Nucleophilic reactions of 1-substituted-2,5-dithiobiureas with chloronated benzo- and naphthoquinones as well as (1,3-dioxo-2,3-dihydro-1(*H*)-inden-2-ylidene)propanedinitrile

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Abstract

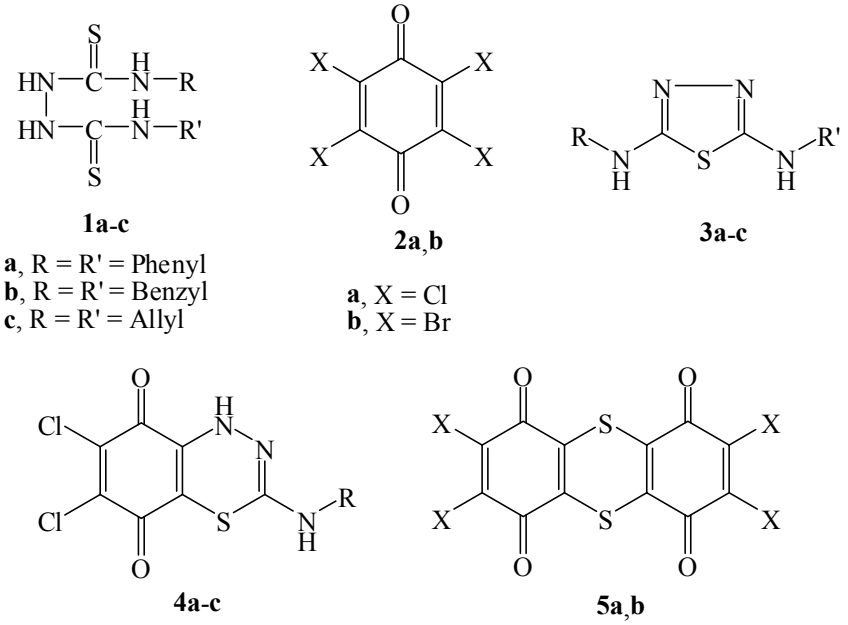
Nucleophilic attack by 1-substituted-2,5-dithiobiureas on C-2, C-3 of 2,3,5,6-tetrachloro-1,4-benzoquinone and 2,3-dichloro-1,4-naphthoquinone initiates the formation of benzo- and naphthoimidazothiadiazolediones. On the other hand, 1-substituted-2,5-dithiobiureas attack 2,3,5,6-tetrachloro-1,4-benzoquinone and 2,3-dichloro-1,4-naphthoquinone at (C-1, C-2, C-4 and C-5) as well as (C-1, C-2, C-3 and C-4), respectively to form benzo- and naphthoimidazothiadiazoles. The reaction of (1,3-dioxo-2,3-dihydro-1(*H*)-indene-2-ylidene)-propanedinitrile with 1-substituted-2,5-dithiobiureas forming the derivatives of (oxoindeno-thiazinylidene)hydrazinecarbothioamide as well as (oxoindenopyrrolylidene)hydrazinecarbo-thioamides. A rationale for the conversions observed is presented.

Keywords: 1-Substituted-2,5-dithiobiureas, chlorinated benzo- and naphthoquinones, (1,3-dioxo-2,3-dihydro-1(*H*)-indene-2-ylidene)propanedinitrile

Introduction

Substituted dithiobiureas act as a key for the synthesis of many organic heterocyclic ring systems. Several authors have investigated under various conditions the heterocyclization of 1-acylthiobiurea,[1] 1,6-disubstituted-2,5-dithiobiureas,[2] and 1-aryl/alkyl-2-thiobiureas.[3] Also, the heterocyclization of compounds having an extended urea like chain such as 1,4- and 2,4-disubstituted thiosemicarbazides have been reported.[4,5] 2,3,5,6-Tetrachloro-1,4-benzoquinone (**2a**) and 2,3-dichloro-1,4-naphthoquinone (**7**) undergo nucleophilic substitution of one or two chlorine atoms by thioacetamide or thiourea,[6-9] thiocarbohydrazide,[10] thiocarbazones,[10] N-substituted thioureas,[11] disubstituted-2,5-dithiobiureas,[12] thiosemicarbazones,[13] and substituted thiosemicarbazides.[14] A large variety of quinones including heterocyclic rings, have been used as synthetic intermediates and in the medicinal,[15-18] as well as dye chemistry.[19-22] Recently, we have reported an efficient transformation of 1,6-disubstituted-2,5-dithiobiureas **1a-c** with **2a**,**b** into

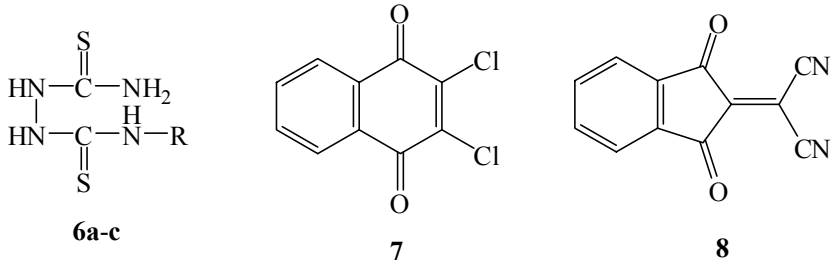
disubstituted-1,3,4-thiadiazoles **3**, benzothiadiazinediones **4** and tetrahalothianthrene derivatives **5** (Chart 1).[12]



3-**5**: **a**, R = Phenyl; **b**, R = Benzyl; **c**, R = Allyl

Chart 1. Previous work on the reaction of 1,6-disubstituted dithiobiureas with **2a,b.**

This paper is focused on the reactions of 1-substituted-2,5-dithiobiureas **6a-c** as a reactive donor with acceptors 2,3,5,6-tetrachloro-1,4-benzoquinone (**2a**), 2,3-dichloro-1,4-naphtho-quinone (**7**) and (1,3-dioxo-2,3-dihydro-1(*H*)-inden-2-ylidene)propanedinitrile (**8**) Figure 1.

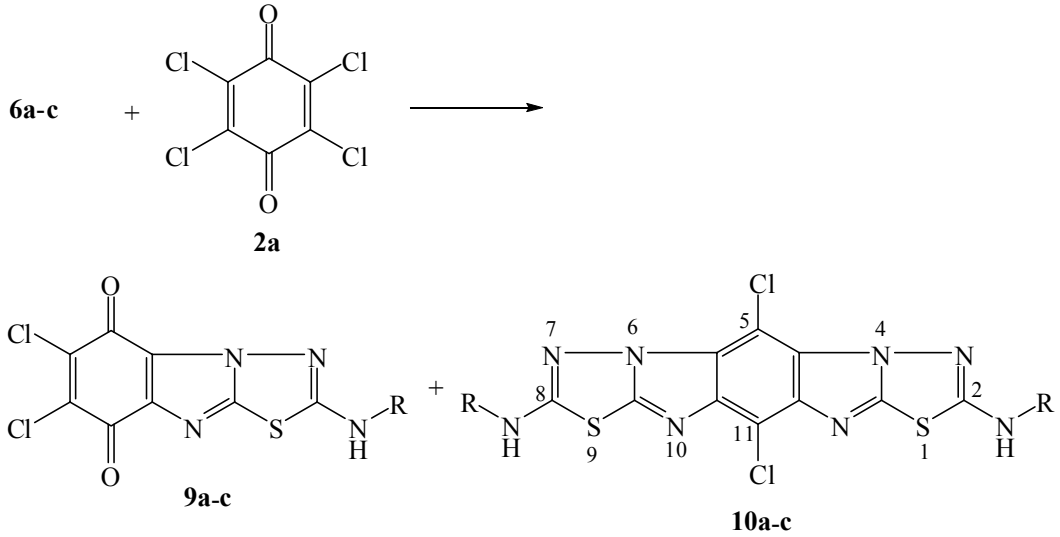


6: **a**, R = Phenyl; **b**, R = Benzyl; **c**, R = Allyl

Figure 1. 1-Substituted-2,5-dithiobiureas and some π-acceptors.

Results and Discussion

Addition of tetrahydrofuran (THF) solutions of **6a-c** to solutions of **2a** (1:2) in the same solvent formed, after standing for 48 hours at room temperature, substituted benzobisimidazo-thiadiazoles **10a-c** as minor (21-24%) and substituted imidazothiadiazolediones **9a-c** as major products (48-54%) (Scheme 1).



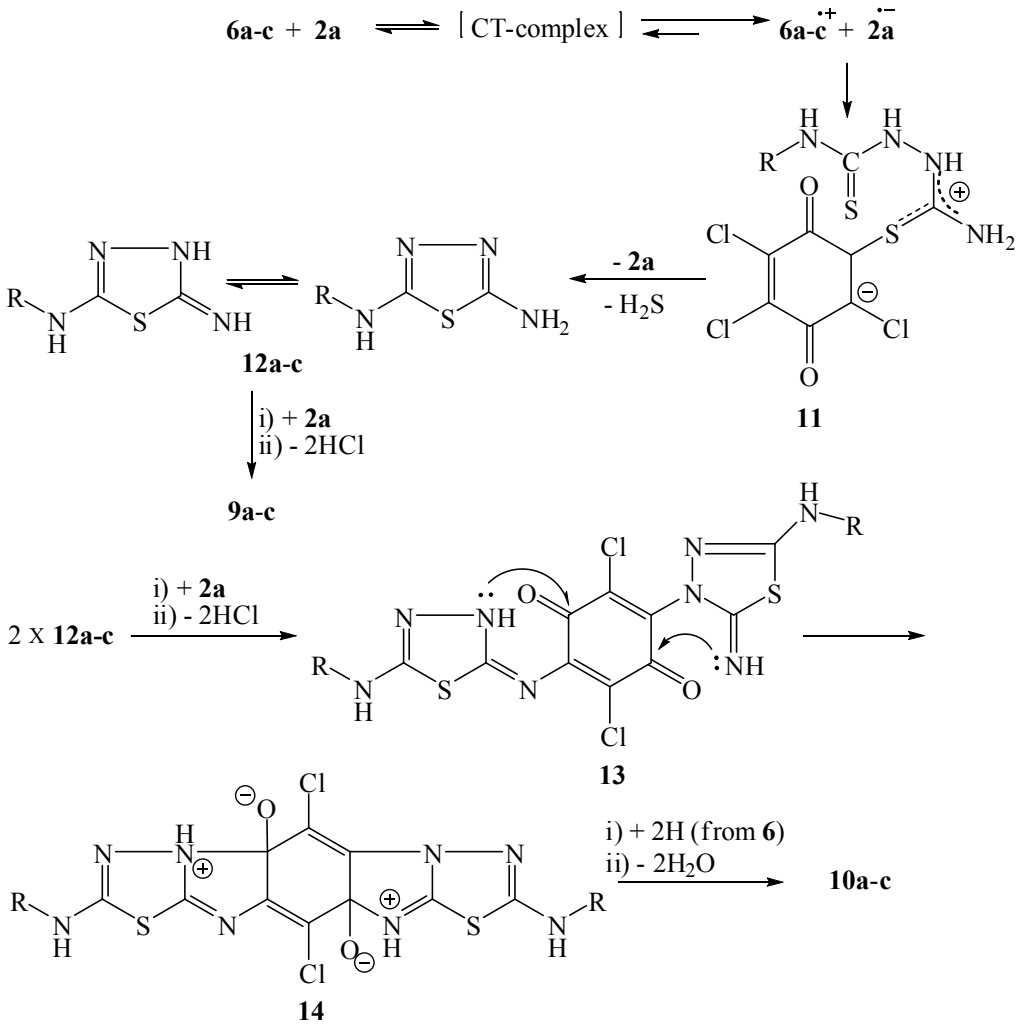
6, **9** and **10**: **a**, R = Phenyl; **b**, R = Benzyl; **c**, R = Allyl

Scheme 1. New products formed during the reaction of 1-substituted dithiobiureas **6a-c** with 2,3,5,6-tetrachloro-1,4-benzoquinone (**2a**).

The structure assignment of the precipitate **10a-c** is based on following data: In their ^{13}C-NMR spectra, the characteristic absorption signal of the two carbon atoms of **2a** at δ = 169.90 ppm,[23] is replaced by signal at δ = 140.78 ppm, which are characteristic for the imidazole-*C*-atoms. In addition, Ph-*C*-Cl appears at 123.89-124.28 ppm, (*C*-2 and *C*-8) at 157.75-157.88 ppm. The IR spectra showed two bands at ν = 3320-3295, and 1625-1620 cm^{-1} for (NH) and (C=N) groups, respectively. The ^{1}H-NMR spectrum of **10c** showed signals at 4.11, 5.16-5.19 and 5.91-5.96 ppm, due to (allyl-CH_2N), (allyl-CH_2=) and (allyl-CH=) group, respectively.

The filtrate from the reaction between **2a** and **6a-c** contains benzoimidazothia-diazolediones **9a-c**. The structural assignment of **9a** was supported by the following spectral data. In its ^{13}C-NMR spectrum, the characteristic resonance signals of carbonyl carbon atoms of **2a** appeared at δ = 171.34 and 171.87 ppm.[9] The ^{1}H-NMR spectrum of **9a** showed one broad signal at 9.84 ppm due to the (NH) attached to the phenyl ring, in addition to the phenyl protons. The IR spectrum of **9a** showed sharp bands at 3280 and 1675 cm^{-1} for (NH) and (CO) groups, respectively. The formation of **9a** was further confirmed by mass spectrometry. Beside the molecular ions at *m/z* = 368/364, the characteristic fragment ion patterns of the substituted dichloro compounds were

observed.[24] It worthy to note that the mass spectra of compounds **9a-c** show the loss of substituted isothiocyanates as well as N_2 from the molecular ions. Formation of substituted and disubstituted benzimidazothiadiazoles **9** and **10** derived from **2a** and **6a-c** may be rationalized as outlined in Scheme 2.

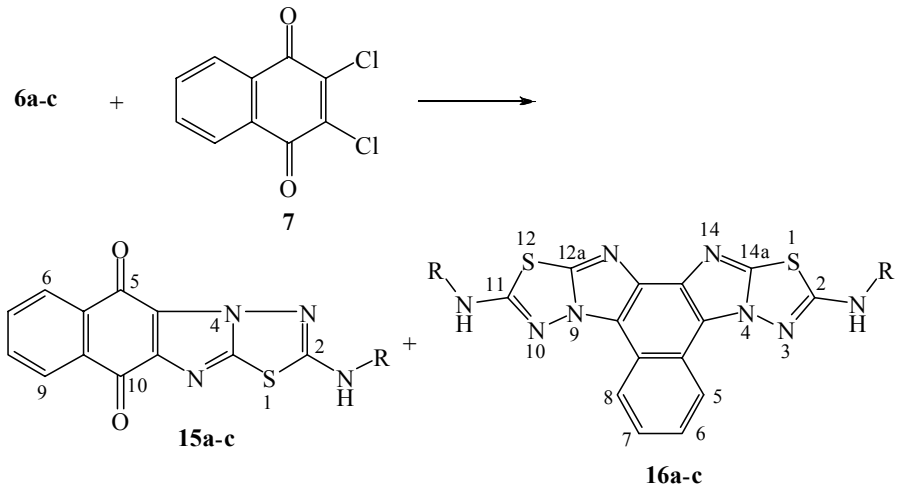


Scheme 2. A rationale for the formation of products **9a-c** and **10a-c**.

Substituted naphthimidazothiadiazolediones **15a-c** and disubstituted naphthobisimidazothiadiazoles **16a-c** were obtained from the reaction of **6a-c** with 2,3-dichloro-1,4-naphthoquinone (**7**) (Scheme 3).

Compounds **15a-c** exhibited two IR absorptions at 3320-3290 (secondary amine), and 1665-1655 cm^{-1} (CO) group, respectively. The ^{13}C-NMR spectra of **15a-c** show absorption signals at 151.86-152.41 and 157.73-158.12 due to (*C*-11a) and (*C*-2), as well as around 179.52 and 179.83 ppm due to quinonoid carbonyl *C*-atoms.

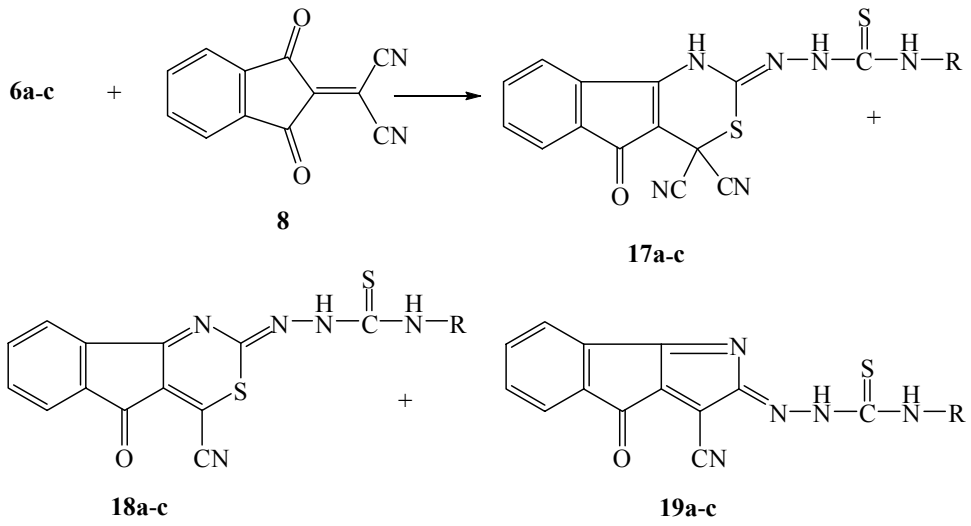
Compounds **16a-c** were obtained as characteristically reddish brown colour crystals. For example **16c**, its molecular structure is supported by the following findings: The gross formula $C_{20}H_{16}N_8S_2$ represents product from one molecule of dichloronaphthoquinone (**7**) and two molecules of **6c** with loss two molecules of HCl and another two of H_2O. The low-field NH-attached to allyl group is present with the aromatic protons, in addition to allyl and aryl protons. In ^{13}C-NMR spectrum, (*C*-12a, *C*-14a) and (*C*-2, *C*-11), resonate at δ = 152.56 and 159.63 ppm, respectively. The presence of allyl group is also evident from ^{13}C-DEPT-NMR spectrum exhibiting positive signal at δ = 135.12 (allyl-*C*H=) and negative signals at 42.96 and 114.88 due to (allyl-*C*H_2N) and (allyl-*C*H_2=), respectively. The EI mass spectrum of **16c** is characterized by molecular ion of low intensity and the loss of 198 a.m.u (representing two molecules of allylisothiocyanate). The resulting fragment ions undergo loss of 30 a.m.u (most likely dinitrogen and hydrogen molecules) followed by the appearance of allyl cation as a base peak at 41.



6, **15** and **16**: **a**, R = Phenyl; **b**, R = Benzyl; **c**, R = Allyl

Scheme 3. New products formed during the reaction of 1-substituted dithiobiureas **6a-c** with 2,3-dichloronaphthoquinone (**7**).

It has been reported earlier that (1,3-dioxo-2,3-dihydro-1(*H*)-inden-2-ylidene)propane-dinitrile (**8**),[25] is isomerized to 2,3-dicyano-1,4-naphthoquinone when brought in contact with electron donors.[26] Compound **8** readily adds *N*-nucleophiles such as primary and tertiary aromatic amines,[27,28] tertiary cyclic amines,[29,30] 1,8-diamino-naphthalene,[31] and thiocarbazones,[10] at the dicyanomethylene carbon atom with the release of HCN. Due to insufficient solubility of **8** in THF, the reaction was carried out in ethyl acetate under reflux, followed by chromatographic separation. The reaction mixture afforded the products **17-19** in Scheme 4 and numerous coloured byproducts each in small quantities.



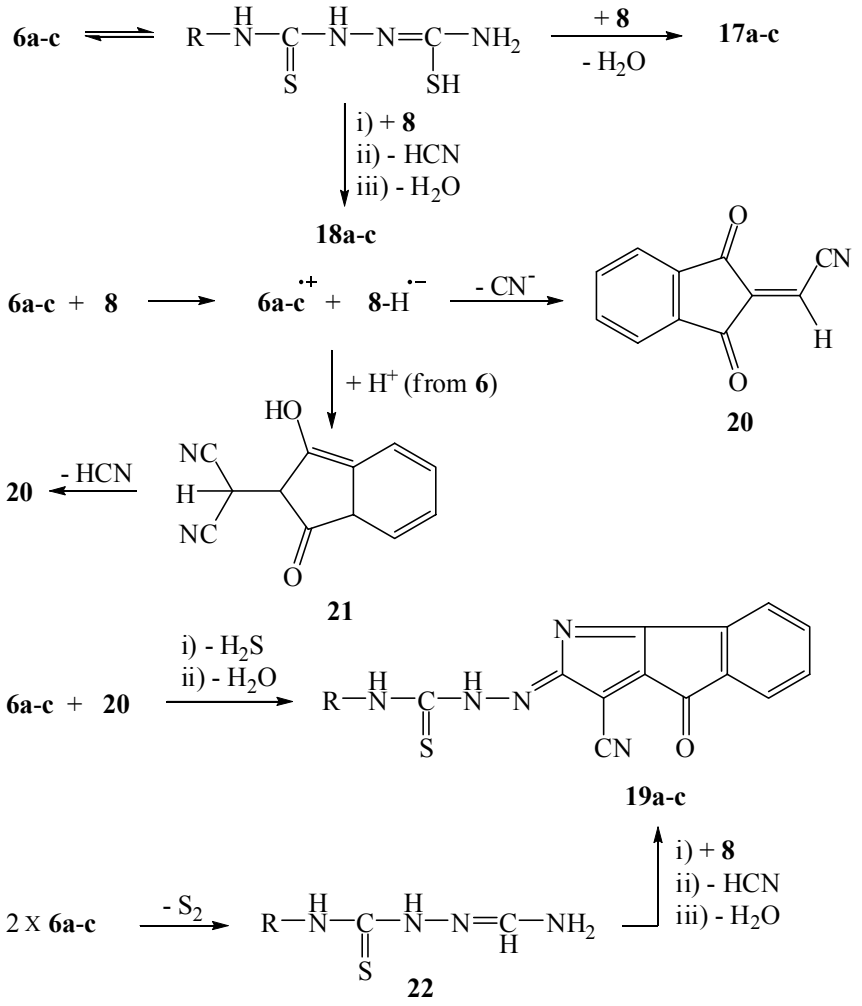
6, **17**, **18 and 19**: **a**, R = Phenyl; **b**, R = Benzyl; **c**, R = Allyl

Scheme 4. New products formed during the reaction of 1-substituted dithiobiureas **6a-c** with (1,3-dioxo-2,3-dihydro-1(h)-indene-2-ylidene)propanedinitrile (**8**).

The structures of **17-19** have assigned on the basis of their IR and NMR spectral data. The gross compositions of **17-19** were derived from satisfactory elemental analyses and the molecular masses. The IR spectra of all compounds showed sharp band due to cyano group at 2220-2210 cm^{-1}, NH absorptions at 3340-3240 cm^{-1}. All products **17-19** were also characterized in their IR spectra by sharp bands at 1575-1565 due to (NH-deformation and C-N stretching) and intense bands in the range of 1360-1345 as well as 990-1010 cm^{-1} assigned to strongly coupled between C=S and C-N vibrations.[32-35] The ^{1}H-NMR spectrum of *N*-phenyl-2-(4,4-dicyano-5-oxoindeno[1,2-*d*][1,3]thiazin-2(1*H*,4*H*,5*H*)ylidene)hydrazinecarbothioamide (**17a**) clearly showed three broad signals at 7.96, 9.73 and 9.89 ppm, due to thiazine-NH, hydrazine-NH and NH attached to phenyl group, besides the aromatic protons. Signals at 31.72 (*C*-4), 107.12 (*C*-4a), 146.43 (*C*-9b), 156.32 (*C*-2), 181.22 (*C*=S) and 195.52 (*C*O) in the ^{13}C-NMR spectrum of **17a** lend further supported of the structure assigned to **18a**. The EI-mass spectra of **18a-c** *m/z* = 281 represents the 2-(4,4-dicyano-5-oxoindeno[1,2-*d*][1,3]thiazin-2(1*H*,4*H*,5*H*)ylidene)-hydrazine fragment formed by release of the corresponding isothiocyanate from the molecular ion. Since fragment ions with the masses of these isothiocyanates are also found. It is concluded that the positive charge may remain alternatively either with the ring or the isothiocyanate fragment. The structure assigned of *N*-benzyl-2-(4-dicyano-5-oxoindeno[1,2-*d*][1,3]thiazin-2(5*H*)-ylidene)hydrazinecarbothioamide (**18b**) is based on the following spectral data: The ^{1}H-NMR spectrum showed two broad signals centered at δ = 8.90, 9.80 ppm due to benzyl-NH and hydrazine-NH, respectively, besides the benzylic-CH_2, and aromatic protons. The ^{13}C-NMR decoupling showed signals at 52.43 (*C*H_2), 145.94 (*C*-3a), 157.43 (*C*-2), 152.74 (*C*-9b), 181.35

(*C*=S) and 195.12 (*C*O). The structure of **18b** was evidently confirmed by mass spectrometrically. Besides the molecular ion at *m/z* = 403 (22 %), the characteristic fragment ion pattern of benzylisothiocyanate at 149 (47), benzoyl group at 105 (81) and benzyl cation at 91 as a base peak.

A minor product (7-11 %) from the reaction between **6a-c** and **8** contains *N*-substituted (oxoindenopyrrolylidene)hydrazinecarbothioamides **19a-c**. As an example, the structural assignment of **19c** was supported by the following spectral data. In its ^{13}C-NMR spectrum, the characteristic resonance signal of the carbonyl carbon atom of indandione **8** appeared at δ = 194.83 ppm.[36] Signals at 121.23, 158.31, 145.92 and 152.29 due to (*C*-3), (*C*-2), (*C*-3a) and (*C*-8b), respectively. The ^{1}H-NMR in DMSO-d_6 of **19c** displayed broadened signals at δ = 4.12 (allyl-CH_2N), 7.79 (allyl-NH) and 9.77 (hydrazine-NH) as well as multiplets at 5.14-5.17 (allyl-CH_2=), 5.90-94 (allyl-CH=) and aromatic protons. The presence of allyl group is also evident from ^{13}C-DEPT-NMR spectrum which exhibits negative signals at δ = 42.83 (allyl-*C*H_2N) and 118.41 (allyl-*C*H_2=) as well as positive signal at 135.16 ppm due to (allyl-*C*H=). The elemental analysis supported the gross composition $C_{16}H_{11}N_5OS$ and the mass spectrum revealed the expected molecular ion. The formation of structure products **17-19** may be rationalized as in Scheme 6. Two routes can be suggested for the formation of cyanomethyleneindanedione **20**. The first, is abstraction of a proton from **6a-c** by the carbanione **8**-$H^{\bullet-}$ to give (1,3-dihydroxyindan-2-ylidene)propanedinitrile **21** which loss a molecules of HCN to form **20**. In second route, cyanide ion released from the anion **8**-$H^{\bullet-}$.[30] Combination of **6a-c** and **20** with the elimination of H_2S and H_2O afforded the substituted (oxoindenopyrrolylidene)hydrazine-carbothioamide **19**. Also, compound **19** may be formed *via* the formation of **22** as an intermediate. Several alternative structures based on the same elemental composition could be eliminated according to previous ^{1}H-NMR and ^{13}C-NMR spectral data.



Scheme 5. A rationale for the formation of products **17-19.**

On the other hand, the reaction of **6a-c** with 2,3-dicyano-1,4-naphthoquinone in ethyl acetate (under our reaction conditions reported with compound **8**) afforded the thiadiazoles **12a-c** and dihydrodicyanonaphthoquinone.

Experimental Section

General Procedures. Mps have been determined using open glass capillaries on a Gallenkamp melting point apparatus and are uncorrected. The IR spectra were recorded with a Shimadzu 408 instrument using potassium bromide pellets. The ^{1}H-NMR (400.134 MHz) and ^{13}C-NMR (100.6 MHz) spectra were measured in DMSO-d_6 using a Bruker AM 400 with TMS as an internal standard. Assignments of carbon resonances have been supported by DEPT experiments. Mass spectra have been obtained with a Varian MAT 311 instrument using electron impact ionization

(70 eV). Elemental analyses have been determined by the Microanalytical Center, Cairo University, Egypt. Preparative layer chromatography (plc): Glass plates (48 cm x 20 cm) were coated with silica gel Merck Pf_{254} (applied as aqueous slurry and air-dried affording a 1mm layer). Zones were detected by indicator fluorescence quenching upon 245 nm illuminations, removed from plates and extracted with acetone.

Materials. 2,3,5,6-Tetrachloro-1,4-benzoquinone (**2a**), and 2,3-dichloro-1,4-naphthoquinone (**7**) (Aldrich) were used as received. 2-(1,3-Dioxo-2,3-dihydro-1(*H*)-inden-2-ylidene)propane-dinitrile (dicyanomethyleneindane-1,3-dione) (**8**) was prepared according to Chatterjee.[25] 1-Substituted-2,5-dithiobiureas **6a-c** were prepared according to published procedures, as were 1-phenyl-2,5-dithiobiurea (**6a**),[37] 1-benzyl-2,5-dithiobiurea (**6b**)[37,38] and 1-allyl-2,5-dithiobiurea (**6c**).[37]

Reaction of 2a with 1-substituted-2,5-dithiobiureas 6a-c

A solution dithiobiureas **6a-c** (1.0 mmole) in 15 ml of dry tetrahydrofuran (THF) was added dropwise to a solution of **2a** (2.0 mmole) in 25 ml of dry THF at room temperature. The reaction mixture becomes deeply blue or purple colour. It was left standing for 48 hours, filtered and the precipitate was washed several times with THF and identified as disubstituted benzo[2,3-*d*:6,5-*d'*]bis(imidazo[2,1-*b*][1,3,4]-thiadiazoles) **10a-c**. The filtrate was concentrated in vacuum and the residue separated by plc using toluene/ethyl acetate (10:1) to give only one zone which was removed and extracted to give substituted benzo[4,5]imidazo[2,1-*b*][1,3,4]thiadiazole-5,8-diones **9a-c**.

2-(Phenylamino)-6,7-dichlorobenzo[4,5]imidazo[2,1-*b*][1,3,4]thiadiazole-5,8-dione (9a). Reddish brown crystals (methanol) (215 mg, 59 %), mp 221-223 ^{o}C. IR; ν_{max} (KBr) cm^{-1} 3280 (NH), 1675 (CO), 1615 (C=N), 1585 (Ar-C=C). ^{1}H-NMR (DMSO-d_6); δ 7.18-7.71 (m, 5H, Ar-H), 9.84 (br, 1H, Phenyl-NH). ^{13}C-NMR (DMSO-d_6); δ 127.86, 128.64, 129.74 (Ar-*C*H), 137.14 (*C*-8a), 137.34 (*C*-4a), 141.11 (Ar-*C*), 143.23 (*C*-6, *C*-7), 152.74 (*C*-9a), 158.26 (*C*-2), 171.34, 171.87 (*C*-5, *C*-8). MS; m/z (%) 368/364 (M^{+}, 26), 328 (21), 292 (12), 229 (18), 201 (24), 150 (31), 135 (52), 91 (64), 77 (100), 65 (52). Anal. Calcd. For $C_{14}H_6Cl_2N_4O_2S$: C, 46.04; H, 1.66; Cl, 19.42; N, 15.34; S, 8.78. Found: C, 45.91; H, 1.79; Cl, 19.64; N, 15.19; S, 8.96.

2-(Benzylamino)-6,7-dichlorobenzo[4,5]imidazo[2,1-*b*][1,3,4]thiadiazole-5,8-dione (9b). Reddish brown crystals (acetonitrile) (205 mg, 54 %), mp 247-249 ^{o}C. IR; ν_{max} (KBr) cm^{-1} 3290 (NH), 1680 (CO), 1620 (C=N), 1580 (Ar-C=C). ^{1}H-NMR (DMSO-d_6); δ 4.61 (s, 2H, CH_2Ph), 7.22-7.49 (m, 5H, Ar-H), 8.78 (br, 1H, benzyl-NH). ^{13}C-NMR (DMSO-d_6); δ 52.56 (*C*H_2Ph), 127.76, 127.98, 128.83 (Ar-*C*H), 137.10 (*C*-8a), 137.27 (*C*-4a), 139.92 (Ar-*C*), 142.96 (*C*-6, *C*-7), 152.68 (*C*-9a), 157.33 (*C*-2), 171.21, 171.79 (*C*-5, *C*-8). MS; m/z (%) 378/382 (M^{+}, 29), 342 (16), 306 (8), 229 (26) 201 (9), 164 (24), 149 (43), 91 (100), 77 (63). Anal. Calcd. For $C_{15}H_8Cl_2N_4O_2S$: C, 47.51; H, 2.13; Cl, 18.70; N, 14.77; S, 8.46. Found: C, 47.29; H, 2.26; Cl, 18.47; N, 14.99; S, 8.67.

2-(Allylamino)-6,7-dichlorobenzo[4,5]imidazo[2,1-*b*][1,3,4]thiadiazole-5,8-dione (9c). Reddish brown crystals (ethanol) (158 mg, 48 %), mp 185-187 °C. IR; ν_{max} (KBr) cm^{-1} 3275 (NH), 2975 (Ali-CH), 1680 (CO), 1610 (C=N). ^{1}H-NMR (DMSO-d_6); δ 4.12 (br, 2H, allyl-CH_2N), 5.19-5.22 (m, 2H, allyl-CH_2=), 5.87-5.94 (m, 1H, allyl-CH=), 7.61 (br, 1H, allyl-NH). ^{13}C-NMR (DMSO-d_6); δ 43.39 (allyl-*C*H_2N), 115.02 (allyl-*C*H_2=), 134.71 (allyl-*C*H=), 136.92 (*C*-8a), 137.29 (*C*-4a), 143.28 (*C*-6, *C*-7), 152.69 (*C*-9a), 158.32 (*C*-2), 171.28, 171.85 (*C*-5, *C*-8). MS; m/z (%) 328/332 (M^+, 34), 292 (27), 256 (18), 229 (24), 201 (9), 114 (27), 99 (61), 41 (100). Anal. Calcd. For $C_{11}H_6Cl_2N_4O_2S$: C, 40.14; H, 1.84; Cl, 21.54, N, 17.02; S, 9.74. Found: C, 39.93; H, 2.04; Cl, 21.76; N, 16.88; S, 9.52.

5,11-Dichloro-2,8-diphenylaminobenzo[2,3-*d*:6,5-*d′*]bis(imidazo[2,1-*b*][1,3,4]thiadiazole) (10a). Blue crystals (acetonitrile) (126 mg, 24 %), mp 289-291 °C. IR; ν_{max} (KBr) cm^{-1} 3310 (NH), 1625 (C=N), 1595 (Ar-C=C). ^{1}H-NMR (DMSO-d_6); δ 7.17-7.71 (m, 10H, Ar-H), 9.88 (br, 2H, phenyl-NH). ^{13}C-NMR (DMSO-d_6); δ 124.18 (*C*-5, *C*-11), 127.82, 128.69, 129.57 (Ar-*C*H), 140.83 (Ar-*C*), 140.86 (*C*-4a, *C*-5a, *C*-10a, *C*-11a), 151.92 (*C*-9a, *C*-12a), 157.88 (*C*-2, *C*-8). MS; m/z (%) 522/526 (M^+, 26), 486 (34), 450 (25), 252 (33), 222 (26), 150 (72), 135 (100), 124 (18), 77 (41). Anal. Calcd. For $C_{22}H_{12}Cl_2N_8S_2$: C, 50.48; H, 2.31; Cl, 13.55; N; 21.41; S, 12.25. Found: C, 50.71; H, 2.17; Cl, 13.32; N, 21.64; S, 12.47.

5,11-Dichloro-2,8-dibenzylaminobenzo[2,3-*d*:6,5-*d′*]bis(imidazo[2,1-*b*][1,3,4]thiadiazole) (10b). Blue crystals (acetonitrile) (116 mg, 21 %), mp 326-328 °C. IR; ν_{max} (KBr) cm^{-1} 3295 (NH), 1620 (C=N), 1590 (Ar-C=C). ^{1}H-NMR (DMSO-d_6); δ 4.58 (s, 4H, CH_2Ph), 7.28-7.57 (m, 10H, Ar-H), 8.92 (br, 2H, benzyl-NH). ^{13}C-NMR (DMSO-d_6); δ 52.56 (*C*H_2Ph), 123.89 (*C*-5, *C*-11), 127.78, 127.98, 128.52 (Ar-*C*H), 140.74 (Ar-*C*), 140.78 (*C*-4a, *C*-5a, *C*-10a, *C*-11a), 152.06 (*C*-9a, *C*-12a), 157.75 (*C*-2, *C*-8). MS; m/z (%) 550/554 (M^+, 22), 478 (26), 252 (19), 222 (11), 164 (29), 149 (81), 91 (100), 77 (56). Anal, calcd. For $C_{24}H_{16}Cl_2N_8S_2$: C, 52.27; H, 2.92; Cl, 12.86; N; 20.32; S, 11.63. Found: C, 52.49; H, 3.09; Cl, 12.63; N, 20.07; S, 11.81.

5,11-Dichloro-2,8-diallylaminobenzo[2,3-*d*:6,5-*d′*]bis(imidazo[2,1-*b*][1,3,4]thiadiazole) (10c). Blue crystals (methanol) (104 mg, 23 %), mp 264-266 °C. IR; ν_{max} (KBr) cm^{-1} 3320 (NH), 2965 (Ali-H), 1625 (C=N), 1595 (Ar-C=C). ^{1}H-NMR (DMSO-d_6); δ 4.11 (br, 4H, allyl-CH_2N), 5.16-5.19 (m, 4H. allyl-CH_2=), 5.91-5.96 (m, 2H, allyl-CH=), 7.78 (br, 2H, allyl-NH). ^{13}C-NMR (DMSO-d_6); δ 43.29 (allyl-*C*H_2N), 114.89 (allyl-*C*H_2=), 123.96 (*C*-5, *C*-11), 134.76 (allyl-*C*H=), 140.79 (*C*-4a, *C*-5a, *C*-10a, *C*-11a), 152.08 (*C*-9a, *C*-12a), 157.83 (*C*-2, *C*-8). MS; m/z (%) 450/454 (M^+, 22), 378 (18), 252 (11), 222 (6), 114 (36), 99 (53), 41 (100). Anal, calcd. For $C_{16}H_{12}Cl_2N_8S_2$: C, 42.58; H, 2.68; Cl, 15.71; N; 24.83; S, 14.21. Found: C, 42.33; H, 2.91; Cl, 15.93; N, 24.59; S, 14.44.

Reaction of 2,3-dichloro-1,4-naphthoquinone (7) with 1-substituted-2,5-dithiobiureas 6a-c

A solution of **6a-c** (1.0 mmole) in 15 ml of dry THF was added to a solution of 2,3-dichloro-1,4-naphthoquinone (**7**) (1.0 mmole). The mixture heated under reflux for 3-5 hours, for 3 h in the reaction of **6a** with **7**, 3.5 h in the reaction of **6b** with **7** and 5 h in the reaction of **6c** with **7** during which time it turned from faint red into deep red or orange. The precipitate disubstituted

aminonaphtho[1,2-*d*:4,3-*d'*]bis(imidazo[2,1-*b*][1,3,4]thiadiazoles) **16a-c** was filtered off which was recrystallized from the proper solvent. The filtrate was concentrated and the residue subjected to plc using toluene/ethyl acetate (1:2) as developing solvent to give numerous zones, the main and intense zone in every case contained substituted aminonaphtho[4,5]imidazo[2,1-*b*][1,3,4]thiadiazole-5,10-diones **15a-c**. The zone was extracted with acetone and recrystallized.

2-Phenylaminonaphtho[4,5]imidazo[2,1-*b*][1,3,4]thiadiazole-5,10-diones (15a). Reddish brown crystals (methanol) (135 mg, 39 %), mp 266-268 ^{o}C. IR; ν_{max} (KBr) cm^{-1} 3320 (NH), 1660 (CO), 1615 (C=N), 1595 (Ar-C=C). ^{1}H-NMR (DMSO-d$_6$); δ 7.22-8.16 (m, 9H, Ar-H), 9.91 (br, 1H, phenyl-NH). ^{13}C-NMR (DMSO-d$_6$); δ 126.96, 127.54, 127.93, 129.53, 132.71 (Ar-*C*H), 134.66, 141.12 (Ar-*C*), 136.88, 137.12 (*C*-10a, *C*-4a), 151.86 (*C*-11a), 157.73 (*C*-2), 179.83 (*C*-5, *C*-10). MS; m/z (%) 346 (M$^+$, 24), 211 (21), 196 (12), 150 (48), 135 (51), 105 (63), 77 (100), 65 (46). Anal. Calcd. For $C_{18}H_{10}N_4O_2S$: C, 62.42; H, 2.91; N, 16.18; S, 9.26. Found: C, 62.26; H, 3.11; N, 16.41; S, 9.06.

2-Benzylaminonaphtho[4,5]imidazo[2,1-*b*][1,3,4]thiadiazole-5,10-diones (15b). Reddish orange crystals (acetonitrile) (130 mg, 36 %), mp 291-293 ^{o}C. IR; ν_{max} (KBr) cm^{-1} 3290 (NH), 1665 (CO), 1610 (C=N), 1585 (Ar-C=C). ^{1}H-NMR (DMSO-d$_6$); δ 4.58 (s, 2H, CH_2Ph), 7.23-8.05 (m, 9H, Ar-H), 8.96 (br, 1H, benzyl-NH). ^{13}C-NMR (DMSO-d$_6$); δ 52.64 (*C*H$_2$Ph), 126.96, 127.71, 127.98, 128.72, 132.61 (Ar-*C*H), 134.65, 139.96 (Ar-*C*), 136.89, 137.39 (*C*-10a, *C*-4a), 152.41 (*C*-11a), 158.11 (*C*-2), 179.72 (*C*-5, *C*-10). MS; m/z (%) 360 (M$^+$, 21), 211 (12), 196 (7), 164 (33), 149 (46), 105 (81), 91 (100), 77 (56), 65 (42). Anal. Calcd. For $C_{19}H_{12}N_4O_2S$: C, 63.32; H, 3.36; N, 15.55; S, 8.90. Found: C, 63.56; H, 3.44; N, 15.31; S, 9.11.

2-Allylaminonaphtho[4,5]imidazo[2,1-*b*][1,3,4]thiadiazole-5,10-diones (15c). Reddish orange crystals (acetonitrile) (118 mg, 38 %), mp 227-229 ^{o}C. IR; ν_{max} (KBr) cm^{-1} 3310 (NH), 2980 (Ali-H), 1665 (CO), 1620 (C=N). ^{1}H-NMR (DMSO-d$_6$); δ 4.16 (br, 2H, allyl-CH_2N), 5.12-5.17 (m, 2H, allyl-CH_2=), 5.88-5.92 (m, 1H, allyl-CH=), 7.56 (br, 1H, allyl-NH). ^{13}C-NMR (DMSO-d$_6$); δ 43.23 (allyl-*C*H$_2$N), 115.06 (allyl-*C*H$_2$=), 126.92, 132.76 (Ar-*C*H), 134.44 (Ar-*C*), 134.83 (allyl-*C*H=), 136.87, 137.26 (*C*-10a, *C*-4a), 152.29 (*C*-11a), 158.12 (*C*-2), 179.59 (*C*-5, *C*-10). MS; m/z (%) 310 (M$^+$, 26), 211 (18), 196 (17), 105 (62), 99 (76), 41 (100). Anal. Calcd. For $C_{15}H_{10}N_4O_2S$: C, 58.05; H, 3.25; N, 18.05; S, 10.33. Found: C, 57.79; H, 3.37; N, 17.81; S, 10.11.

2,11-Diphenylaminonaphtho[1,2-*d*:4,3-*d'*]bis(imidazo[2,1-*b*][1,3,4]thiadiazole) (16a). Reddish brown crystals (methanol) (222 mg, 44 %), mp 306-308 ^{o}C. IR; ν_{max} (KBr) cm^{-1} 3330 (NH), 1620 (C=N), 1585 (Ar-C=C). ^{1}H-NMR (DMSO-d$_6$); δ 7.16-8.19 (m, 14H, Ar-H), 9.92 (br, 2H, phenyl-NH). ^{13}C-NMR (DMSO-d$_6$); δ 126.83, 127.12, 127.96, 128.57, 129.42 (Ar-*C*H), 129.93, 131.84, 141.53 (Ar-*C*), 151.57 (*C*-12a, *C*-14a), 157.93 (*C*-2, *C*-11). MS; m/z (%) 504 (M$^+$, 18), 369 (6), 234 (14), 204 (16), 176 (23), 135 (76), 77 (100), 65 (36). Anal. Calcd. For $C_{26}H_{16}N_8S_2$: C, 61.89; H, 3.20; N, 22.21; S, 12.71. Found: C, 62.12; H, 3.06; N, 22.44; S, 12.95.

2,11-Dibenzylaminonaphtho[1,2-*d*:4,3-*d'*]bis(imidazo[2,1-*b*][1,3,4]thiadiazole) (16b). Reddish brown crystals (methanol) (218 mg, 41 %), mp 334-336 ^{o}C. IR; ν_{max} (KBr) cm^{-1} 3315 (NH), 1625 (C=N), 1590 (Ar-C=C). ^{1}H-NMR (DMSO-d$_6$); δ 4.63 (S, 2H, CH_2Ph), 7.23-8.16 (m,

14H, Ar-H), 8.94 (br, 2H, benzyl-NH). ^{13}C-NMR (DMSO-d_6); δ 52.39 (*C*H_2Ph), 126.78, 126.97, 127.26, 127.88, 128.53 (Ar-*C*H), 129.89, 130.85, 139.96 (Ar-*C*), 152.31 (*C*-12a, *C*-14a), 159.61 (*C*-2, *C*-11). MS; m/z (%) 532 (M^+, 12), 384 (16), 204 (9), 164 (26), 149 (63), 91 (100), 71 (56), 65 (37). Anal. Calcd. For $C_{28}H_{20}N_8S_2$: C, 63.14; H, 3.78; N, 21.04; S, 12.04. Found: C, 62.93; H, 3.86; N, 20.85; S, 11.81.

2,11-Diallylaminonaphtho[1,2-*d*:4,3-*d'*]bis(imidazo[2,1-*b*][1,3,4]thiadiazole) (16c). Reddish brown crystals (acetonitrile) (199 mg, 46 %), mp 275-277 °C. IR; ν_{max} (KBr) cm^{-1} 3290 (NH), 2970 (Ali-H), 1620 (C=N). ^{1}H-NMR (DMSO-d_6); δ 4.12 (br, 4H, allyl-CH_2N), 5.16-5.20 (m, 4H, allyl-CH_2=), 5.90-5.93 (m, 2H, allyl-CH=), 7.34-8.19 (m, 6H, Ar-H and allyl-NH). ^{13}C-NMR (DMSO-d_6); δ 42.96 (allyl-*C*H_2N), 114.88 (allyl-*C*H_2=), 135.12 (allyl-*C*H=), 127.43, 127.96 (Ar-*C*H), 129.76, 130.87 (Ar-*C*), 152.56(*C*-12a, *C*-14a), 159.63 (*C*-2, *C*-11). MS; m/z (%) 432 (M^+, 12), 234 (16), 204 (11), 128 (16), 99 (69), 74 (33), 41 (100). Anal. Calcd. For $C_{20}H_{16}N_8S_2$: C, 55.54; H, 3.73; N, 25.91; S, 14.83. Found: C, 55.76; H, 3.57; N, 26.14; S, 15.09.

Reaction of 1-substituted-2,5-dithiobiureas 6a-c with (1,3-dioxo-2,3-dihydro-1(*H*)-inden-2-ylidene)propanedinitrile (8)

To a solution of 1.0 mmole of **6a-c** in 20 ml dry ethyl acetate, 416 mg (2.0 mmole) of **8** were added. Within two minutes, the initially yellow solution first turned to reddish brown and then brown, the mixture was stirred for 3 hours at 20 °C. The mixture was left standing for 48 hours at room temperature, concentrated and subjected to plc using cyclohexane/ethyl acetate (3:1) to give numerous coloured zones. The three intense of which were removed and extracted. The fastest migrating one contained *N*-substituted (oxoindeno-pyrrolylidene)hydrazinecarbothioamides **19a-c**, the second zone (which is always characterized by orange colour) contained (4-cyano-5-oxoindenothiazinylidene)*N*-substituted hydrazine-carbothioamide **18a-c**. The slowest migrating zone contained 2-(4,4-dicyano-5-oxoindeno-thiazinylidene)*N*-substituted carbothioamides **17a-c**. Extractions of zones with acetone and recrystallized.

***N*-Phenyl-2-(4,4-dicyano-5-oxoindeno[1,2-*d*][1,3]thiazin-2-(1*H*,4*H*,5*H*)-ylidene)hydrazine-carbothioamide (17a).** Reddish brown crystals (acetonitrile) (204 mg, 49 %), mp 301-303 °C. IR; ν_{max} (KBr) cm^{-1} 3340, 3310, 3280 (NH), 2210 (CN), 1730 (CO), 1635 (C=N), 1570 (NH def. and C-N str.), 1345, 1010 (C=S, C-N), ^{1}H-NMR (DMSO-d_6); δ 7.21-7.72 (m, 9H, Ar-H), 7.96 (br, 1H, thiazine-NH), 9.73 (br, 1H, hydrazine-NH), 9.89 (br, 1H, phenyl-NH). ^{13}C-NMR (DMSO-d_6); δ 31.27 (*C*-4), 107.12 (*C*-4a), 117.96 (*C*N), 126.34, 126.67, 127.51, 128.46, 128.92, 129.26, 129.83 (Ar-*C*H), 135.76, 136.66, 138.57 (Ar-*C*), 146.43 (*C*-9b), 156.32 (*C*-2), 181.22 (*C*=S), 195.52 (*C*O). MS; m/z (%) 416 (M^+, 26), 281 (31), 266 (24), 253 (11), 150 (26), 135 (49), 105 (83), 77 (100). Anal. Clacd. For $C_{20}H_{12}N_6OS_2$: C, 57.68; H, 2.90; N, 20.18; S, 15.40. Found: C, 57.87; H, 3.09; N, 20.41; S, 15.63.

***N*-Benzyl-2-(4,4-dicyano-5-oxoindeno[1,2-*d*][1,3]thiazin-2-(1*H*,4*H*,5*H*)-ylidene)hydrazine-carbothioamide (17b).** Reddish brown crystals (ethyl acetate) (194 mg, 45 %), mp 329-331 °C. IR; ν_{max} (KBr) cm^{-1} 3325, 3300, 3280 (NH), 2220 (CN), 1720 (CO), 1630 (C=N), 1575 (NH def.

and C-N str.), 1355, 990 (C=S, C-N), ^{1}H-NMR (DMSO-d_6); δ 4.65 (s, 2H, CH_2Ph), 7.23-7.57 (m, 9H, Ar-H), 7.92 (br, 1H, thiazine-NH), 8.91 (br, 1H, hydrazine-NH), 9.75 (br, 1H, benzyl-NH). ^{13}C-NMR (DMSO-d_6); δ 31.67 (*C*-4), 106.89 (*C*-4a), 118.12 (*C*N), 126.42, 126.79, 126.99, 127.74, 128.56, 129.66 (Ar-*C*H), 135.62, 136.44, 138.34 (Ar-*C*), 147.11 (*C*-9b), 156.88 (*C*-2), 181.06 (*C*=S), 195.36 (*C*O). MS; m/z (%) 430 (M^+, 34), 281 (28), 266 (9), 238 (21), 164 (35), 149 (66), 105 (58), 91 (100), 77 (63), 65 (44). Anal. Clacd. For $C_{21}H_{14}N_6OS_2$: C, 58.59; H, 3.28; N, 19.52; S, 14.90. Found: C, 58.36; H, 3.11; N, 19.74; S, 15.16.

***N*-Allyl-2-(4,4-dicyano-5-oxoindeno[1,2-*d*][1,3]thiazin-2-(1*H*,4*H*,5*H*)-ylidene)hydrazine-carbothioamide (17c).** Reddish brown crystals (ethanol) (167 mg, 44 %), mp 272-274 °C. IR; ν_{max} (KBr) cm^{-1} 3335, 3310, 3290 (NH), 2215 (CN), 1725 (CO), 1580 (C=N), 1570 (NH def. and C-N str.), 1350, 1010 (C=S, C-N), ^{1}H-NMR (DMSO-d_6); δ 4.12 (br, 2H, allyl-CH_2N), 5.11-5.14 (m, 2H, allyl-CH_2=), 5.90-5.93 (m, 1H, allyl-CH=), 7.36-7.67 (m, 5H, Ar-H and allyl-NH), 7.95 (br, 1H, thiazine-NH), 9.79 (br, 1H, hydrazine-NH). ^{13}C-NMR (DMSO-d_6); δ 31.52 (*C*-4), 44.12 (allyl-*C*H_2N), 107.14 (*C*-4a), 117.93 (*C*N), 118.13 (allyl-*C*H_2=), 126.89, 126.37, 128.49, 129.38 (Ar-*C*H), 134.82 (allyl-*C*H=), 135.86, 136.88 (Ar-*C*), 146.96 (*C*-9b), 157.29 (*C*-2), 181.66 (*C*=S), 195.66 (*C*O). MS; m/z (%) 380 (M^+, 42), 281 (23), 266 (16), 238 (23), 105 (100), 77 (83), 41 (93). Anal. Clacd. For $C_{17}H_{12}N_6OS_2$: C, 53.67; H, 3.18; N, 22.09; S, 16.86. Found: C, 53.45; H, 3.33; N, 21.82; S, 16.64.

***N*-Phenyl-2(4-cyano-5-oxoindeno[1,2-*d*][1,3]thiazin-2(5*H*)-ylidene)hydrazinecarbothio-amide (18a).** Orange crystals (ethanol) (121 mg, 31 %), mp 278-280 °C. IR; ν_{max} (KBr) cm^{-1} 3330, 3260 (NH), 2220 (CN), 1720 (CO), 1635 (C=N), 1570 (NH def. and C-N str.), 1360, 1000 (C=S, C-N). ^{1}H-NMR (DMSO-d_6); δ 7.24-8.05 (m, 9H, Ar-H), 9.78 (br, 1H, hydrazine-NH), 9.88 (br, 1H, phenyl-NH). ^{13}C-NMR (DMSO-d_6); δ 117.94 (*C*N), 126.69, 126.83, 126.97, 127.44, 128.56, 129.79, 129.93 (Ar-*C*H), 137.12, 138.14, 139.36 (Ar-*C*), 146.32 (*C*-4a), 152.88 (*C*-9b), 157.56 (*C*-2), 181.29 (*C*=S), 194.86 (*C*O). MS; m/z (%) 389 (M^+, 16), 254 (27), 239 (31), 150 (42), 135 (66), 105 (100), 77 (83). Anal. Clacd. For $C_{19}H_{11}N_5OS_2$: C, 58.60; H, 2.85; N, 17.98; S, 16.47. Found: C, 58.83; H, 3.04; N, 18.17; S, 16.24.

***N*-Benzyl-2(4-cyano-5-oxoindeno[1,2-*d*][1,3]thiazin-2(5*H*)-ylidene)hydrazinecarbothio-amide (18b).** Orange crystals (methanol) (117 mg, 29 %), mp 305-307 °C. IR; ν_{max} (KBr) cm^{-1} 3315, 3270 (NH), 2210 (CN), 1730 (CO), 1630 (C=N), 1565 (NH def. and C-N str.), 1355, 995 (C=S, C-N). ^{1}H-NMR (DMSO-d_6); δ 4.62 (s, 2H, CH_2Ph), 7.26-8.00 (m, 9H, Ar-H), 8.90 (br, 1H, benzyl-NH), 9.80 (br, 1H, hydrazine-NH). ^{13}C-NMR (DMSO-d_6); δ 52.43 (*C*H_2Ph), 118.29 (*C*N), 126.76, 126.93, 127.45, 127.71, 128.66, 129.54, 129.86 (Ar-*C*H), 135.66, 136.71, 137.92 (Ar-*C*), 145.94 (*C*-4a), 152.74 (*C*-9b), 157.43 (*C*-2), 181.35 (*C*=S), 195.12 (*C*O). MS; m/z (%) 403 (M^+, 22), 254 (19), 239 (6), 211 (29), 164 (32), 149 (47), 105 (81), 91 (100), 76 (63). Anal. Clacd. For $C_{20}H_{13}N_5OS_2$: C, 59.54; H, 3.25; N, 17.36; S, 15.89. Found: C, 59.76; H, 3.07; N, 17.59; S, 16.14.

***N*-Allyl-2(4-cyano-5-oxoindeno[1,2-*d*][1,3]thiazin-2(5*H*)-ylidene)hydrazinecarbothioamide (18c).** Orange crystals (acetonitrile) (102 mg, 29 %), mp 249-251 °C. IR; ν_{max} (KBr) cm^{-1} 3320,

3265 (NH), 2215 (CN), 1725 (CO), 1620 (C=N), 1575 (NH def. and C-N str.), 1360, 995 (C=S, C-N). ^{1}H-NMR (DMSO-d_6); δ 4.08 (br, 2H, allyl-CH_2N), 5.16-5.19 (m, 2H, allyl-CH_2), 5.88-5.92 (m, 1H, allyl-CH=), 7.59-8.05 (m, 5H, Ar-H and allyl-NH), 9.78 (br, 1H, hydrazine-NH). ^{13}C-NMR (DMSO-d_6); δ 43.29 (allyl-*C*H_2N), 117.66 (allyl-*C*H_2=), 117.93 (*C*N), 127.73, 128.64 (Ar-*C*H), 129.73, 130.11 (Ar-*C*), 134.79 (allyl-*C*H=), 146.24 (*C*-4a), 153.11 (*C*-9b), 158.12 (*C*-2), 178.93 (*C*=S), 194.77 (*C*O). MS; m/z (%) 353 (M^+, 25), 254 (18), 239 (24), 114 (41), 105 (73), 99 (84), 77 (62), 41 (100). Anal. Clacd. For $C_{16}H_{11}N_5OS_2$: C, 54.37; H, 3.14; N, 19.82; S, 18.15. Found: C, 54.52; H, 2.96; N, 20.09; S, 18.38.

***N*-Phenyl-2(3-cyano-4-oxoindeno[1,2-*b*]pyrrol-2(4*H*)-ylidene)hydrazinecarbothioamide (19a).** Pale red crystals (methanol) (39 mg, 11 %), mp 250-252 °C. IR; ν_{max} (KBr) cm^{-1} 3335, 3240 (NH), 2220 (CN), 1730 (CO), 1635 (C=N), 1600 (Ar-C=C), 1565 (NH def. and C-N str.), 1360, 1005 (C=S, C-N). ^{1}H-NMR (DMSO-d_6); δ 7.18-7.95 (m, 9H, Ar-H), 9.78 (br, 1H, hydrazine-NH), 9.91 (br, 1H, phenyl-NH). ^{13}C-NMR (DMSO-d_6); δ 117.86 (*C*N), 121.11 (*C*-3), 126.75, 126.93, 127.14, 128.48, 129.15, 129.78, 129.98 (Ar-*C*H), 135.81, 136.46, 139.22 (Ar-*C*), 147.12 (*C*-3a), 153.12 (*C*-8b), 158.36 (*C*-2), 181.53 (*C*=S), 194.69 (*C*O). MS; m/z (%) 357 (M^+, 43), 222 (29), 167 (23), 150 (36), 135 (57), 105 (74), 76 (100). Anal. Calcd. For $C_{19}H_{11}N_5OS$: C, 63.85; H, 3.10; N, 19.60; S, 8.97. Found: C, 64.08; H, 2.94; N, 19.79; S, 9.13.

***N*-Benzyl-2(3-cyano-4-oxoindeno[1,2-*b*]pyrrol-2(4*H*)-ylidene)hydrazinecarbothioamide (19b).** Orange crystals (acetonitrile) (26 mg, 7 %), mp 275-277 °C. IR; ν_{max} (KBr) cm^{-1} 3320, 3260 (NH), 2210 (CN), 1725 (CO), 1635 (C=N), 1600 (Ar-C=C), 1570 (NH def. and C-N str.), 1355, 995 (C=S, C-N). ^{1}H-NMR (DMSO-d_6); δ 4.61 (s, 2H, CH_2Ph), 7.23-8.00 (m, 9H, Ar-H), 8.88 (br, 1H, benzyl-NH), 9.76 (br, 1H, hydrazine-NH). ^{13}C-NMR (DMSO-d_6); δ 118.19 (*C*N), 120.96 (*C*-3), 126.79, 126.92, 127.22, 127.74, 128.56, 129.26, 129.89 (Ar-*C*H), 135.78, 136.39, 139.29 (Ar-*C*), 146.14 (*C*-3a), 152.66 (*C*-8b), 157.53 (*C*-2), 181.52 (*C*=S), 194.94 (*C*O). MS; m/z (%) 371 (M^+, 36), 222 (28), 167 (24), 164 (18), 149 (54), 105 (86), 91 (100), 76 (62), 65 (47). Anal. Calcd. For $C_{20}H_{13}N_5OS$: C, 64.68; H, 3.53; N, 18.86; S, 8.63. Found: C, 64.44; H, 3.76; N, 19.11; S, 8.39.

***N*-Allyl-2(3-cyano-4-oxoindeno[1,2-*b*]pyrrol-2(4*H*)-ylidene)hydrazinecarbothioamide (19c).** Red crystals (methanol) (32 mg, 10 %), mp 226-228 °C. IR; ν_{max} (KBr) cm^{-1} 3330, 3270 (NH), 2215 (CN), 1720 (CO), 1630 (C=N), 1575 (NH def. and C-N str.), 1350, 1010 (C=S, C-N). ^{1}H-NMR (DMSO-d_6); δ 4.12 (br, 2H, allyl-CH_2N), 5.14-5.17 (m, 2H, allyl-CH_2=), 5.90-5.94 (m, 1H, allyl-CH=), 7.52-7.95 (m, 5H, Ar-H and allyl-NH), 9.77 (br, 1H, hydrazine-NH). ^{13}C-NMR (DMSO-d_6); δ 42.83 (allyl-*C*H_2N), 117.95 (*C*N), 118.41 (allyl-*C*H_2=), 121.23 (*C*-3), 126.76, 126.95, 129.58, 129.97 (Ar-*C*H), 135.16 (allyl-*C*H=), 135.74, 136.55 (Ar-*C*), 145.92 (*C*-3a), 152.29 (*C*-8b), 158.31 (*C*-2), 179.22 (*C*=S), 194.83 (*C*O). MS; m/z (%) 321 (M^+, 38), 222 (27), 167 (19), 105 (91), 99 (64), 41 (100). Anal. Calcd. For $C_{16}H_{11}N_5OS$: C, 59.80; H, 3.45; N, 21.79; S, 9.98. Found: C, 59.57; H, 3.64; N, 22.05; S, 10.14.

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