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RESEARCH ARTICLE

Indazole, oxathiadiazole, and thiadiazine derivatives from thiosemicarbazides

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4-Substituted thiosemicarbazides **1a–c** reacted with 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ, **2**), 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL-*p*, **6**) and 2,3-dichloro-1,4-naphthoquinone (DCHNQ, **7**) in ethyl acetate with admission of air and form the derivatives of 1,5,2,3-oxathiadiazole **8a–c**, indazole **9a–c**, 1,3,4-thiadiazine-6-one **10a–c**, 1,3,4-thiadiazaphenanthren-9-one **11a–c**, naphtho[1,2-*e*:4,3-è]bis[1,3,4]thiadiazine **12** and dibenzo[*b,i*]thianthrene-5,7,12,14-tetraone **13**. A rationale for the conversions observed is presented.

Keywords: Thiosemicarbazides; Quinones; Indazole; Oxathiadiazole derivatives; Thiadiazine derivatives

1. Introduction

The chemistry of nucleophilic substitution of halogenated *p*-quinones continues to be of interest for the synthesis of many heterocycles. 2,3,5,6-Tetrachlorobenzoquinone (chloranil, **6**) and 2,3-dichloro-1,4-naphthoquinone **7** undergo substitution of one or two chlorine atoms by primary amines [1–3], aminoacids [4], and aziridines [5, 6] as well as bisamines [7]. In the reactions of **6** and **7** with pyrazoles [8–10], imidazoles [8] and triazoles [8, 11–13] all chlorine atoms present may be replaced by the heterocyclic residues. 2,5-Bis(arylamino)-3,6-dichloro-*p*-benzoquinones have been used to synthesize triphenodioxazines [14]. Amides and thioamides were added to **6** and **7** to produce two related heterocyclic dione series in excellent yield [15–21]. The reaction of **6** and **7** with N^1,N^2-diaryl-amidines to give benzimidazole and indole derivatives has been reported [22, 23]. Heterocyclization of thiosemicarbazide and dithiocarbazate derivatives during the reaction with benzo- and naphthoquinones as well as α-haloketones, different successful approach for the synthesis of thiadiazole [9, 10], thiadiazine [9, 10, 24–28], oxathiadiazole [29] and pyrazolophthalazinol [29] derivatives.

Recently, it has been reported that 4-phenyl- and 4-benzylthiosemicarbazides **1a,b** reacted with **2** in ethyl acetate with charge-transfer complex (CT) formation, ultimately giving a mixture of oxathiadiazole and 1,2,3,4-dithiadiazole-2,2-dioxide derivatives **3**, **4** (scheme 1) [30].

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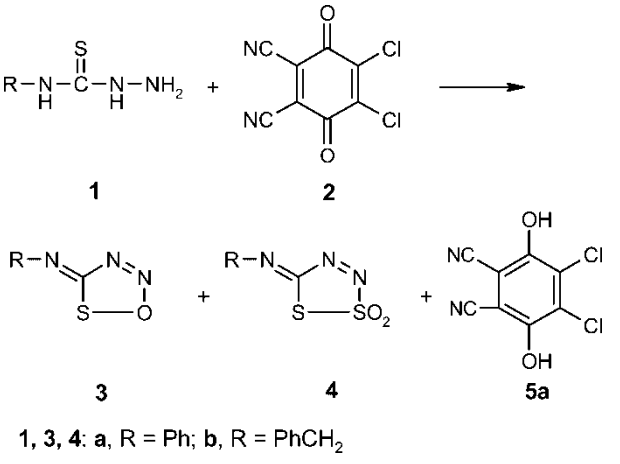


SCHEME 1 Previous work on the reaction of **2** with 4-substituted thiosemicarbazides **1a**,**b**.

2. Result and discussion

We report here the results of our recent investigations on the reaction of 4-substituted thiosemicarbazides **1a–c** with benzo- and naphthoquinones **2, 6** and **7**. These results are compared with those obtained earlier [30]. Equimolar solutions of **2** and **1a–c** in ethyl acetate, upon standing for 48 hours at room temperature, formed oxathiadiazole **8a–c** as major products (21–26%) and indazole derivatives **9a–c** as minor products (11–18%) in addition to the hydroquinone (**5a**) (figure 1).

In an attempt to improve the yield of **8** and **9**; **2** was treated with two equivalent of **1a–c** under the same experimental condition. The oxathiadiazole and indazole derivatives **8** and **9** were obtained in (34–38%) and (23–27%) yield, respectively (table 1).

The structural assignment of oxathiadiazole **8a** is based on the following spectral data: the IR spectrum showed a broad band at υ_{max} 3355, 3320 and 1620 cm^{-1} for the (NH) and (C=N) groups, respectively. The ^1H NMR displayed two broad singlet one at δ 8.58 ppm and the other at 11.85 ppm due to (NHPh) and (oxathiadiazole-NH). The ^{13}C NMR spectrum showed only one carbon at δ 157.18 ppm for (oxathiadiazole-C-4) in addition to the aromatic carbons. The mass spectrum and the satisfactory elemental analysis confirmed its structure assignments.

The IR spectrum (KBr) of **9c** showed characteristic absorption for the hydroxyl and (NH) groups at υ_{max} 3410–3230 cm^{-1}, whereas at 2220 cm^{-1} for the cyano group. The ^1H NMR

Table 1. The reaction of thiosemicarbazides **1a–c** with benzo-and naphthoquinones **2**, **6** and **7***.

Reaction	Molar ratio	Time (h)	Products (yield %)
1a + **2**	2:1	48	**5a** (34) + **8a** (38) + **9a** (19)
1a + **2**	2:1	48	**5a** (31) + **8b** (35) + **9b** (17)
1a + **2**	2:1	48	**5a** (37) + **8a** (34) + **9c** (16)
1a + **6**	1:1	72	**5b** (29) + **8a** (41) + **10a** (19)
1a + **6**	1:1	72	**5b** (32) + **8b** (38) + **10b** (17)
1a + **6**	1:1	72	**5b** (37) + **8c** (35) + **10c** (16)
1a + **7**	1:1	72	**11a** (22) + **12a** (31) + **13** (36)
1a + **7**	1:1	72	**11b** (19) + **12b** (30) + **13** (38)
1a + **7**	1:1	72	**11c** (20) + **12c** (28) + **13** (39)

*Ethyl acetate was used as the solvent for all the reaction and at room temperature.

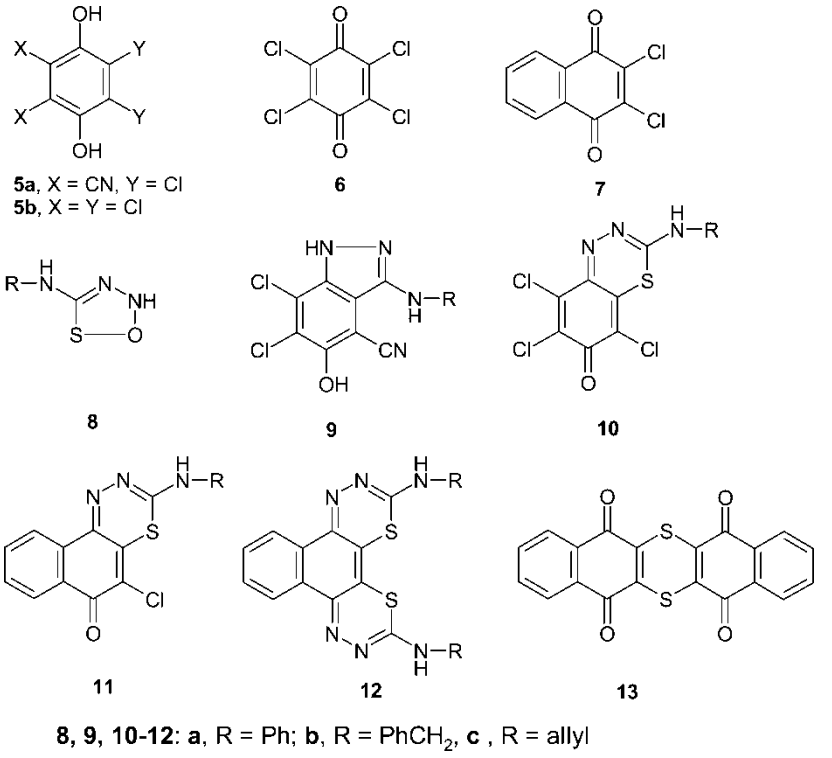


Figure 1. New products formed during the reaction of 4-substituted thiosemicarbazides and benzo- as well as naphthoquinones.

spectrum showed three broad signals at δ 7.52, 9.41 and 11.40 due to (allyl-NH), (OH) and (indazole-NH), respectively. The ^{13}C NMR decoupling showed a signal at δ 154.33 ppm for aromatic quaternary carbon atom bearing a hydroxyl group [31], signals at 121.48, 121.93 and 153.88 for indazole (C-6, 7 and 3) in addition to signals at 43.42, 114.93 and 134.87 for (allyl-CH_2N), (allyl-CH_2=) and (allyl-CH=), respectively.

Addition of ethyl acetate solution of **1a–c** to equimolar quantity of another electron poor (chloranil, **6**) in ethyl acetate upon standing for 72 hours with admission of air at room temperature, a green color was observed which gradually changed to brown. When the reaction was followed spectrophotometrically an absorption maximum was observed in the visible region at 588–562 nm and was assigned to the formation of an unstable charge-transfer complex (CTC), since both the thiosemicarbazides **1a–c** and chloranil **6** alone did not absorb in this region.

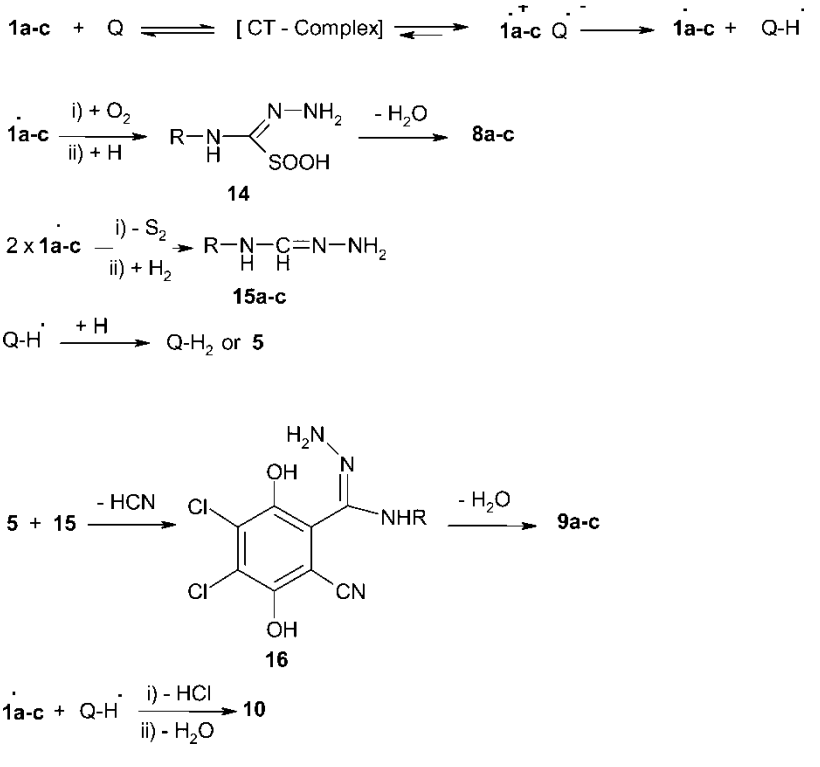
The separation of the reaction mixture by preparative layer chromatography (plc) yielded the oxathiadiazole **8a-c** (35–41%), the thiadiazine **10** (16–19%) and 2,3,5,6-tetrachloro-1,4-hydroquinone (**5b**) (26–29%). The IR spectrum of **10a** showed sharp band at υ_{max} 3330 cm^{-1} and 1680 cm^{-1} for the secondary amino group and one of the carbonyl group of the quinone system respectively. The ^{1}H NMR spectrum revealed a broad singlet δ 8.67 ppm for the (NHPh) proton and a multiplet at 7.12–7.54 ppm, which is characteristic of phenyl protons. The ^{13}C NMR spectrum showed the presence of one carbonyl group at δ 170.11 ppm and (thiadiazine-C-3 and C-8a) at 158.94 ppm and 159.73 ppm, respectively. The structure of **10a** was evidently confirmed by mass spectrometrically. Besides the molecular ion at m/z 363/357, the characteristic fragment ion pattern of the substituted trichloro compounds was observed [32].

The formation of the products observed may be rationalized as in scheme 2. At first an unstable CTC is formed followed by the formation of radicals **1**˙ **a–c** and **Q-H**˙. The radical ˙**1a–c** pick up a molecule of oxygen followed by abstraction of hydrogen atom to give the intermediate **14** which cyclize to oxathiadiazole **8a–c** after elimination a molecule of H_2O. On the other hand, the radical **1**˙**a–c** being a precursor to compound **15** which could be reacted with hydroquinone **5a** with elimination a molecule of HCN and another of H_2O to give the indazole derivatives **9a–c**.

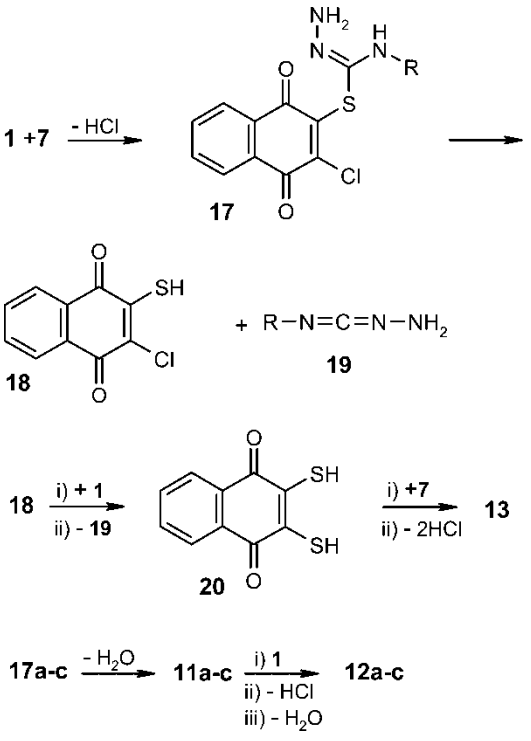
2,3-Dichloro-1,4-naphthoquinone **7** was chosen to compare its reactivity towards the thiosemicarbazides **1a–c** with chloranil **6**. As it has been described in the literature that the **7** resembles **6** in most of its substitution reactions, especially with compounds containing nucleophilic nitrogen (amines, amino acids, pyrazoles, imidazoles, etc) [1–13]. From this point of view one might expect that thiosemicarbazides **1a–c** should react with **6** similarly like **7**, but the results were completely different. Not only the electron affinity of the acceptors is the reason for the instability of the CT-complexes and subsequent chemical reaction but also the ease of undergoing reduction to hydroquinones as an important factor.

Mixing equimolar amounts of **1a–c** and **7** in ethyl acetate for 72 hours led to the formation of thiadiazine, naphthobisthiadiazine derivatives as well as dibenzo[*b*,*i*]thianthrene-5,7,12,14-tetraone (**11**–**13**) (scheme 3).

Assignment of **12a–c** and **13a–c** were based on their spectral data. The thiadiazine derivative **11a** exhibited two IR-absorption bands at υ_{max} 3360 cm^{-1} (secondary amine) and 1690 cm^{-1} (carbonyl group of naphthoquinone), respectively. The ^{13}C NMR spectrum showed absorption



SCHEME 2 A rationale for the formation of products **8–10**.



SCHEME 3 A rationale for the formation of products **11**–**13**.

signals at δ 156.12 ppm and 158.93 ppm for (thiadiazine-C-2,4a) as well as two signals at 124.18 ppm and 177.83 ppm for (thiadiazine-C-10a) and ketonic carbon atom.

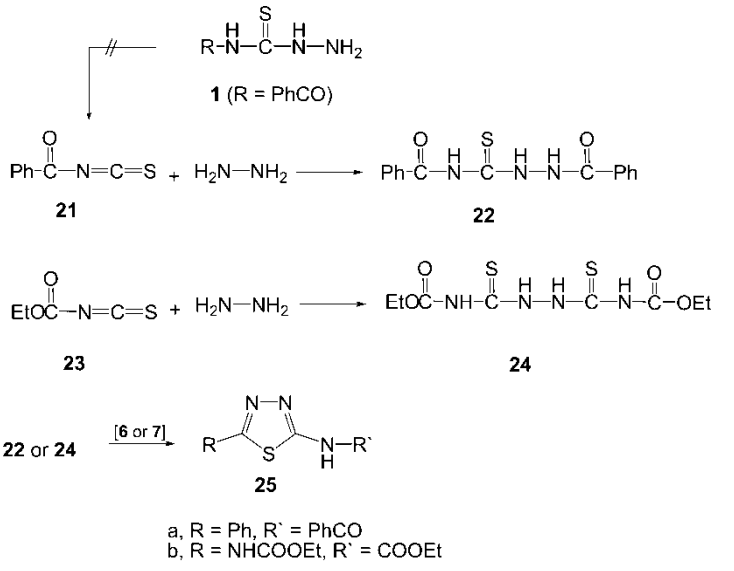
Upon transformation of **11a** to **12a**, the naphthoquinone (C=O) absorption is replaced by a new IR band at υ_{max} 1630 cm^{-1} (C=N) and the ^{13}C NMR spectrum clearly shows the absence of carbonyl group, further signals in the experimental part. Several alternative structures based on the same elemental composition could be eliminated according to previous ^{1}H NMR and ^{13}C NMR spectral data.

In the most cases the presence of air is very important to allow the formation of the reaction products, because under argon the interaction between benzo- or naphthoquinones (**2**, **6**, **7**) and thiosemicarbazides **1a–c** does give CT-complexes which decompose and do not follow the previous sequence of chemical reactions.

The formation of structure products **11–13** may be rationalized through the successive substitution of both chlorine atoms *via* the intermediates **16–19**.

On the other hand, mixing equimolar amounts of each of hydrazine and benzoylisothiocyanate (**21**) in DMF at room temperature resulted in an excellent yield of 1,4-dibenzoylthiosemicarbazide (**22**) rather than in the formation of compound **1** (R=PhCO) [33]. Also, mixing equimolar amounts of hydrazine and ethoxycarbonylisothiocyanate (**23**) in DMF at room temperature gave 1,6-bis-(ethoxycarbonyl)bithiourea **24** (scheme 4) [34].

Compounds **22** and **24** were too sparingly soluble in ethyl acetate as the solvent of reaction with **2**, **6** and **7**, but soluble in DMF. Treatment of **22** or **24** with two molar equivalents of **2** in DMF resulted in formation of a precipitate, which by washing with ethyl acetate yielded a dark-brown solid, which in turn, did not melt below 350 °C, was insoluble in all common solvents and was not characterized further. The formation of polymers from **2** in the presence



SCHEME 4 Products formed during the reaction of 1,4-dibenzoylthiosemicarbazide **22** and 1,6-bis-(ethoxycarbonyl)bithiourea **24** with **6** and **7**.

of alcohols, phenols and amines has been observed [35] and most of the nitrile groups seem to be involved in the polymerization [36].

Addition of two equivalents of **6** or **7** to a solution of **22** or **24** in DMF as a solvent at room temperature resulted in a green colouration of the solution that quickly turned into brown. Concentration of the preparative runs resulted in formation of colourless precipitates of thiadiazole derivatives **25a** [37] and **25b** [34].

3. Conclusion

The reactions and products presented here provide insight into the spontaneous reactions between the electron donating thiosemicarbazides **1a–c** and electron acceptors; benzo- as well as naphthoquinones **2**, **6** and **7**. In a fairly complex and multistep process, an interesting heterocyclic compounds (indazole, oxathiadiazole and thiadiazine derivatives) are formed from **1a–c**. The results reported were supplement the rich chemistry of thiosemicarbazides **1a–c.**

4. Experimental section

4.1 *General information*

Melting points have been determined using open capillaries on a Gallen Kamp melting point apparatus and are uncorrected. Elemental analyses were determined by Microanalytical Center, Cairo University, Egypt. The IR spectra were recorded with Shimadzue 408 or Bruker Vector 22 FT-IR instruments using potassium bromide. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra (DMSO-d_6 and $CDCl_3$ as solvents, TMS as internal standard) were obtained on a Bruker WM 300 instrument. Assignment of carbon resonances has been supported by DEPT

experiments. Mass spectra were recorded on a double focussing AMD 604 spectrometer in EI Mode at (70 eV) ionization energy. UV-vis spectra were measured on a Perkin-Elmer Lambda 2 spectrophotometer using 1.0 cm stoppered silica cells. Preparative layer chromatography (plc) used air dried 1.0 mm thick layers of slurry applied silica gel, Merck Pf_{254} on 48 cm wide and 20 cm high glass plates using the solvents listed. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm light and eluted with acetone.

4.2 *Starting materials*

2,3-Dicyano-5,6-dichloro-1,4-benzoquinone (DDQ, **2**), 2,3,5,6-tetra-chloro-1,4-benzoquinone (chloranil, **6**) and 2,3-dichloro-1,4-naphthoquinone (**7**) (Aldrich) were used as received. 4-Substituted thiosemicarbazides **1a–c** were prepared according to the literature [38–41], as were 4-phenylthiosemicarbazide (**1a**) [38, 39], 4-benzylthiosemicarbazide (**1b**) [39, 40] and 4-(2-propenyl) thiosemicarbazide (**1c**) [40, 41].

4.3 *Reaction of 1a–c with (DDQ, 2)*

A solution of **1a–c** (2 mmol) in 20 ml of dry ethyl acetate is added dropwise to solution of **2** (1.0 mmol) in 10 ml of dry ethyl acetate at room temperature. The reaction mixture becomes deeply blue and quickly turns into a brown color. It was left standing for 48 hours, concentrated in *vacuo* and the residue separated by (plc) using cyclohexane/ethyl acetate (5:1) into three zones. The fastest zone contained the oxathiadiazole **8a–c**, the second zone contained the indazole derivatives **9a–c** and the slowest one contained the dihydroquinone (**5a**).

4.3.1 (2H-[1,5,2,3]Oxathiadiazol-4-yl)phenylamine (8a). Was obtained as colourless crystals, mp 210–212 °C (ethanol).

δ_H (300.13 MHz, $CDCl_3$): 7.10–7.16, 7.30–7.53 (m, 5H, Ar-H), 8.58 (br, s, 1H, NHPh), 11.85 (br, s, 1H, oxathiadiazole-NH). δ_C (75.47 MHz, $CDCl_3$): 125.82, 128.93, 129.30, 142.71 (Ar-C), 157.18 (C-4). ν_{max} (cm^{-1}): 3355, 3320 (NH), 3070 (Ar-CH), 1620 (C=N), 1580 (Ar-C=C) cm^{-1}. EI+mass spectrum (m/z, %): 181 (M^+, 44%), 179 (100%), 151 (87%), 135 (47%), 91 (27%), 77 (88%). C, H, N, O, S (%): found: C, 46.37; H, 3.96; N, 23.10; S, 17.86. $C_7H_7N_3OS$ (181.21) requires C, 46.39; H, 3.89; N, 23.19; S, 17.69.

4.3.2 (2H-[1,5,2,3]Oxathiadiazole-4-yl)benzylamine (8b). Was obtained as colourless crystals, mp 235–237 °C (acetonitrile).

δ_H (300.13 MHz, $CDCl_3$): 4.67 (br, s, 2H, $PhCH_2$), 7.15–7.53 (m, 5H, Ar-H), 8.42 (br, s, 1H, $NHCH_2Ph$), 11.92 (br, s, 1H, oxathiadiazole-NH). δ_C (75.47 MHz, $CDCl_3$): 50.34 (CH_2Ph), 126.53, 127.14, 128.33, 142.41 (Ar-C), 156.93 (C-4). ν_{max} (cm^{-1}): 3348, 3318 (NH), 3060 (Ar-CH), 2960 (Ali-CH), 1625 (C=N), 1590 (Ar-C=C) cm^{-1}. EI+mass spectrum (m/z, %): 195 (M^+, 35), 193 (100%), 165 (61%), 149 (49%), 102 (36%), 77 (80%). C, H, N, O, S (%): found C, 49.09; H, 4.81; N, 21.65; S, 16.29. $C_8H_9N_3OS$ (195.24) requires C, 49.21; H, 4.65; N, 21.52; S, 16.42.

4.3.3 (2H-[1,5,3,2]Oxathiadiazole-4-yl)allylamine (8c). Was obtained as colourless crystals, mp 163–165 °C (ethanol).

δ_H (300.13 MHz, $CDCl_3$): 4.10 (br, s, 2H, allyl-CH_2N), 5.12–5.16 (m, 2H, allyl-CH_2=), 5.92–5.98 (m, 1H, allyl-CH=), 7.57 (br, s, 1H, allyl-NH), 11.82 (br, s, 1H, oxathiadiazole-NH). δ_C (75.47 MHz, $CDCl_3$): 43.22 (allyl-CH_2N), 115.61 (allyl-CH_2=), 135.18 (allyl-CH=), 157.88 (C-4). ν_{max} (cm^{-1}): 3340, 3310 (NH), 2960, 2880 (Ali-CH), 1620 (C=N). EI+mass spectrum (m/z, %): 145 (M^+, 28), 143 (100%), 115 (62%), 99 (83%), 41 (53%). C, H, N, O, S (%): found C, 32.91; H, 4.94; N, 29.12; S, 21.93. $C_4H_7N_3OS$ (145.18) require C, 33.09; H, 4.86; N, 28.94; S, 22.09.

4.3.4 1H-4-Cyano-6,7-dichloro-5-hydroxy-3-phenylaminoindazole (9a). Was obtained as yellow crystals, mp 271–273 °C (methanol).

δ_H (300.13 MHz, DMSO-d_6): 7.12–7.52 (m, 5H, Ar-H), 8.64 (br, s, 1H, NHPh), 9.46 (br, s, 1H, OH), 11.48 (br, s, 1H, indazole-NH). δ_C (75.47 MHz, DMSO-d_6): 118.77 (CN), 121.41, 122.11 (indazole-C-6,7), 133.82 (C-7a), 126.15, 127.18, 128.33, 142.44 (Ar-C), 154.18 (C-3), 155.21 (C-5). ν_{max} (cm^{-1}): 3410–3220 (OH, NH), 2220 (CN), 1625 (Ar-C=N), 1590 (Ar-C=C). EI+mass spectrum (m/z, %) 322/318 (M^+, 33), 284 (22%), 248 (19%), 221 (27%), 191 (18%), 91 (24%), 77 (54%), 65 (100%). C, H, Cl, N, O (%): found C, 52.83; H, 2.42; N, 17.39; Cl, 22.36. $C_{14}H_8Cl_2N_4O$ (319.15) require C, 52.69; H, 2.53; N, 17.56; Cl, 22.22.

4.3.5 1H-3-Benzylamino-4-cyano-6,7-dichloro-5-hydroxyindazole (9b). Was obtained as yellow crystals, mp 296–298 °C (methanol).

δ_H (300.13 MHz, DMSO-d_6): 4.64 (br, s, 2H, CH_2Ph), 7.16–7.58 (m, 5H, Ar-H), 8.48 (br, s, 1H, NHCH_2Ph), 9.38 (br, s, 1H, OH), 11.41 (br, s, 1H, indazole-NH). ν_{max} (cm^{-1}): 3425–3220 (OH, NH), 2218 (CN), 1630 (Ar-C=N), 1585 (Ar-C=C). EI+mass spectrum (m/z, %): 336/332 (M^+, 14), 298 (18%), 262 (21%), 234 (9%), 105 (33%), 77 (43%), 65 (100%). C, H, Cl, N, O (%): found C, 53.89; H, 3.16; N, 16.96; Cl, 21.41. $C_{15}H_{10}Cl_2N_4O$ (333.18) require C, 54.07; H, 3.04; N, 16.82; Cl, 21.28.

4.3.6 1H-3-Allylamino-4-cyano-6,7-dichloro-5-hydroxyindazole (9c). Was obtained as pall yellow crystals, mp 202–204 °C (ethanol).

δ_H (300.13 MHz, DMSO-d_6): 4.22 (m, 2H, allyl-CH_2N), 5.18–5.23 (m, 2H, allyl-CH_2=), 5.85–5.93 (m, 1H, allyl-CH=), 7.52 (br, s, 1H, allyl-NH), 9.41 (br, s, 1H, OH), 11.40 (br, s, 1H, indazole-NH). δ_C (75.47 MHz, DMSO-d_6): 43.42 (allyl-CH_2N), 114.93 (allyl-CH_2=), 134.87 (allyl-CH=), 118.68 (CN), 121.48, 121.93 (indazole-C-6,7), 133.74 (C-7a), 153.88 (C-3), 154.33 (C-5). ν_{max} (cm^{-1}): 3410–3230 (OH, NH), 2926 (Ali-CH), 2220 (CN), 1615 (C=N), 1590 (Ar-C=C. EI+mass spectrum (m/z, %): 286/282 (M^+, 14), 248 (9%), 212 (4%), 185 (22%), 155 (24%), 56 (53%), 41 (100%). C, H, Cl, N, O (%): found C, 46.49; H, 2.98; N, 19.91; Cl, 24.88. $C_{11}H_8Cl_2N_4O$ (283.12) require C, 46.67; H, 2.85; N, 19.79; Cl, 25.04.

4.4 *Reaction of 1a–c with (chloranil, 6)*

A solution of **1a–c** (1.0 mmol) in 15 ml of dry ethyl acetate was added dropwise with stirring to a solution of chloranil, **6** (1.0 mmol) in 15 ml of dry ethyl acetate. The reaction color changed gradually from green to purple and later turns into brown color. The stirring was continued for 72 hour with admission of air to complete the reaction. The reaction mixture was concentrated and the residue was then separated by (plc) using a suitable solvent mixture eluent cyclohexane/ethyl acetate (4:1) to give numerous colored zones, the three intense of which were removed and extracted. The fastest migrating one contained the oxathiadiazoles **8a–c**, the second zone, which quenched all indicator fluorescence upon exposure to 254 nm UV-light,

contained 2,3,5,6-tetrachloro-1,4-hydroquinone (**5b**) and finally the slowest migrating zone (which is always characterized by orange color) contained the thiadiazine derivatives **10a–c**.

4.4.1 5,7,8-Trichloro-3-phenylaminobenzo[1,3,4]thiadiazine-6-one (10a). Was obtained as orange crystals, mp 293–295 °C (acetonitrile).

δ_H (300.13 MHz, DMSO-d_6): 7.12–7.54 (m, 5H, Ar-H), 8.67 (br, s, 1H, NHPh). δ_C (75.47 MHz, DMSO-d_6): 125.16, 128.53, 129.34, 142.71 (Ar-C), 138.14, 141.22, 147.18 (C-8,7,5), 132.28 (C-4a), 158.94 (C-3), 159.73 (C-8a), 170.11 (C=O). ν_{max} (cm^{-1}): 3330 (NH), 1680 (C=O), 1600 (C=N), 1580 (Ar-C=C). EI + mass spectrum (m/z, %): 363/357 (M^+, 21), 286 (18%), 250 (11%), 135 (22%), 115 (31%), 91 (84%), 77 (100%). C, H, Cl, N, O, S (%): found C, 43.69; H, 1.76; N, 11.56; S, 9.08; Cl, 29.52. $C_{13}H_6Cl_3N_3OS$ (358.63) require C, 43.54; H, 1.69; N, 11.72; S, 8.92; Cl, 29.66.

4.4.2 3-Benzylamino-5,7,8-trichlorobenzo[1,3,4]thiadiazin-6-one (10b). Was obtained as orange crystals, mp 308–310 °C (methanol).

δ_H (300.13 MHz, DMSO-d_6): 4.64 (br, s, 2H, CH_2Ph), 7.18–7.58 (m, 5H, Ar-H), 8.42 (br, s, 1H, $NHCH_2Ph$). δ_C (75.47 MHz, DMSO-d_6): 49.38 (CH_2Ph), 126.54, 127.18, 128.36, 142.43 (Ar-C), 138.12, 141.28 and 147.44 (C-8,7,5), 132.61 (C-4a), 158.72 (C-3), 159.63 (C-8a), 169.96 (C=O). ν_{max} (cm^{-1}): 3320 (NH), 1675 (C=O), 1610 (C=N), 1590 (Ar-C=C). EI+mass spectrum (m/z, %): 377/371 (M^+, 19), 300 (16%), 264 (9%), 149 (48%), 115 (26%), 77 (100%). C, H, Cl, N, O, S (%): found C, 44.96; H, 2.28; N, 11.41; S, 8.46; Cl, 28.68. $C_{14}H_8Cl_3N_3OS$ (372.66) require C, 45.12; H, 2.16; N, 11.28; S, 8.60; Cl, 28.54.

4.4.3 3-Allylamino-5,7,8-trichlorobenzo[1,3,4]thiadiazin-6-one (10c). Was obtained as orange crystals, mp 233–235 °C (ethanol).

δ_H (300.13 MHz, DMSO-d_6): 4.33 (br, s, 2H, allyl-CH_2N), 5.16–5.18 (m, 2H, allyl-CH_2=), 5.88–5.96 (m, 1H, allyl-CH=), 7.58 (br, s, 1H, allyl-NH). δ_C (75.47 MHz, DMSO-d_6): 43.81 (allyl-CH_2N), 114.96 (allyl-CH_2=), 134.82 (allyl-CH=), 132.18 (C-4a), 138.26, 141.52, 147.14 (C-8,7,5), 158.86 (C-3), 159.44 (C-8a), 170.21 (C=O). ν_{max} (cm^{-1}): 3340 (NH), 2960, 2880 (Ali-CH), 1675 (C=O), 1600 (C=N). EI+mass spectrum (m/z, %): 327/321 (M^+, 21), 285 (11%), 214 (14%), 115 (36%), 99 (100%), 41 (86%). C, H, Cl, N, O, S (%): found C, 37.10; H, 1.98; N, 12.88; S, 10.11; Cl, 33.12. $C_{10}H_6Cl_3N_3OS$ (322.60) requires C, 37.23; H, 1.87; N, 13.03; S, 9.94; Cl, 32.97.

4.5 *Reaction of 1a–c with 7*

A solution of **1a–c** (1.0 mmol) in 15 ml of dry ethyl acetate was added dropwise with stirring to a solution of **7** (1.0 mmol) in 15 ml of dry ethyl acetate. The reaction mixture was stirring for 72 hours, during which time it turned from faint orange into deep blue. The precipitate dibenzo[*b,i*]thianthrene-5,7,12,14-tetraone **13** was filtered and washed several times with ethyl acetate. The filtrate was concentrated *in vacuo* and the residue separated by (plc) using cyclohexane/ethyl acetate (2:1) into two zones. The fastest zone contained **11a–c** and the slowest migrating zone contained naphthobisthiadiazine derivatives **12a–c**.

4.5.1 10-Chloro-2-phenylamino-1-thia-3,4-diazaphenanthren-9-one (11a). Was obtained as orange crystals, mp 266–268 °C (ethanol).

δ_H (300.13 MHz, DMSO-d_6): 6.94, 7.4–7.73 (all m, 9H, Ar-H), 8.70 (br, s, 1H, NHPh). δ_C (75.47 MHz, DMSO-d_6): 122.76, 124.43, 129.32, 129.56, 129.84, 131.32, 132.44, 134.41, 137.22, 142.73 (Ar-C), 124.18 (C-10a), 136.12 (C-5), 156.12 (C-2), 158.93 (C-4a), 177.83 (C=O). ν_{max} (cm^{-1}): 3360 (NH), 3070 (Ar-CH), 1690 (C=O), 1620 (C=N). EI+mass spectrum (m/z, %): 341/339 (M^+, 34), 303 (18), 275 (9), 140 (16), 91 (83), 77 (76), 65 (100). C, H, Cl, N, O, S (%): found C, 59.93; H, 3.08; N, 12.49; S, 9.31. $C_{17}H_{10}ClN_3OS$ (339.80) requires C, 60.09; H, 2.97; N, 12.37; S, 9.44; Cl, 10.43.

4.5.2 2-Benzylamino-10-chloro-1-thia-3,4-diazaphenanthren-9-one (11b). Was obtained as orange crystals, mp 284–286 °C (acetonitrile).

δ_H (300.13 MHz, DMSO-d_6): 4.61 (br, s, 2H, CH_2Ph), 6.92, 7.12, 7.40–7.68 (all m, 9H, Ar-H); 8.48 (br, s, 1H, $NHCH_2Ph$). δ_C (75.47 MHz, DMSO-d_6): 48.92 (CH_2Ph), 126.53, 127.11, 128.33, 129.55, 129.88, 131.34, 132.48, 134.41, 137.22, 141.83 (Ar-C), 124.33 (C-10a), 155.88 (C-2), 158.76 (C-4a) and 178.41 (C=O). ν_{max} (cm^{-1}): 3345 (NH), 2980 (Ali-CH), 1685 (C=O), 1610 (C=N). EI+mass spectrum (m/z, %): 355/353 (M^+, 23), 317 (14%), 289 (6%), 140 (21%), 91 (73%), 77 (56%), 65 (100%). C, H, Cl, N, O, S (%): found C, 61.26; H, 3.54; N, 11.69; S, 8.94; Cl, 9.88. $C_{18}H_{12}ClN_3OS$ (353.83) required C, 61.10; H, 3.42; N, 11.88; S, 9.06; Cl, 10.02.

4.5.3 2-Allylamino-10-chloro-1-thia-3,4-diazaphenonthren-9-one (11c). Was obtained as orange crystals, mp 191–193 °C (ethanol).

δ_H (300.13 MHz, DMSO-d_6): 4.21 (m, 2H, allyl-CH_2N), 5.16–5.19 (m, 2H, allyl-CH_2=), 5.96–6.04 (m, 1H, allyl-CH=), 6.96, 7.11–7.38 (m, 4H, Ar-H), 7.53 (br, s, 1H, allyl-NH). δ_C (75.47 MHz, DMSO-d_6): 43.64 (allyl-CH_2N), 115.11 (allyl-CH_2=), 135.14 (allyl-CH=), 129.53, 129.84, 131.34, 132.44, 134.56 (Ar-C), 124.16 (C-10a), 156.72 (C-2), 158.93 (C-4a), 177.14 (C=O). ν_{max} (cm^{-1}): 3350 (NH), 2974, 2865 (Ali-CH), 1690 (C=O), 1600 (C=N). EI+mass spectrum (m/z, %): 305/303 (M^+, 26), 267 (14%), 140 (26%), 99 (53%), 41 (100%). C, H, CL, N, O, S (%): found C, 55.48; H, 3.21; N, 13.96; S, 10.71; Cl, 11.52. $C_{14}H_{10}ClN_3OS$ (303.77) requires C, 55.35; H, 3.32; N, 13.83; S, 10.56; Cl, 11.67.

4.5.4 2,11-Diphenylaminonaphtho[1,2-e:4,3-è]bis[1,3,4]thiadiazine (12a). Was obtained as reddish orange crystals, mp 322-324 °C (methanol).

δ_H (300.13 MHz, DMSO-d_6): 6.92, 7.10, 7.42–7.68 (all, m, 14H, Ar-H), 8.66 (br, s, 2H, 2NHPh). δ_C (75.47 MHz, DMSO-d_6): 125.11, 128.56, 129.36, 129.58, 130.88, 131.74, 141.18 (Ar-C), 156.59 (C-2, 11), 158.76 (C-4a). ν_{max} (cm^{-1}): 3360 (NH), 1630 (C=N), 1590 (Ar-C=C). EI+mass specrum (m/z, %): 452 (M^+, 43), 424 (12%), 396 (8%), 327 (31%), 182 (11%), 126 (9%), 91 (53%), 77 (83%), 65 (100%). C, H, N, S (%): found C, 63.53; H, 3.73; N, 18.71; S, 14.02. $C_{24}H_{16}N_6S_2$ (452.55) requires C, 63.70; H, 3.56; N, 18.57; S, 14.17.

4.5.5 2,11-Dibenzylaminonaphtho[1,2-e:4,3-è]bis[1,3,4]thiadiazine (12b). Was obtained as reddish orange crystals, mp 331–333 °C (methanol).

δ_H (300.13 MHz, DMSO-d_6): 4.63 (br, s, 2H, CH_2Ph), 7.05, 7.16, 7.42–7.65 (all m, 14H, Ar-H), 8.48 (br, s, 2H, $2NHCH_2Ph$). δ_C (75.47 MHz, DMSO-d_6): 48.83 (CH_2Ph), 126.51, 127.11, 128.33, 129.18, 130.94, 131.76, 140.88 (Ar-C), 156.12 (C-2, 11), 159.60 (C-4a, 9a). ν_{max} (cm^{-1}): 3376 (NH), 1625 (C=N), 1660 (Ar-C=C). EI+mass spectrum (m/z, %): 480 (M^+, 36), 331 (12%), 182 (18%), 154 (22%), 126 (9%), 91 (74%), 77 (56%), 65 (100%). C,

H, N, S (%): found C, 65.12; H, 4.03; N, 17.63; S, 13.51. $C_{26}H_{20}N_6S_2$ (480.61) requires C, 64.98; H, 4.19; N, 17.49; S, 13.34.

4.5.6 2,11-Diallylaminonaphtho[1,2-e:4,3-è]bis[1,3,4]thiadiazine (12c). Was obtained as pall reddish orange crystals, mp 287–289 °C (ethanol).

δ_H (300.13 MHz, DMSO-d_6): 4.18 (m, 2H, allyl-CH_2N), 5.18–5.20 (m, 2H, allyl-CH_2=), 5.92–5.96 (m, 1H, allyl-CH=), 6.96–7.20 (m, 4H, Ar-H). ν_{max} (cm^{-1}): 3360 (NH), 1630 (C=N), 1595 (Ar-C=C). EI+mass specrum (m/z, %): 380 (M^+, 44), 281 (16%), 253 (22%), 99 (100%), 41 (56%). C, H, N, S (%): found C, 56.93; H, 4.11; N, 21.94; S, 17.04. $C_{18}H_{16}N_6S_2$ (380.49) requires C, 56.82; H, 4.24; N, 22.09; S, 16.86.

4.5.7 Dibenzo[b,i]thianthrene-5,7,12,14-tetraone (13). Was obtained as blue crystals, mp 312–314 °C (lit 308–310 °C) [42].

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