2). Then, another nucleophilic attack of the remaining aromatic NH to the C-3 in **9a–i**, followed by elimination of another molecule of HCl, gives the stable heterocyclic compounds **7a–i**. It is believed that attachment by the SH group proceeds faster compared to the aromatic amine, therefore we propose that the reaction can be shown by the steps as in scheme 2.

We have thus demonstrated a very convenient procedure to synthesize fused thiazoles from the reaction of aroylphenylthioureas with π-acceptor quinones. The advantages of this method are the reasonable yields and the ease with which the reaction can be carried out as a

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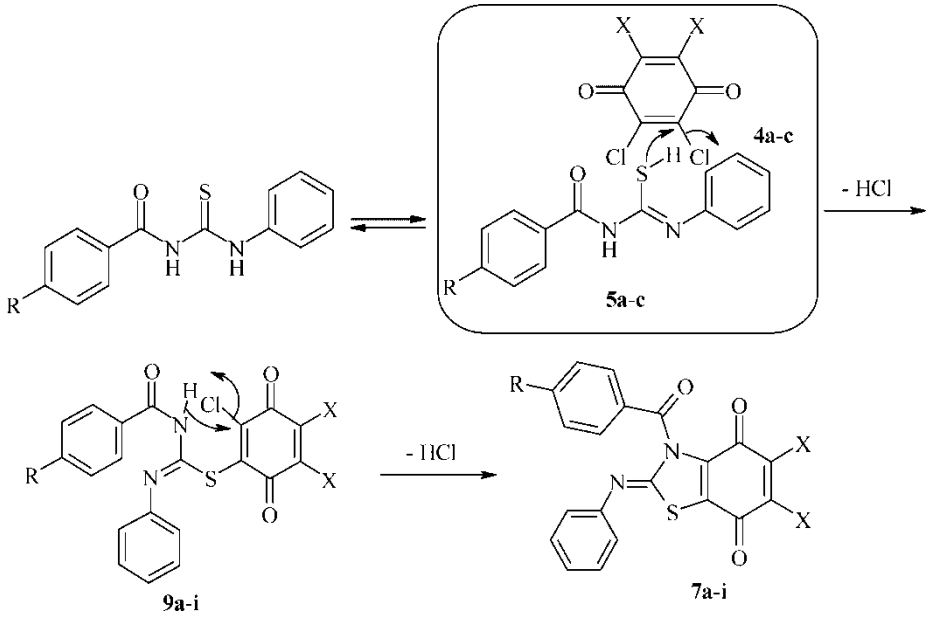

SCHEME 2 Mechanistic pathways in the synthesis of fused thiazoldiones **7a–i**.

one-pot procedure with readily available starting materials. New fused thiazoles will continue to contribute to fascinating developments in the field of heterocyclic chemistry.

3. Experimental section

3.1 *General information*

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra (Bruker AM 400, ^{1}H: 400.13 MHz, ^{13}C: 100.6 MHz) were obtained from DMSO-d_6 solutions. Coupling constants are expressed in Hz. Elemental analyses were carried at the Assuit Microanalysis Center of Assuit University. Mass spectroscopy was performed with a Finnigan MAT 8430 spectrometer at 70 eV, Institute of Organic Chemistry, Technical University-Braunschweig, Germany. IR spectra were run on a Shimadzu 470 spectrometer using KBr pellets.

3.2 *Starting materials*

Aroylphenylthioureas **5a–c** were prepared according to the literature [29]. 2,3,4,6-Tetrachloro-1,4-benzoquinone (CHL-*p*, **4a**) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, **4b**) were bought from Merck, whereas 2,3-dichloro-1,4-naphthoquinone (**4c**, DCHNQ) was bought from Fluka.

3.3 *General procedure*

A 250 cm^3 two-necked round bottom flask was flame-dried under N_2 atmosphere and then cooled to room temerature. Into this flask, were placed dry dimethylformamide (100 mL) and 2 mmols of both **4a–c** and **5a–c**. The mixture was gently refluxed under stirring for 10–14 h

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(the reaction was monitored by TLC analyses). The solvent was evaporated to a third of its volume and the precipitate formed was filtered off. Compounds **7a–i** were obtained after recrystallization from the stated solvents.

3.3.1 5,6-Dichloro-(*E*)-[3-(4′-methoxybenzoyl)-2-phenylimino]-2,3-dihydro-1,3-benzothiazole-4,7-dione (7a). Was obtained as yellow crystals (0.64 g, 70%), mp 238–240 °C (DMF/ethanol).

δ_H (400 MHz, DMSO-d_6): 3.85 (3 H, s, OCH_3), 6.85 (2 H, dd, *J* 8.0, 1.2 Hz), 7.34–7.42 (1 H, m), 7.59–7.65 (2 H, m), 7.95–8.07 (2H, m), 8.20 (2 H, dd, *J* 7.8, 1.3 Hz). δ_C (100.6 MHz, DMSO-d_6): 51.0 (OCH_3), 124.6 (*C*-5), 126.0 (*C*-6), 126.8 (Ph−*C*H, *C*H-4′), 127.2, 128.0, 128.7 (2 Ar−*C*H), 132.8, 133.0 (Ar−*C*-3′ and -7′), 134.0 (Ar−*C*−CO), 134.6 (2 Ar−*C*H), 139.0 (Ar−*C*−N), 140.0 (Ar−*C*−OCH_3), 150.0 (*C*-2), 160.9 (N*C*O), 174.6 (*C*-4), 177.0 (*C*-7). ν_{max} (cm^{-1}): 3040–2980 (Ar−CH, w), 2950–2870 (aliph.−CH, m), 1692–1685 (C=O, s), 1592 (C=N, s), 1490 (C=C, m), 1450 (s), 920 (m). λ_{max} (CH_3CN, lg ε, nm): 420 (3.9). EI + mass spectrum (m/z, %): 461 ([M + 2], 28%), 459 ([M^+], 100%), 458 (30%), 428 (22%), 388 (20%), 360 (22%), 354 (26%), 325 (48%), 323 (50%), 238 (62%), 236 (60%), 159 (48%), 136 (20%), 129 (18%), 91 (22%), 77 (20%). C H N (%): found C 54.85, H 2.60, Cl 15.33, N 6.15, S 7.00. $C_{21}H_{12}Cl_2N_2O_4S$ requires C 54.92, H 2.63, Cl 15.44, N 6.10, S 6.98.

3.3.2 5,6-Dichloro-(*E*)-[3-(4′-methylbenzoyl)-2-phenylimino]-2,3-dihydro-1,3-benzothiazole-4,7-dione (7b). Was obtained as yellow crystals (0.58 g, 65%), mp 268–270 °C (ethanol).

δ_H (400 MHz, DMSO-d_6): 2.30 (3 H, s, CH_3), 6.80 (2 H, dd, *J* 8.0, 1.4 Hz), 7.25–7.28 (1 H, m), 7.54–7.60 (2 H, m), 7.70–7.80 (2 H, m), 8.12 (2 H, dd, *J* 8.0, 1.4 Hz). δ_C (100.6 MHz, DMSO-d_6): 2.8 (CH_3), 124.2 (*C*-5), 126.4 (*C*-6), 126.4 (Ph−*C*H, *C*H-4′), 127.0, 128.2, 128.5 (2 Ar−*C*H), 129.7, 132.0 (Ar−*C*-3′ and -7′), 133.6 (Ar−*C*−CO), 134.0 (2 Ar−*C*H), 134.6 (Ar−*C*−CH_3), 138.9 (Ar−*C*−N), 149.6 (*C*-2), 160.4 (N*C*O), 174.6 (*C*-4), 176.8 (*C*-7). ν_{max} (cm^{-1}): 3030–2970 (Ar−CH, w), 2930–2890 (aliph.−CH, m), 1690–1682 (C=O, s), 1590 (C=N, s), 1490 (C=C, m), 1450 (s), 920 (s). λ_{max} (CH_3CN, nm, lg ε): 416 (3.7). EI + mass spectrum (m/z, %): 445 ([M + 2], 28%), 443 ([M^+], 100%), 442 (26%), 428 (24%), 406 (18%), 395 (28%), 365 (18%), 323 (54%), 246 (24%), 234 (44%), 136 (24%), 129 (20%), 91 (24%), 77 (18%). C, H, N (%): found C 56.80, H 2.70, Cl 15.90, N 6.30, S, 7.30. $C_{21}H_{12}Cl_2N_2O_3S$ requires C 56.90, H 2.73, Cl 15.99, N 6.32, S 7.23.

3.3.3 5,6-Dichloro-(*E*)-[3′-benzoyl-2-phenylimino]-2,3-dihydro-1,3-benzothiazole-4,7-dione (7c). Was obtained as pale yellow crystals (0.51 g, 60%), mp 215–217 °C (ethyl acetate).

δ_H (400 MHz, DMSO-d_6): 6.72–6.90 (3 H, m), 7.50–7.60 (2 H, m), 7.72–8.00 (3 H, m), 8.14 (2 H, dd, *J* 8.0, 1.4 Hz). δ_C (100.6 MHz, DMSO-d_6): 124.0 (*C*-5), 126.0 (*C*-6), 126.0, 126.8 (Ar−*C*H), 127.0, 127.4, 128.0 (2 Ar−*C*H), 130.8, 132.0 (Ar−*C*-3′ and -7′), 134.0 (Ar−*C*−CO), 134.0 (2 Ar−*C*H), 138.0 (Ar−*C*−N), 148.5 (*C*-2), 160.4 (N*C*O), 174.2 (*C*-4), 176.0 (*C*-7). ν_{max} (cm^{-1}): 3046–2980 (Ar−CH, m), 1690–1680 (C=O, s), 1592 (C=N, s), 1494 (C=C, m), 1440 (m), 920 (m). λ_{max} (CH_3CN, nm, lg ε): 412 (3.6). EI + mass spectrum (m/z, %): 431 ([M + 2], 28%), 429 ([M^+], 100%), 427 (28%), 393 (28%), 358 (24%), 324 (52%), 244 (40%), 236 (60%), 212 (22%), 176 (18%), 129 (24%), 105 (56%), 91 (26%), 77 (60%). C, H, N (%): found C 55.90, H 2.29, Cl 16.50, N 6.48, S 7.42. $C_{20}H_{10}Cl_2N_2O_3S$ requires C 55.96, H 2.35, Cl 16.52, N 6.53, S 7.47.

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3.3.4 5,6-Dicyano-(*E*)-[3-(4′-methoxybenzoyl)-2-phenylimino]-2,3-dihydro-1,3-benzothiazole-4,7-dione (7d). Was obtained as yellow crystals (0.60 g, 68%), mp 256–258 °C (acetone).

δ_H (400 MHz, DMSO-d_6): 3.90 (3 H, s, OCH_3), 6.85 (2 H, dd, *J* 8.0, 1.2 Hz), 7.34–7.42 (1 H, m), 7.59–7.65 (2 H, m), 7.95–8.07 (m, 2 H), 8.20 (dd, 2 H, *J* = 7.8, 1.3 Hz). δ_C (100.6 MHz, DMSO-d_6): 51.0 (O*C*H$_3$), 113.2, 113.4 (CN), 123.5 (*C*-5), 124.6 (*C*-6), 126.8 (Ph−*C*H, *C*H-4′), 127.2, 128.0, 128.7 (2 Ar−*C*H), 132.0, 132.8 (Ar−*C*-3′, -7′), 134.0 (Ar−*C*−CO), 134.6 (2 Ar−*C*H), 139.0 (Ar−*C*−N), 140.0 (Ar−*C*−OCH$_3$), 150.0 (*C*-2), 160.9 (N*C*O), 174.0 (*C*-4), 175.5 (*C*-7). ν_{max} (cm^{-1}): 3040–2980 (Ar-CH, m), 2950–2870 (aliph.−CH, m), 1692–1685 (C=O, s), 1592 (C=N, s), 1490 (C=C, m), 1450 (s), 920 (m). λ_{max} (CH$_3$CN, nm, lg ε): 420 (3.9). EI + mass spectrum (m/z, %): 440 [M$^+$], 100), 425 (18%), 410 (28%), 334 (34%), 304 (58%), 280 (16%), 190 (34%), 176 (20%), 144 (40%), 129 (24%), 105 (40%), 91 (24%), 77 (26%). C, H, N (%): found C 62.80, H 2.70, N 12.80, S 7.30. $C_{23}H_{12}N_4O_4S$ requires C 62.72, H 2.75, N 12.72, S 7.28.

3.3.5 5,6-Dicyano-(*E*)-[3-(4′-methylbenzoyl)-2-phenylimino]-2,3-dihydro-1,3-benzothiazole-4,7-dione (7e). Was obtained as pale brown crystals (0.55 g, 65%), mp 240–242 °C (ethyl acetate).

δ_H (400 MHz, DMSO-d_6): 2.40 (3 H, s, *C*H_3), 6.80 (2 H, dd, *J* 8.0, 1.4 Hz), 7.32–7.40 (1 H, m), 7.60–7.64 (2 H, m), 7.92–8.04 (2 H, m), 8.22 (2 H, dd, *J* 7.8, 1.3 Hz). δ_C (100.6 MHz, DMSO-d_6): 23.4 (*C*H$_3$), 113.0, 113.2 (CN), 123.2 (*C*-5), 124.2 (*C*-6), 126.6 (Ph−*C*H, CH-4′), 127.0, 128.2, 128.4 (2 Ar−*C*H), 132.6, 132.8 (Ar−*C*-3′ and -7′), 134.2 (Ar-*C*-CO), 134.0 (2 Ar-*C*H), 134.4 (Ar−*C*−CH$_3$), 139.6 (Ar-*C*-N), 150.4 (*C*-2), 160.6 (N*C*O), 173.9 (*C*-4), 175.8 (*C*-7). ν_{max} (cm^{-1}): 3052–2976 (Ar-CH, m), 2980–2890 (aliph.−CH, m), 2220–2212 (CN, m), 1690–1682 (C=O, s), 1590 (C=N, m), 1490 (C=C, m), 1452 (m), 922 (m). λ_{max}(CH$_2$Cl$_2$, nm, lg ε): 416 (3.6). EI + mass spectrum (m/z, %): 424 ([M$^+$], 100%), 410 (28%), 372 (26%), 346 (24%), 304 (48%), 278 (18%), 252 (24%), 190 (30%), 176 (18%), 144 (20%), 129 (18%), 105 (54%), 91 (16%), 77 (20%). C, H, N (%): found C, 65.00; H, 2.80; N, 13.24; S, 7.60. $C_{23}H_{12}N_4O_3S$ requires C 65.09, H 2.85, N 13.20, S 7.55.

3.3.6 5,6-Dicyano-(*E*)-[3-benzoyl-2-phenylimino]-2,3-dihydro-1,3-benzothiazole-4,7-dione (7f). Was obtained as red crystals (0.52 g, 63%), mp > 300 °C (DMF/ethanol).

δ_H (400 MHz, DMSO-d_6): 6.65–6.84 (3 H, m), 7.46–7.58 (2 H, m), 7.70–7.96 (3 H, m), 8.18 (2 H, dd, *J* 8.0, 1.2 Hz). δ_C (100.6 MHz, DMSO-d_6): 112.2, 112.6 (CN), 123.0 (*C*-5), 124.0 (*C*-6), 126.2, 126.4 (Ar−*C*H), 127.0, 127.2, 127.4 (2 Ar−*C*H), 132.0, 132.4 (Ar−*C*-3′ and -7′), 134.0 (Ar−*C*−CO), 134.4 (2 Ar−*C*H), 139.2 (Ar−*C*−N), 148.8 (*C*-2), 160.8 (N*C*O), 174.8 (*C*-4), 175.0 (*C*-7). ν_{max} (cm^{-1}): 3050–2960 (Ar−CH, w), 2218–2210 (CN), 1690–1680 (C=O, s), 1590 (C=N, m), 1498 (C=C, s), 1440 (s), 920 (s). λ_{max} (CH$_2$Cl$_2$, nm, lg ε): 410 (3.4). EI + mass spectrum (m/z, %): 410 [M$^+$], 100%), 384 (30%), 358 (18%), 332 (24%), 304 (48%), 228 (60%), 214 (20%), 176 (24%), 129 (20%), 105 (62%), 91 (24%), 77 (24%). C, H, N (%): found C 64.50, H 2.50, N 13.60, S, 7.80. $C_{22}H_{10}N_4O_3S$ requires C 64.39, H 2.46, N 13.65, S 7.81.

3.3.7 (*E*)-[3-(4′-Methoxybenzoyl)-2-phenylimino]-2,3-dihydro-naphtho-[2,3-*d*] thiazole-4,9-dione (7g). Was obtained as orange crystals (0.69 g, 78%), mp 280–282 °C (DMF/ethanol).

δ_H (400 MHz, DMSO-d_6): 3.92 (3 H, s, OCH$_3$), 6.82 (2 H, dd, *J* 8.0, 1.4 Hz), 7.35–7.45 (2 H, m), 7.50–7.65 (3 H, m), 7.72–7.80 (3 H, m), 7.94–8.07 (2 H, m), 8.24 (1 H, dd, *J* 8.0, 1.4 Hz).

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δ_C (100.6 MHz, DMSO-d_6): 51.6 (O*C*H_3), 126.8 (Ph−*C*H−4′), 127.0, 128.2 (2 Ph−*C*H), 128.6 (2 Ar−*C*H-2′), 129.2, 129.8, 130.6, 132.0 (naph-*C*H), 132.4, 132.8 (Ar−*C*-3′, -9′), 133.4, 134.2 (*C* − 4′ and -8′), 134.8 (Ar−*C*−CO), 136.0 (2 Ar−*C*H-3′), 139.4 (Ar−C−N), 142.0 (Ar−C−OCH_3), 154.0 (*C*-2), 162.9 (N*C*O), 174.4 (*C*-4), 176.0 (*C*-7). ν_{max} (cm^{-1}): 3065–2960 (Ar−CH, m), 2950–2870 (aliph.−CH, m), 1690–1682 (C=O, s), 1600 (C=N, s), 1520 (C=C, m), 1420 (m), 920 (s). λ_{max} (CH_3CN, nm, lg ε): 460 (4.4). EI + mass spectrum (m/z, %): 440 ([M^+], 100%), 424 (22%), 410 (18%), 363 (30%), 335 (16%), 303 (22%), 136 (24%), 106 (40%), 77 (22%), 51 (20%). C, H, N (%): found C 68.05, H 3.60, N 6.30, S 7.34. $C_{25}H_{16}N_2O_4S$ requires C 68.17, H 3.66, N 6.36, S 7.28.

3.3.8 (*E*)-[3-(4′-Methylbenzoyl)-2-phenylimino]-2,3-dihydro-naphtho-[2,3-*d*]thiazole-4,9-dione (7h). Was obtained as yellow crystals (0.63 g, 74%), mp 290–292 °C (DMF/ethanol).

δ_H (400 MHz, DMSO-d_6): 2.40 (3 H, s, CH_3), 6.80 (2 H, dd, *J* 8.0, 1.4 Hz), 7.32–7.42 (2 H, m), 7.50–7.64 (3 H, m), 7.70–7.76 (3 H, m), 7.90–8.04 (2 H, m), 8.20 (dd, 1 H, *J* 8.0, 1.4 Hz). δ_C (100.6 MHz, DMSO-d_6): 22.8 (*C*H_3), 126.4 (Ph−*C*H-4′), 127.2, 128.0 (2 Ph−*C*H), 128.4 (2 Ar−*C*H-2′), 129.0, 129.4, 130.2, 132.2 (naph-*C*H), 132.6, 133.0 (Ar−*C*-3′, -9′), 133.2, 134.0 (C-4′ and −8′), 134.6 (Ar−*C*−CO), 135.8 (2 Ar−*C*H-3′), 138.6 (Ar−*C*−CH_3), 139.0 (Ar−*C*−N), 154.0 (*C*-2), 162.8 (N*C*O), 174.6 (*C*-4), 176.6 (*C*-9). ν_{max} (cm^{-1}): 3060–2940 (Ar−CH, m), 2940–2850 (aliph.−CH, m), 1692–1680 (C=O, s), 1600 (C=N, m), 1520 (C=C, m), 1422 (m), 920 (s). λ_{max} (CH_3CN, nm, lg ε): 448 nm (4.2). EI + mass spectrum (m/z, %): 424 ([M^+], 100%), 409 (22%), 365 (20%), 346 (40%), 325 (18%), 304 (20%), 226 (14%), 136 (20%), 105 (46%), 77 (24%), 51 (20%). C, H, N (%): found C 70.60, H 3.80, N 6.60, S 7.48. $C_{25}H_{16}N_2O_3S$ requires C 70.74, H 3.80, N 6.60, S 7.55.

3.3.9 (*E*)-[3-Benzoyl-2-phenylimino]-2,3-dihydro-naphtho-[2,3-*d*]thiazole-4,9-dione (7i). Was obtained as orange crystals (0.57 g, 70%), mp >300 °C (ethanol).

δ_H (400 MHz, DMSO-d_6): 6.80–7.40 (5 H, m), 7.60–7.72 (5 H, m), 7.90–8.18 (4 H, m). δ_C (100.6 MHz, DMSO-d_6): 125.4 (bz−*C*H-4′), 126.0 (Ph−*C*H-4′), 126.8 (2 Ph−*C*H), 127.0 (2 bz-*C*H-2′), 127.6 (2 Ph−*C*H), 128.0 (2 bz-*C*H-3′), 128.4, 128.8, 129.4, 130.8 (naph-*C*H), 131.8, 132.4 (Ar−*C*-3′ and 9′), 133.0, 133.6 (*C*-4′ and -8′), 134.4 (Ar−*C*−CO), 139.0 (Ar−*C*−N), 150.6 (*C*-2), 162.6 (N*C*O), 174.2 (*C*-4), 176.0 (*C*-9). ν_{max} (cm^{-1}): 3060–2976 (Ar−CH, s), 1690–1680 (C=O, s), 1590 (C=N, m), 1490 (C=C, m), 1450 (m), 920 (s). λ_{max}, (CH_3CN, nm, lg ε): 434 (3.6). EI + mass spectrum (m/z, %): 410 ([M^+], 100%), 332 (40%), 305 (56%), 290 (18%), 214 (22%), 182 (18%), 136 (24%), 105 (80%), 91 (24%), 77 (30%). C, H, N (%): found C 70.20, H 3.50, N 6.90, S 7.90. $C_{24}H_{14}N_2O_3S$ requires C 70.23, H 3.44, N 6.82, S 7.81.

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Acknowledgement

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

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