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 naphthoimidazothiadiazoles. 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)-inden-2-ylidene)-propanedinitrile with 1-substituted-2,5-dithiobiureas forming the derivatives of (oxoindeno-thiazinylidene)hydrazinecarbothioamide as well as (oxoindenopyrrolylidene)hydrazinecarbothioamides. 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)-inden-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).\(^2\)

![Chart 1](image)

**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-naphthoquinone (7) and (1,3-dioxo-2,3-dihydro-1(H)-inden-2-ylidene)propanedinitrile (8) Figure 1.

![Figure 1](image)

**Figure 1.** 1-Substituted-2,5-dithiobiureas and some \(\pi\)-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 benzobisimidazothiadiazoles 10a-c as minor (21-24%) and substituted imidazothiadiazolediones 9a-c as major products (48-54%) (Scheme 1).

![Scheme 1](image)

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 $\delta = 169.90$ ppm,23 is replaced by signal at $\delta = 140.78$ 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 $\nu = 3320-3295$, and 1625-1620 cm$^{-1}$ for (NH) and (C=N) groups, respectively. The 1H-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. It worthy to note that the mass spectra of compounds 9a-c show the loss of substituted isothiocyanates as well as N₂ 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 naphthimidazothiadiazoliones 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 ¹³C-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_{8}S_{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_{2}O. 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 \(\delta = 152.56\) and 159.63 ppm, respectively. The presence of allyl group is also evident from \(^{13}\)C-DEPT-NMR spectrum exhibiting positive signal at \(\delta = 135.12\) (allyl-CH=) and negative signals at 42.96 and 114.88 due to (allyl-CH_{2}N) and (allyl-CH_{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.

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)propanedinitrile (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.
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 been 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 bands 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 cm⁻¹ due to (NH-deformation and C-N stretching) and intense bands in the range of 1360-1345 cm⁻¹ as well as 990-1010 cm⁻¹ assigned to strongly coupled between C=S and C-N vibrations. The ¹H-NMR spectrum of N-phenyl-2-(4,4-dicyano-5-oxoindeno[1,2-d][1,3]thiazin-2(1H,4H,5H)-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 (CO) in the ¹³C-NMR spectrum of 17a lend further support of the structure assigned to 17a. 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(1H,4H,5H)-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(5H)-ylidene)hydrazinecarbothioamide (18b) is based on the following spectral data: The ¹H-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-CH₂, and aromatic protons. The ¹³C-NMR decoupling showed signals at 52.43 (CH₃), 145.94 (C-3a), 157.43 (C-2), 152.74 (C-9b), 181.35
(C=S) and 195.12 (CO). 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), benzyol 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 13C-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 1H-NMR in DMSO-d6 of 19c displayed broadened signals at δ = 4.12 (allyl-CH2N), 7.79 (allyl-NH) and 9.77 (hydrazine-NH) as well as multiplets at 5.14-5.17 (allyl-CH2=), 5.90-94 (allyl-CH=) and aromatic protons. The presence of allyl group is also evident from 13C-DEPT-NMR spectrum which exhibits negative signals at δ = 42.83 (allyl-CH2N) and 118.41 (allyl-CH2=) as well as positive signal at 135.16 ppm due to (allyl-CH=). The elemental analysis supported the gross composition C16H11N5OS 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 cyanomethylenedindanedione 20. The first, is abstraction of a proton from 6a-c by the carbanione 8-H\(^-\) 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\(^-\).30 Combination of 6a-c and 20 with the elimination of H2S and H2O afforded the substituted (oxoindenopyrrolylidene)hydrazinecarbothioamide 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 1H-NMR and 13C-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 PF254 (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)propanedinitrile (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 °C. IR: ν max (KBr) cm⁻¹ 3280 (NH), 1675 (CO), 1615 (C=N), 1585 (Ar-C=C). ¹H-NMR (DMSO-d₆); δ 7.18-7.71 (m, 5H, Ar-H), 9.84 (br, 1H, Phenyl-NH). ¹³C-NMR (DMSO-d₆); δ 127.86, 128.64, 129.74 (Ar-CH), 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), 328 (21), 229 (18), 201 (24), 150 (31), 135 (52), 91 (64), 77 (100), 65 (52). Anal. Calcd. For C₁₄H₆Cl₂N₄O₂S: 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 °C. IR: ν max (KBr) cm⁻¹ 3290 (NH), 1680 (CO), 1620 (C=N), 1580 (Ar-C=C). ¹H-NMR (DMSO-d₆); δ 4.61 (s, 2H, CH₂Ph), 7.22-7.49 (m, 5H, Ar-H), 8.78 (br, 1H, benzyl-NH). ¹³C-NMR (DMSO-d₆); δ 52.56 (CH₂Ph), 127.76, 127.98, 128.83 (Ar-CH), 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 C₁₅H₁₂Cl₂N₄O₂S: 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-dichlorobenz[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\text{max} (KBr) cm\textsuperscript{-1} 3275 (NH), 2975 (Allyl-CH), 1680 (CO), 1610 (C=N). \textsuperscript{1}H-NMR (DMSO-d\textsubscript{6}): δ 4.12 (br, 2H, allyl-CH\textsubscript{2}N), 5.19-5.22 (m, 2H, allyl-CH\textsubscript{2}=), 5.87-5.94 (m, 1H, allyl-CH=), 7.61 (br, 1H, allyl-NH). \textsuperscript{13}C-NMR (DMSO-d\textsubscript{6}): δ 43.39 (allyl-C\textsubscript{H}2N), 115.02 (allyl-C\textsubscript{H}2=), 134.71 (allyl-CH\textsubscript{2}=), 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\textsuperscript{+}, 34), 292 (27), 256 (18), 229 (24), 201 (9), 114 (27), 99 (61), 41 (100). Anal. Calcd. For C\textsubscript{11}H\textsubscript{6}Cl\textsubscript{2}N\textsubscript{4}O\textsubscript{2}S: 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, 17.02; S, 9.52.

5,11-Dichloro-2,8-diphenylaminobenz[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\text{max} (KBr) cm\textsuperscript{-1} 3310 (NH), 1625 (C=N), 1595 (Ar-C=C). \textsuperscript{1}H-NMR (DMSO-d\textsubscript{6}): δ 7.17-7.71 (m, 10H, Ar-H), 9.88 (br, 2H, phenyl-NH). \textsuperscript{13}C-NMR (DMSO-d\textsubscript{6}): δ 124.18 (C-5, C-11), 127.82, 128.69, 129.57 (Ar-C\textsubscript{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\textsuperscript{+}, 26), 486 (34), 450 (25), 252 (33), 222 (26), 150 (72), 135 (100), 124 (18), 77 (41). Anal. Calcd. For C\textsubscript{22}H\textsubscript{12}Cl\textsubscript{2}N\textsubscript{8}S\textsubscript{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-dibenzylaminobenz[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\text{max} (KBr) cm\textsuperscript{-1} 3295 (NH), 1620 (C=N), 1590 (Ar-C=C). \textsuperscript{1}H-NMR (DMSO-d\textsubscript{6}): δ 4.58 (s, 4H, CH\textsubscript{2}Ph), 7.28-7.57 (m, 10H, Ar-H), 8.92 (br, 2H, benzyl-NH). \textsuperscript{13}C-NMR (DMSO-d\textsubscript{6}): δ 52.56 (C\textsubscript{H}2Ph), 123.89 (C-5, C-11), 127.78, 127.98, 128.52 (Ar-C), 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\textsuperscript{+}, 22), 478 (26), 252 (26), 222 (26), 150 (72), 135 (100), 124 (18), 77 (41). Anal. Calcd. For C\textsubscript{24}H\textsubscript{16}Cl\textsubscript{2}N\textsubscript{8}S\textsubscript{2}: C, 52.27; H, 2.92; Cl, 12.86; N, 20.46; S, 12.47.

5,11-Dichloro-2,8-diallylaminobenz[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\text{max} (KBr) cm\textsuperscript{-1} 3320 (NH), 2965 (Ali-H), 1625 (C=N), 1595 (Ar-C=C). \textsuperscript{1}H-NMR (DMSO-d\textsubscript{6}): δ 4.11 (br, 4H, allyl-CH\textsubscript{2}N), 5.16-5.19 (m, 4H, allyl-CH=), 5.91-5.96 (m, 2H, allyl-CH=), 7.78 (br, 2H, allyl-NH). \textsuperscript{13}C-NMR (DMSO-d\textsubscript{6}): δ 43.29 (allyl-C\textsubscript{H}2N), 114.89 (allyl-CH\textsubscript{2}=), 123.96 (C-5, C-11), 134.76 (allyl-CH=), 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\textsuperscript{+}, 22), 378 (18), 252 (11), 222 (6), 114 (36), 99 (53), 41 (100). Anal. Calcd. For C\textsubscript{16}H\textsubscript{12}Cl\textsubscript{2}N\textsubscript{8}S\textsubscript{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 °C. IR; νmax (KBr) cm⁻¹ 3320 (NH), 1660 (CO), 1595 (Ar-C=N). ¹H-NMR (DMSO-d₆); δ 7.22-8.16 (m, 9H, Ar-H), 9.91 (br, 1H, phenyl-NH). ¹³C-NMR (DMSO-d₆); δ 126.96, 127.54, 127.93, 129.53, 132.71 (Ar-CH), 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 C₁₈H₁₀N₄O₂S: 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 °C. IR; νmax (KBr) cm⁻¹ 3290 (NH), 1665 (CO), 1610 (C=N). ¹H-NMR (DMSO-d₆); δ 4.58 (s, 2H, CH₂Ph), 7.23-8.05 (m, 9H, Ar-H), 8.96 (br, 1H, benzyl-NH). ¹³C-NMR (DMSO-d₆); δ 52.64 (CH₂Ph), 126.96, 127.71, 127.98, 128.72, 132.61 (Ar-CH), 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), 99 (76), 41 (100). Anal. Calcd. For C₁₉H₁₂N₄O₂S: 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 °C. IR; νmax (KBr) cm⁻¹ 3310 (NH), 2980 (Ally-H), 1665 (CO), 1595 (Ar-C=N). ¹H-NMR (DMSO-d₆); δ 4.16 (br, 2H, allyl-CH₂N), 5.12-5.17 (m, 2H, allyl-CH₂Ph), 5.88-5.92 (m, 1H, allyl-CH =), 7.56 (br, 1H, allyl-NH). ¹³C-NMR (DMSO-d₆); δ 43.23 (allyl-CH₂N), 115.06 (allyl-CH₂Ph), 126.92, 132.76 (Ar-CH), 134.44 (Ar-C), 134.83 (allyl-CH =), 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 C₁₅H₁₀N₄O₂S: 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.

2,11-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 266-268 °C. IR; νmax (KBr) cm⁻¹ 3330 (NH), 1620 (C=N), 1585 (Ar-C=N). ¹H-NMR (DMSO-d₆); δ 7.16-8.19 (m, 14H, Ar-H), 9.92 (br, 2H, phenyl-NH). ¹³C-NMR (DMSO-d₆); δ 126.83, 127.12, 127.96, 128.57, 129.42 (Ar-CH), 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 C₂₆H₁₆N₆S₂: 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 °C. IR; νmax (KBr) cm⁻¹ 3315 (NH), 1625 (C=N), 1590 (Ar-C=N). ¹H-NMR (DMSO-d₆); δ 4.63 (s, 2H, CH₂Ph), 7.23-8.16 (m,
14H, Ar-H), 8.94 (br, 2H, benzyl-NH). 13C-NMR (DMSO-d6); δ 52.39 (CH2Ph), 126.78, 126.97, 127.26, 127.88, 128.53 (Ar-CH), 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 C28H20N8S2: 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-Diallylamnonaphtho[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). 1H-NMR (DMSO-d6); δ 4.12 (br, 4H, allyl-CH2N), 5.16-5.20 (m, 4H, allyl-CH2=), 5.90-5.93 (m, 2H, allyl-CH=), 7.34-8.19 (m, 6H, Ar-H and allyl-NH). 13C-NMR (DMSO-d6); δ 42.96 (allyl-CH2N), 114.88 (allyl-CH2=), 135.12 (allyl-CH=), 127.43, 127.96 (Ar-C), 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 C20H16N8S2: 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-pyrolylidene)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-oxoindenothiazinylidene)N-substituted carbothioamides 17a-c. Extractions of zones with acetone and recrystallized.

N-Phenyl-2-(4,4-dicyano-5-oxoinden[1,2-d][1,3]thiazin-2-(1H,4H,5H)-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), 9.73 (br, 1H, thiazine-NH), 9.89 (br, 1H, phenyl-NH). 13C-NMR (DMSO-d6); δ 31.27 (C=4), 107.12 (C=4a), 117.96 (CN), 126.34, 126.67, 127.51, 128.46, 128.92, 129.26, 129.83 (Ar-CH), 135.76, 136.66, 138.57 (Ar-C), 146.43 (C=9b), 156.32 (C=9c), 181.22 (C=S), 195.52 (CO). MS; m/z (%) 416 (M+, 26), 281 (31), 266 (24), 253 (11), 150 (26), 135 (49), 105 (83), 77 (100). Anal. Calcd. For C20H12N6OS2: C, 55.76; H, 3.57; N, 25.28; S, 15.09. Found: C, 57.87; H, 3.09; N, 20.41; S, 15.63.

N-Benzyl-2-(4,4-dicyano-5-oxoinden[1,2-d][1,3]thiazin-2-(1H,4H,5H)-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$_2$Ph), 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 (CN), 126.42, 126.79, 126.99, 127.74, 128.56, 129.66 (Ar-CH), 135.62, 136.44, 138.34 (Ar-C), 147.11 (C-9b), 156.88 (C-2), 181.06 (C=S), 195.36 (CO). 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$_6$O$_2$: 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-(1H,4H,5H)-ylidene)hydrazinecarbothioamide (17c). Reddish brown crystals (ethanol) (167 mg, 44 %), mp 272-274 °C. IR; ν$_{\text{max}}$ (KBr) cm$^{-1}$ 3335, 3310, 3290 (NH), 2215 (CN), 1725 (CO), 1580 (C=N), 1570 (NH def. and C-N str.), 1355, 1010 (C=S, C-N), $^1$H-NMR (DMSO-d$_6$); δ 4.12 (br, 2H, allyl-CH$_2$N), 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$_2$H$_2$N), 107.14 (C-4a), 117.93 (CN), 118.13 (allyl-CH$_2$=), 126.89, 126.37, 128.49, 129.38 (Ar-CH), 134.82 (allyl-CH=), 135.86, 136.88 (Ar-C), 146.96 (C-9b), 157.29 (C-2), 181.66 (C=S), 195.66 (CO). 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$_6$O$_2$: 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(5H)-ylidene)hydrazinecarbothioamide (18a). Orange crystals (ethanol) (121 mg, 31 %), mp 278-280 °C. IR; ν$_{\text{max}}$ (KBr) cm$^{-1}$ 3330, 3260 (NH), 2215 (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 (CN), 126.69, 126.83, 126.97, 127.44, 129.79, 129.93 (Ar-CH), 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 (CO). 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$_5$O$_2$: 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(5H)-ylidene)hydrazinecarbothioamide (18b). Orange crystals (methanol) (117 mg, 29 %), mp 305-307 °C. IR; ν$_{\text{max}}$ (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$_2$Ph), 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 (CH$_2$Ph), 118.29 (CN), 126.76, 126.93, 127.45, 127.71, 128.66, 129.54, 129.86 (Ar-CH), 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 (CO). 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$_5$O$_2$: 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(5H)-ylidene)hydrazinecarbothioamide (18c). Orange crystals (acetonitrile) (102 mg, 29 %), mp 249-251 °C. IR; ν$_{\text{max}}$ (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$_2$N), 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$_2$H$_2$N), 117.66 (allyl-C$_2$H=), 117.93 (CN), 127.73, 128.64 (Ar-CH), 129.73, 130.11 (Ar-C), 134.79 (allyl-CH=), 146.24 (C-4a), 153.11 (C-9b), 158.12 (C-2), 178.93 (C=S), 194.77 (CO). 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$_5$OS$_2$: 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(4H)-ylidene)hydrazinecarbothioamide (19a). Pale red crystals (methanol) (39 mg, 11 %), mp 250-252 °C. IR; $\nu_{\text{max}}$ (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-CH), 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 (CO). MS; m/z (%) 357 (M +, 43), 222 (29), 167 (30), 135 (57), 105 (74), 76 (100). Anal. Calcd. For C$_{19}$H$_{11}$N$_5$OS: 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(4H)-ylidene)hydrazinecarbothioamide (19b). Orange crystals (acetonitrile) (26 mg, 7 %), mp 275-277 °C. IR; $\nu_{\text{max}}$ (KBr) cm$^{-1}$ 3320, 3260 (NH), 2210 (CN), 1720 (CO), 1635 (C=N), 1600 (Ar-C=C), 1565 (NH def. and C-N str.), 1355, 995 (C=S, C-N). $^1$H-NMR (DMSO-d$_6$): δ 4.61 (s, 2H, CH$_2$Ph), 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-CH), 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 (CO). 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$_5$OS: C, 64.68; H, 3.53; N, 18.86; S, 8.63. Found: C, 64.48; H, 3.76; N, 19.11; S, 8.39.

N-Allyl-2(3-cyano-4-oxoindeno[1,2-b]pyrrol-2(4H)-ylidene)hydrazinecarbothioamide (19c). Red crystals (methanol) (32 mg, 10 %), mp 226-228 °C. IR; $\nu_{\text{max}}$ (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$_2$N), 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-CH$_2$N), 117.95 (CN), 118.41 (allyl-CH$_2$=), 121.23 (C-3), 126.76, 126.95, 129.58, 129.97 (Ar-CH), 135.16 (allyl-CH=), 135.74, 136.55 (Ar-C), 145.92 (C-3a), 152.29 (C-8b), 158.31 (C-2), 179.22 (C=S), 194.83 (CO). MS; m/z (%) 321 (M +, 38), 222 (27), 167 (19), 105 (91), 99 (64), 41 (100). Anal. Calcd. For C$_{16}$H$_{11}$N$_5$OS: 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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References