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A variety of 1,4-thiazines, thiazoles, 1,4-dithines and 2,2'-bithiazoles containing fused naphthoquinone and related rings have been prepared. The compounds include several novel chromophoric heterocyclic system and their visible absorption spectra are discussed.

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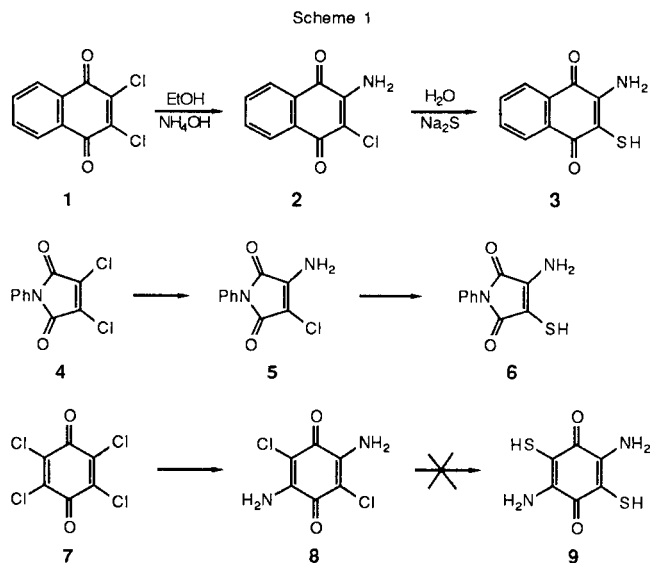
The chemistry of quinones is of considerable interest: the class includes many natural products and numerous important synthetic products [1-2]. A large variety of quinones, including many with fused heterocyclic rings, have been used as synthetic intermediates and in medicinal and industrial chemistry. Quinones are particularly important in dye chemistry [3], and many quinone dyes are commercially available. Recently, quinone-type dyestuffs have received increasing attention because of the search for new infrared dyes for optical recording media [4-5]. We have recently reported novel chromophoric heterocycles based on naphthoquinones and maleimides [6] in our search for new dyestuffs [7-10] using the theory of merostabilization of the excited state [11-14]. The present work represents a further extension of this search for derivatives of naphthoquinone and related systems with fused heterocyclic rings.

2,3-Dichloro-1,4-naphthoquinone **1** was readily converted into 2-amino-3-chloro-1,4-naphthoquinone **2** by ammonium hydroxide as previously described [15]. Heating **2** with sodium sulfide in water followed by acidification with dilute hydrochloric acid afforded 2-mercapto-3-amino-1,4-

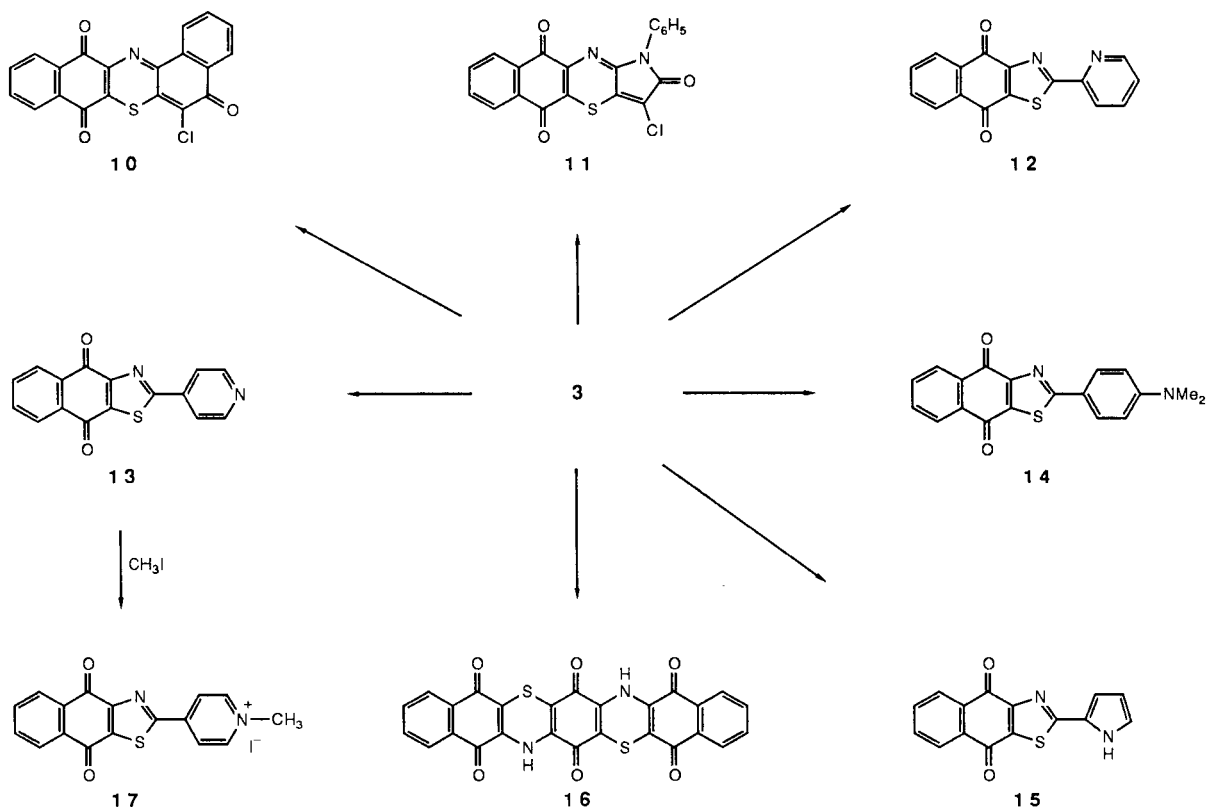
naphthoquinone **3** in 78% yield. In a similar manner, 2-mercapto-3-amino-*N*-phenylmaleimide **6** was prepared from 2,3-dichloro-*N*-phenylmaleimide **4** in two steps *via* 2-amino-3-chloro-*N*-phenylmaleimide **5** as shown in Scheme 1. Compounds **3**, **5** and **6** were characterized by ¹H and ¹³C nmr, ir spectra and by elemental analyses. An attempt to prepare 2,5-dimercapto-3,6-diamino-1,4-benzoquinone **9** by the same sequence failed, although 2,5-diamino-3,6-dichloro-1,4-benzoquinone was easily obtained.

Interest in 1,4-benzothiazine dyestuff chemistry has increased since the identification of the natural trichochrome pigments suggested that the benzothiazine system might form the basis of new dyes of possible commercial interest [16-17]. However, relatively little synthetic activity has been reported in this area, Thomson and his co-workers condensed 2-mercapto-3-amino-1,4-naphthoquinone with ω -bromoacetophenone to form 3-phenyl-3,4-dihydro-3-hydroxy-2*H*-naphtho[2,3-*b*]-1,4-thiazine-5,10-dione [18]. We describe in this paper the synthesis of naphthoquinone-1,4-thiazine derivatives by the nucleophilic substitution of 2-mercapto-3-amino-1,4-naphthoquinone **3** and compounds containing active chlorine atoms. Compound **3** reacted with 2,3-dichloro-1,4-naphthoquinone **1** in ethanol to give a red solid. This sparingly soluble product was assigned the 1,4-thiazine structure **10** based on analysis and ir spectra. The reaction pattern is similar to some known reactions of 2,3-dichloro-1,4-naphthoquinone **1** with binucleophiles such as *o*-aminothiophenol [19]. Similarly, 2-mercapto-3-amino-1,4-naphthoquinone with 2,3-dichloro-*N*-phenylmaleimide **4** and with 2,3,5,6-tetrachloro-1,4-benzoquinone afforded 1,4-thiazines **11** and **16**, respectively (Scheme 2); **11** and **16** both form sparingly soluble red crystals, and their structures were deduced by elemental analyses and by ir spectra.

Many naphthoquinone-fused thiazoles have previously been prepared from the *in situ* reactions of 2-mercapto-3-amino-1,4-naphthoquinone sodium salt (from 2-amino-3-chloro-1,4-naphthoquinone and sodium sulfide but without isolation) and appropriate aldehydes [20-21]. We



Scheme 2



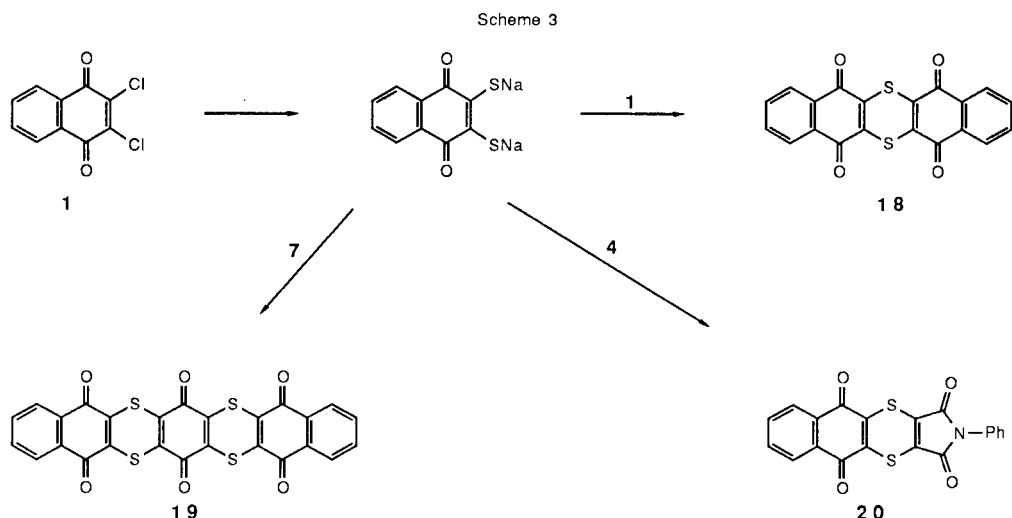
have now investigated analogous reactions with other aldehydes in order to find novel dyes. 4-Dimethylaminobenzaldehyde, pyrrole-2-carboxaldehyde and 2- or 4-pyridinecarboxaldehyde gave the expected thiazole derivatives **14**, **15**, **12**, and **13** in good yields (Scheme 2). 2-(4-Dimethylaminophenyl)-4,9-dioxonaphtho[2,3-*d*]thiazole hydrochloride **14** forms attractive bluish-purple needles. The ir, ^1H and ^{13}C nmr spectra and elemental analyses of these compounds agree with the structures. Two different carbonyl groups appear at around 180 ppm in ^{13}C nmr spectra and 1670 and 1650 cm^{-1} in the ir spectra. Quarternization of 2-(4-pyridyl)-4,9-dioxonaphtho[2,3-*d*]thiazole **13** with methyl iodide in dimethylformamide produced the corresponding pyridinium iodide **17**, but the 2-pyridyl isomer **12** did not react.

All these novel fused heterocyclic compounds contain the naphthoquinone chromophore, and furthermore, possess donor-acceptor substitution, thus merostabilization of their excited state should operate, and they are indeed deeply colored (red or purple) in the solid state. The visible absorption spectra were recorded in ethanol. For the 1,4-thiazine derivatives **10**, **11** and **16**, the absorption maximums occur at 490, 476 and 480 nm, respectively, and for the condensed thiazole derivatives **14** and **15**, at

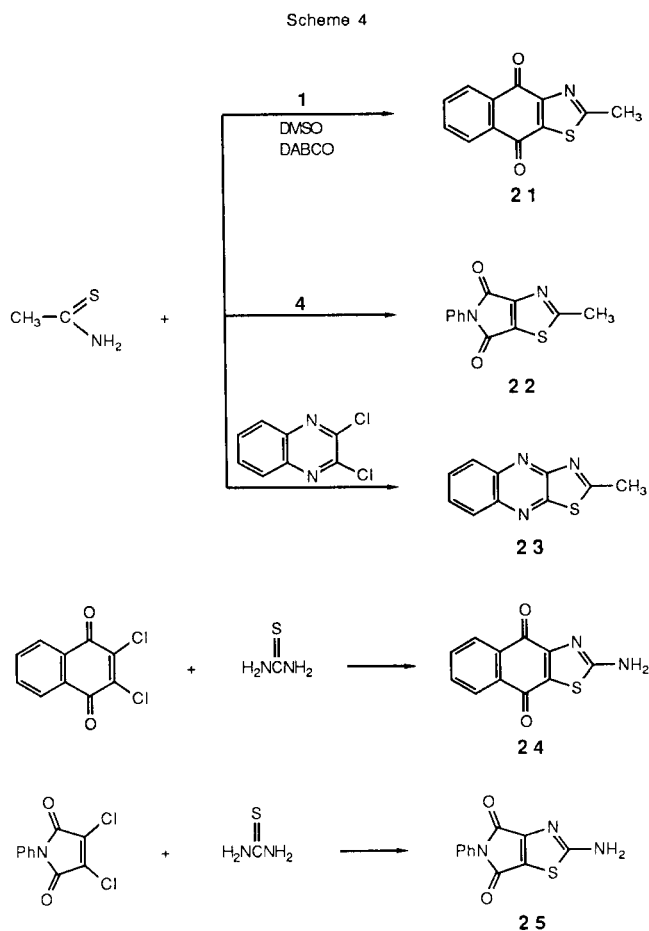
516 nm and 460 nm, respectively. However, the extinction coefficients of these compounds are not very high.

2,3-Dichloro-1,4-naphthoquinone reacted with a large excess of sodium sulfide in aqueous solution to give a deep green solution, which is, presumably, the sodium salt of 2,3-dimercapto-1,4-naphthoquinone. This deep green solution, without isolation, reacts further with an additional mole of 2,3-dichloro-1,4-naphthoquinone in aqueous dimethyl formamide to produce a purple powder, assigned the 5,7,12,14-tetraoxodibenzo[*b,d*]thianthrene structure **18**. This compound was previously prepared [22] by treatment of 2,3-dichloro-1,4-naphthoquinone with sodium sulfide followed by oxidation. By heating 2,3-dimercapto-1,4-naphthoquinone sodium salt with 2,3,5,6-tetrachloro-1,4-benzoquinone or 2,3-dichloro-*N*-phenylmaleimide in aqueous dimethylformamide, the expected 1,4-dithiins **19** and **20**, respectively, were afforded as purple solids. Both were characterized by ir and nmr spectra and by elemental analyses.

Beckert and Fablan [23] recently reacted aliphatic thioamides and oxalyl bisarylimido chlorides, the intermediate 2-methyl- Δ^2 -thiazoline-4,5-diimides underwent oxidative dimerization in dimethyl sulfoxide and in the presence of 1,4-diazabicyclo[2.2.2]octane produced tetramethine



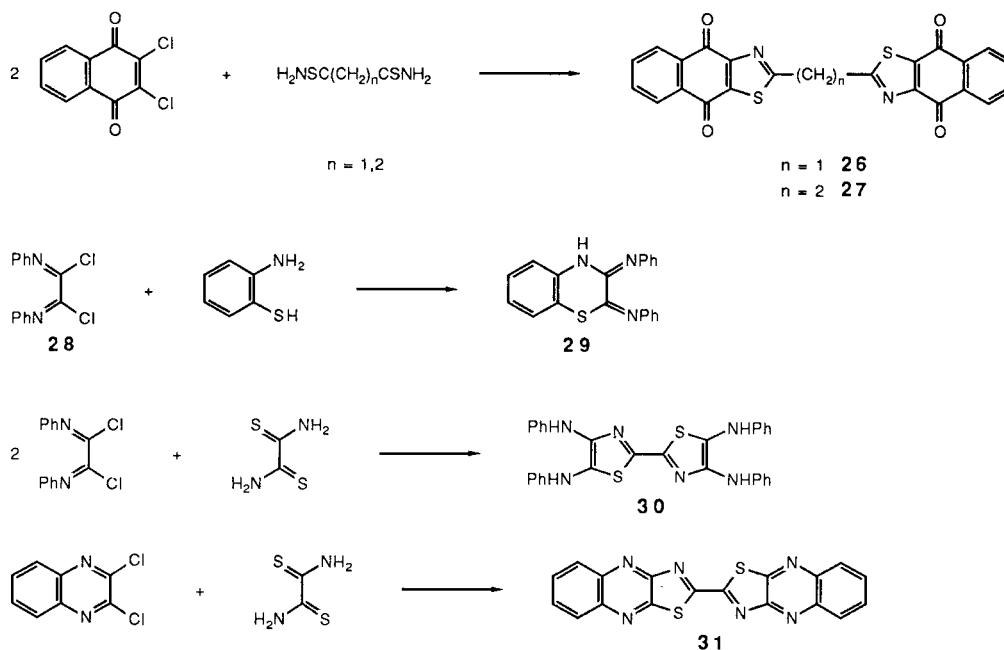
bridged heterocycles. We have now examined analogous reactions between thioacetamide, dithioamides or thiourea and compounds containing active chlorine atoms. Thioacetamide reacted with 2,3-dichloro-1,4-naphthoquinone under the same conditions as those of Beckert to



result in a redish brown solid, assigned as 2-methylnaphtho[2,3-*d*]thiazole-4,9-dione based on analysis and the ir spectra identical with the literature data [24]. This reaction is the same as that from heating the starting material in ethanol by Hamman [24]. No oxidative dimerization reaction was seen. Similarly, reaction of thioacetamide with 2,3-dichloro-*N*-phenylmaleimide afforded **21** as yellow solid, and with 2,3-dichloroquinoxaline produced compound **22** (Scheme 4). The structures of the poorly soluble products **20-22** were supported by ir spectra and by elemental analyses. In a similar manner, the reactions of thiourea with 2,3-dichloronaphthoquinone and with 2,3-dichloro-*N*-phenylmaleimide were also carried out: the thiazole derivatives **23** and **24** were formed as red solids. The ir spectra all show bands in the range 1700-1660, 1650-1630 and 1610-1600 cm^{-1} characteristic of ν (C=O) and ν (C=C) in quinones.

We recently reported [6] that 2,3-dichloro-1,4-naphthoquinone underwent nucleophilic substitution with a variety of binucleophiles, such as *o*-phenyldiamine, *o*-aminothiophenol and dithioamide to produce colored compounds. We now find that *o*-aminothiophenol reacts with oxalyl bisphenylimido chloride **28** to form a red 1,4-thiazine derivative **29**. Dithiomalonamide and dithiosuccinamide, having two functional thioamide groups, could condense with two moles of 2,3-dichloro-1,4-naphthoquinone to give the red bisnaphtho[2,3-*d*]thiazole-4,9-diones **26** and **27**. The methylene groups in compounds **26** and **27** show signals at 3.55 and 2.85 ppm in the ^1H nmr spectra. Reaction of dithioamide with two moles of oxalyl bisphenylimido chloride **28** afforded the brown tetraphenylamino-2,2'-bithiazole derivative **30** similar to the reaction of dithioamide with 2,3-dichloro-1,4-naphthoquinone previously described by Hamman [24], and with 2,3-dichloroquinoxaline, a black compound **30** was produced.

Scheme 5



The uv-visible spectra of these thiazole compounds show absorption maxima around 470-510 nm with rather low extinction coefficients.

EXPERIMENTAL

Melting points of the products were measured on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. The ir spectra are of potassium bromide discs or in bromoform using a Perkin-Elmer 283 B spectrometer. The ^1H nmr spectra were obtained with a Varian EM 360L spectrometer using tetramethylsilane as an internal standard. The ^{13}C nmr spectra were recorded with a FX-100 (25.0 MHz) spectrometer. The solvent for nmr spectral determinations was DMSO- d_6 , unless otherwise noted. Visible spectra were measured on a Perkin-Elmer 330 spectrophotometer. Elemental analyses were carried out under the supervision of Dr. R. King of this department.

The following compounds were prepared by the literature method quoted: 2-amino-3-chloro-1,4-naphthoquinone **2**, mp 196-198° (lit [15] mp 195-196°); 2,5-diamino-3,6-dichloro-1,4-benzoquinone **3**, mp >300° (lit [25] mp >300°); 2,3-dichloro-*N*-phenylmaleimide **4**, mp 201-203° (lit [26] mp 201-202°).

2-Mercapto-3-amino-1,4-naphthoquinone (3)

2-Amino-3-chloro-1,4-naphthoquinone (4.15 g, 20 mmoles) was heated with sodium sulfide hydrate (7.0 g) in water (70 ml) for 45 minutes, and the solution turned deep blue. After cooling the solution was neutralized with dilute hydrochloric acid, the resulting dark red solid was filtered and recrystallized from dimethylformamide-ethanol (1:1 v/v) to give red crystals, mp 290-292° (lit [24] 293-295°); ^1H nmr: 8.51 (s, 1H, SH), 7.60-8.30 (m, 6H, ArH and NH₂); ^{13}C nmr: 179.9 (C=O), 178.6 (C=O), 153.5, 135.1, 133.1, 132.6, 132.1, 130.2, 126.2, 106.8; ir (potassium bromide): 3350, 1660, 1610, 780 cm^{-1} ; uv/vis (ethanol): 465 (8200).

Anal. Calcd. for C₁₀H₇NO₂S: C, 58.54; H, 3.41; N, 6.82. Found: C, 58.24; H, 3.62; N, 6.58.

2-Amino-3-chloro-*N*-phenylmaleimide (5)

2,3-Dichloro-*N*-phenylmaleimide (11.4 g, 50 mmoles) was heated with concentrated ammonium hydroxide (60 ml) in aqueous ethanol (200 ml) for 4 hours and during this time ammonia gas was passed through the solution. Nitrogen gas was then bubbled through the hot solution to remove ammonia. After cooling to 0°, the resulting crystals were collected by filtration and washed with water to give pale yellow plates (40%), mp 190-192°; ^1H nmr: 9.65 (br s, 2H, NH₂), 7.20-7.65 (m, 5H, ArH); ^{13}C nmr: 167.3 (C=O), 165.6 (C=O), 136.7, 135.5, 127.0, 123.7, 122.4, 92.1; ir (bromoform): 3250, 1720, 1700, 1640, 1585, 1500, 740 cm^{-1} .

Anal. Calcd. for C₁₀H₇ClN₂O₂: C, 53.93; H, 3.15; N, 12.58. Found: C, 53.71; H, 2.89; N, 12.34.

2-Mercapto-3-amino-*N*-phenylmaleimide (6)

The preparative procedure was the same as that of **3**, yellow plates, yield 52%, mp 91-93°; ^1H nmr: 7.05-7.60 (m, 5H, ArH), 6.70 (br, 3H, NH₂ and SH); ^{13}C nmr: 166.5 (C=O), 163.8 (C=O), 135.1, 134.7, 128.8, 124.5, 111.3, 105.1; ir (bromoform): 3350, 3200, 1700, 1680, 1600, 1510 cm^{-1} .

Anal. Calcd. for C₁₀H₈N₂O₂S: C, 54.55; H, 3.64; N, 12.73. Found: C, 54.17; H, 3.85; N, 12.50.

6-Chloro-5,8,13-trioxobisnaphtho[1,2-b:2,3-e]-1,4-thiazine (10)

The reaction mixture of 2-mercapto-3-amino-1,4-naphthoquinone **3** (10 mmoles) and 2,3-dichloro-1,4-naphthoquinone (10 mmoles) was refluxed in ethanol for one day. After cooling, the red solid was collected and washed with water and then with ethanol, yield 70%, mp 201-203°, not soluble in the nmr solvent; ir (bromoform): 1675, 1590, 1520, 1270, 820, 780 cm^{-1} ; uv/vis (ethanol): 490 nm (8900).

Anal. Calcd. for C₂₀H₈ClNO₃S: C, 69.46; H, 2.27; N, 4.05. Found: C, 69.10; H, 1.98; N, 3.94.

1*H*-1-Phenyl-3-chloro-2,5,10-trioxopyrro[4,5-*b*]naphtho[2,3-*e*]-1,4-thiazine (11)

The preparation was as above, yield 51%, mp 191-193°; ^1H nmr (DMSO- d_6 -trifluoroacetic acid): 7.40-7.90 (m); ir (bromoform): 1710, 1660, 1585, 1520, 1385, 1270, 730 cm^{-1} ; uv/vis (ethanol): 476 nm (7100), 400 nm (9000).

Anal. Calcd. for C₂₀H₈ClN₂O₃S: C, 61.10; H, 2.32; N, 7.10. Found: C, 61.45; H, 2.60; N, 6.81.

5,7,9,14,16,18-Hexaoxo-8*H*,17*H*-dibenzo[*b,m*]triphenodithiazine (16)

This compound was obtained as a red powder, yield 58%, mp 275-278°; ir (bromoform): 3500, 1680, 1610, 1585, 1525, 1300, 1270, 720 cm^{-1} ; uv/vis (ethanol): 480 nm (12600).

Anal. Calcd. for $\text{C}_{26}\text{H}_{10}\text{N}_2\text{O}_2\text{S}_2$: C, 61.18; H, 1.98; N, 5.46. Found: C, 60.91; H, 2.20; N, 5.18.

2-(2-Pyridyl)-4,9-dioxonaphtho[2,3-*d*]thiazole (12).

The preparation was the same as above, yield 69%, mp >250°; ^1H nmr: 8.25-8.00 (m, 2H), 7.80-7.45 (m, 6H); ir (bromoform): 1680, 1665, 1615, 1595, 1500 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 65.75; H, 2.74; N, 9.59. Found: C, 65.48; H, 2.98; N, 9.25.

2-(4-Pyridyl)-4,9-dioxonaphtho[2,3-*d*]thiazole (13).

2-Amino-3-chloro-1,4-naphthoquinone (1.80 g) was refluxed with sodium sulfide hydrate (2.50 g) in water (20 ml) for 30 minutes. To the resulting deep blue solution, 4-pyridinecarboxaldehyde (1.07 g) was added, followed by the addition of glacial acetic acid (2 ml). The mixture was heated for 30 minutes and then diluted with ethanol and cooled. The precipitate was collected and recrystallized from ethanol (1.15 g, 65%), mp >250°; ^1H nmr: 8.10 (d, 2H), 7.85-7.45 (m, 6H); ir (bromoform): 1670, 1650, 1620, 1600, 1580 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 65.75; H, 2.74; N, 9.59. Found: C, 66.10; H, 2.58; N, 9.40.

2-(4-Dimethylaminophenyl)-4,9-dioxonaphtho[2,3-*d*]thiazole (14).

2-Amino-3-chloro-1,4-naphthoquinone (3.2 g) was refluxed with sodium sulfide hydrate (5.0 g) in water (50 ml) for 30 minutes. Then *p*-dimethylaminobenzaldehyde (2.25 g) and glacial acetic acid (4 ml) was added to this resulting deep blue solution and the mixture was heated for 30 minutes. After cooling, the precipitate was filtered and recrystallized from dimethylformamide to afford bluish purple needles (4.1 g, 82%), mp >300°; ^1H nmr: 8.35-8.65 (m, 4H, ArH), 7.90-8.27 (m, 4H, ArH), 3.67 (s, 6H, NMe_2); ^{13}C nmr: 181.3 (C=O), 180.8 (C=O), 157.2, 156.2, 148.2, 147.1, 145.6, 137.7, 136.3, 135.8, 135.1, 132.7, 130.4, 129.9, 124.3, 49.5; ir (potassium bromide): 1670, 1645, 1600, 1490, 1320, 950, 810 cm^{-1} ; uv/vis (ethanol): 516 nm (11000).

Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_2\text{S}\cdot\text{HCl}$: C, 61.54; H, 3.96; N, 7.56. Found: C, 61.81; H, 3.69; N, 7.32.

2-(2-Pyrrolyl)-4,9-dioxonaphtho[2,3-*d*]thiazole (15).

The preparation was the same as above, reddish violet needles, mp >250°; ^1H nmr (DMSO- d_6 -trifluoroacetic acid): 7.90-8.40 (m, 4H), 7.15-7.35 (m, 2H), 6.40-6.60 (m, 1H); ir (bromoform): 3400, 1665, 1650, 1560 cm^{-1} ; uv/vis (ethanol): 460 nm (4900).

Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 64.29; H, 2.86; N, 10.00. Found: C, 64.01; H, 2.98; N, 9.69.

2-(*N*-Methyl-4-pyridinium)-4,9-dioxonaphtho[2,3-*d*]thiazole Iodide (17).

2-(4-Pyridyl)-4,9-dioxonaphtho[2,3-*d*]thiazole (13, 0.62 g) was refluxed with excess methyl iodide in dimethylformamide for 3 hours. The addition of a small amount of ether after cooling and filtration afforded a brown solid which on recrystallization from dimethylformamide/ethanol gave the pyridinium iodide 17 (0.68 g, 74%), mp >250°; ^1H nmr: 8.50 (d, 2H, PyH), 7.80-7.45 (m, 6H), 4.15 (s, 3H, CH_3); ir (bromoform): 1685, 1660, 1620, 1600, 1505 cm^{-1} .

Anal. Calcd. for $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_2\text{S}$: C, 47.00; H, 2.53; N, 6.45. Found: C, 46.68; H, 2.22; N, 6.15.

5,7,12,14-Tetraoxodibenzo[*b*,*d*]thianthrene (18).

This compound was obtained as a purple powder, mp 306-308° (lit [22] 302°); ir (potassium bromide): 1650, 1580, 1530, 1280, 790 cm^{-1} ; uv/vis (ethanol): 488 nm (4500).

Anal. Calcd. for $\text{C}_{22}\text{H}_8\text{O}_4\text{S}_2$: C, 63.83; H, 2.13. Found: C, 63.65; H, 2.45. 5,7,9,14,16,18-Hexaoxobisnaphtho[2,3-*b*:2,3-*b'*]benzo[1,2-*e*:4,5-*e'*]bis[1,4]-thiin (19).

This compound was obtained as a purple powder, 41%, mp 320-323°; ir (bromoform): 1660, 1585, 1530, 1475, 1310, 1280, 870, 790 cm^{-1} ; uv/vis (ethanol): 490 nm (5700).

Anal. Calcd. for $\text{C}_{26}\text{H}_8\text{O}_6\text{S}_2$: C, 57.05; H, 1.43. Found: C, 56.69; H, 1.25.

2-Phenyl-1,3,5,10-tetraoxo-2*H*-naphtho[2',3':5,6][1,4]dithiino[2,3-*c*]pyrrole (20).

This compound was obtained as a purple powder, 52%, mp 308-310°; ^1H nmr (trifluoroacetic acid): 8.40-7.35 (m, ArH); ir (bromoform): 1710, 1665, 1620, 1590, 1510, 1320, 850, 780 cm^{-1} ; uv/vis (ethanol): 470 nm (7000).

Anal. Calcd. for $\text{C}_{20}\text{H}_8\text{NO}_4\text{S}_2$: C, 61.38; H, 2.30; N, 3.58. Found: C, 60.98; H, 2.56; N, 3.31.

2-Methylnaphtho[2,3-*d*]thiazole-4,9-dione (21).

The reaction mixture of thioacetamide (10 mmoles), 2,3-dichloro-1,4-naphthoquinone (10 mmoles) and 1,4-diazabicyclo[2.2.2]octane in dimethyl sulfide (30 mmoles) was heated and stirred at 120° for 5 hours. Addition of ethanol after cooling afforded a brown solid which was washed with water and ethanol (62%), mp >300° (lit [24] 318-320°); ir (bromoform): 1670, 1650, 1600, 1520, 1300, 870 cm^{-1} ; uv/vis (ethanol): 495 nm (4000).

2-Methyl-1,3-thiazole-4,5-dicarboxylic Acid *N*-Phenylimide (22).

This compound was prepared as above, greenish yellow powder, 58%, mp >250°; ir (bromoform): 1700, 1670, 1610, 1130, 760 cm^{-1} ; uv/vis (ethanol): 425 nm (5200).

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 62.61; H, 3.28; N, 11.47. Found: C, 62.85; H, 3.17; N, 11.81.

2-Methylthiazolo[4,5-*b*]quinoxaline (23).

This compound was obtained as a deep yellow powder, yield 49%, mp >250°; ir (bromoform): 1640, 1605, 1520, 850, 750 cm^{-1} ; uv/vis (ethanol): 430 nm (7200).

Anal. Calcd. for $\text{C}_{10}\text{H}_7\text{N}_3\text{S}$: C, 59.70; H, 3.48; N, 20.91. Found: C, 59.95; H, 3.25; N, 20.70.

2-Aminonaphtho[2,3-*d*]thiazole-4,9-dione (24).

This compound was obtained as a violet powder, 45%, mp >300° (lit [24] 333°); ^1H nmr (DMSO- d_6 -trifluoroacetic acid): 7.85-8.25 (m, ArH); ir (bromoform): 3330, 1665, 1650, 1610 cm^{-1} ; uv/vis (ethanol): 505 nm (2500).

Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{N}_2\text{O}_2\text{S}$: C, 57.39; H, 2.61; N, 12.10. Found: C, 57.51; H, 2.57; N, 12.25.

2-Amino-1,3-thiazole-4,5-dicarboxylic Acid *N*-Phenylimide (25).

This compound was obtained as a greenish yellow powder, yield 59%, mp >300°; ir (bromoform): 3350, 1696, 1660, 1615, 1510, 790 cm^{-1} ; uv/vis (ethanol): 425 (4600).

Anal. Calcd. for $\text{C}_{11}\text{H}_7\text{N}_3\text{O}_2\text{S}$: C, 53.88; H, 2.86; N, 17.14. Found: C, 53.59; H, 2.98; N, 16.91.

1,2-Bis(4,9-dioxonaphtho[2,3-*d*]thiazol-2-yl)ethane (27).

A mixture of 2,3-dichloro-1,4-naphthoquinone (10 mmoles), dithio-succinamide (10 mmoles) and potassium carbonate was refluxed in ethanol (40 ml) for 5 hours. The resulting reddish brown solid was collected and washed with water and ethanol, yield 71%; mp 241-244° dec; ^1H nmr (trifluoroacetic acid): 7.85-8.25 (m, 4H, ArH), 7.30-7.80 (m, 4H, ArH), 2.80 (s, 4H, CH_2); ir (bromoform): 1670, 1655, 1615, 1580, 1500, 875 cm^{-1} ; uv/vis (ethanol): 490 nm (5700).

Anal. Calcd. for $\text{C}_{24}\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2$: C, 63.16; H, 2.63; N, 6.14. Found: C, 63.45; H, 2.79; N, 5.95.

Bis(4,9-dioxonaphtho[2,3-*d*]thiazol-2-yl)methane (26).

This compound was obtained as a brown powder, 49%, mp >300°; ^1H nmr (trifluoroacetic acid): 8.20-7.40 (m, ArH), 3.55 (s, 2H, CH_2); ir (bromoform): 1675, 1660, 1620, 1580, 1510, 880 cm^{-1} ; uv/vis (ethanol): 495 nm (6500).

Anal. Calcd. for $C_{23}H_{10}N_2O_4S_2$: C, 62.44; H, 2.26; N, 6.33. Found: C, 62.19; H, 2.48; N, 6.15.

1*H*-2,3-Diphenylimino-1,4-benzothiazine (29).

This compound was obtained as yellow needles, 48%, mp >250°; 1H nmr (trifluoroacetic acid): 7.95-7.40 (m, ArH); ir (bromoform): 3350, 3050, 1620, 1580, 1500, 950, 860 cm^{-1} ; uv/vis (ethanol): 386 nm (5900).

Anal. Calcd. for $C_{20}H_{15}N_3S$: C, 72.96; H, 4.56; N, 12.77. Found: C, 72.60; H, 4.79; N, 12.51.

4,4',5,5'-Tetraphenylamino-2,2'-bithiazole (30).

This compound was obtained as a brown powder, 52%, mp >300°; ir (bromoform): 3400, 3050, 1650, 1610, 1520, 1200, 840, 750 cm^{-1} .

Anal. Calcd. for $C_{30}H_{22}N_6S_2 \cdot HCl$: C, 63.95; H, 4.40; N, 13.35. Found: C, 64.30; H, 4.31; N, 13.57.

2,2'-Bisthiazolo[4,5-*b*]quinoxaline (31).

This compound was obtained as a brown powder, 42%, mp >250°; ir (bromoform): 1640, 1600, 1525, 1220, 960, 820 cm^{-1} .

Anal. Calcd. for $C_{18}H_8N_6S_2$: C, 58.06; H, 2.15; N, 22.58. Found: C, 58.34; H, 2.28; N, 22.60.

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