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The synthesis and spectral properties of novel thioquinone dyes

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Abstract

9,10-Dichloro-2,3,5,6-tetrahydrobenzo[*b*][1,4,7]trithionine-8,11-dione (**3**) and 2,3,5,6,10,11,13,14-octahydrobenzo[1,2-*b*:4,5-*b*′]bis[1,4,7]-trithionine-8,16-dione (**4**) were synthesized from the reaction of *p*-chloranil with bis(2-mercaptoethyl) sulfide. The reaction of *p*-chloranil with 1-mercapto-2-propanol and with naphthalene-2-thiol as well as with 6-mercapto-1-hexanol yielded novel compounds. The structures of the compounds were characterized by elemental analysis, UV/vis, FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopies.

Keywords: Thioquinone dyes; Tetrathiabenzoquinone; Chloranil; Benzoquinone thio-crown ether

1. Introduction

Tetrathiabenzoquinone compounds are used in the dye industry. Some thioquinone dye molecules are employed as organic nonlinear optical (NLO) materials [2], organic photoconductors (OPC) and emitters for electroluminescence (EL) [1]. Mercapto quinones are valuable fungicides [3], the quinone structure being present in numerous natural products that display antitumor, antifungal, antimalarial and antibacterial activities [4]. Tetraalkylmercapto-*p*-benzoquinones are used as additives in engine lubricants [5,6]. Bis(ethylenedithio)-1,4-benzoquinone and tetrathiotetracene behave as weak π-electron acceptors due to the electronic and steric effects of the fused group electrons and form a charge-transfer complex [7]. *p*-Benzoquinone derivatives are synthesized from fluoranil and chloranil; amphoteric redox potentials of the compounds with donor- and acceptor-substituents have been investigated [8].

The synthesis of the following compounds have been reported: tetrathioethylquinone, lead salt of tetrathioethylhydroquinone and acetic acid $[C_6(SC_2H_5)_4(OPbOCOCH_3)_2]$, tetrathioethylhydroquinone dibenzoate $[C_6(SC_2H_5)_4(OCOC_6H_5)_2]$, and dithioethyldiethoxy-hydroquinone dibenzoate $[C_6(SC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2]$ [9].

Isomer substituted quinone compounds have been prepared by the reactions of *p*-chloranil with NaOEt and NaOAr [10]. Tetrathiabenzoquinone compounds were synthesized from the reaction of *p*-chloranil with linear-chain ethyl mercaptane, dodecyl mercaptane and aromatic structure benzyl mercaptane, *p*-methylthiophenol [3]. Cyclic thioquinone compounds have been obtained from *p*-chloranil with dithiols $HS-(CH_2)_2-SH$, $HS-(CH_2)_3-SH$, *o*-$C_6H_4(SH)_2$, $HS-CH(CH_3)-CH_2-SH$ and $HO-CH_2-CH_2-SH$ [1]. The solid state spectra of cyclic thioquinones have been investigated [11]

The aim of this study is to synthesize and establish the structure of these novel compounds.

2. Results and discussion

We have previously reported the crown ethers generated from the reaction of *p*-chloranil with 2,2′-oxydiethanethiol [4]. In this study, the novel benzoquinone thio-crown ethers **3** and **4** were prepared from the reaction of *p*-chloranil (**1**) with bis(2-mercaptoethyl) sulfide (**2**) at room temperature in the presence of sodium carbonate in ethanol (Scheme 1).

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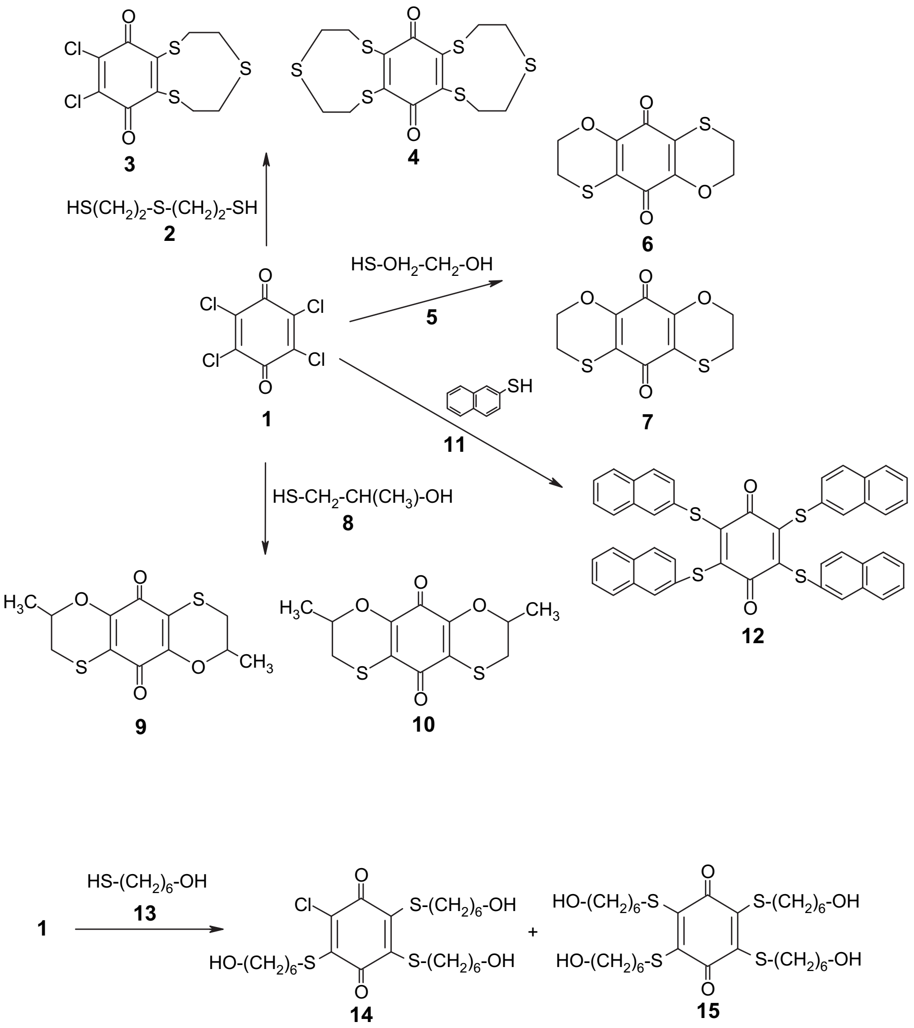

Scheme 1.

The IR spectra of compounds **3** and **4** showed characteristic carbonyl bands ($>$C=O) at 1660 and 1620 cm^{-1}, respectively.

The two isomers, **6**, **7** were obtained by reacting 2-mercaptoethanol (**5**) with *p*-chloranil (**1**); **6** has been synthesized before [1] whereas **7** is a new and stable product. The IR spectra of **6** and **7** showed different behaviour; that of **6** showed a $>$C=O group band at 1630 cm^{-1} and that of **7** displayed split bands due to the conjugated group effect at 1620, 1650 cm^{-1} for the $>$C=O group. The ^{13}C NMR spectrum of **6** gave a carbon signal at 176.20 ppm (O–C–*CO*–C–S) while that of **7** showed two carbon signals for the carbonyl groups at 170.65 ppm (S–C–*CO*–C–S) and 180.35 ppm (O–C–*CO*–C–O).

1-Mercapto-2-propanol (**8**) reacted with *p*-chloranil (**1**) furnished the new compounds **9** and **10**. The IR spectrum of **9** showed a band at 1650 cm^{-1} for the $>$C=O group and, for that of **10** split bands were observed due to the conjugated group effect at 1630, 1660 cm^{-1} for the $>$C=O group. The ^{13}C NMR spectrum of **9** showed a carbon signal at 176.32 ppm (O–C–*CO*–C–S) while **10** gave two carbon signals for the carbonyl groups at 170.71 ppm (S–C–*CO*–C–S) and 180.24 ppm (O–C–*CO*–C–O).

2,3,5,6-Tetrakis(naphalen-1-ylthio)cyclohexa-2,5-diene-1,4-dione (**12**) was prepared by reacting *p*-chloranil with naphthalene-2-thiol (**11**). The IR spectrum of compound **12** showed a characteristic $>$C=O group band at 1650 cm^{-1}.

The reaction of *p*-chloranil (**1**) with 6-mercapto-1-hexanol (**13**) resulted in the formation of new compounds **14** and **15** without heating (Scheme 1). The IR spectra showed hydroxyl bands (HO) at 3370, 3410 cm^{-1} and characteristic carbonyl bands ($>$C=O) at 1660, 1640 cm^{-1} for **14**, **15**, respectively.

These compounds **3**, **4**, **7**, **9**, **10**, **12**, **14** and **15** are new, stable and coloured dyes. The structure of the novel compounds were determined by microanalysis and spectroscopic data.

3. Experimental

3.1. Apparatus

Melting points were measured on a Buchi B-540 melting point apparatus and are uncorrected. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser. Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Shimadzu FT-IR-8101 spectrometer. UV spectra were recorded using a TU-1901 UV/vis spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Varian$^{\text{UNITY}}$ INOVA operating at 500 MHz and mass spectra were obtained on a Thermo Advantage MAX LC/MS/MS spectrometer. Products were isolated by column chromatography on silica gel (Fluka Silica gel 60, particle size: 63–200 μm). Merck TLC plates (silica 60F$_{254}$) were used, employing detection with UV light at 254 nm.

3.2. Procedures

3.2.1. Method A

Sodium carbonate was dissolved in ethanol and to the resulting solution was added *p*-chloranil followed by the thiol. The ensuing reaction mixture was refluxed for 5 h and concentrated [7]. The residue was extracted in a Soxhlet extractor with dichloromethane. After recovery of the solvent, the crude product was purified by chromatography.

3.2.2. Method B

Sodium carbonate was dissolved in ethanol and *p*-chloranil and the thiol were added slowly. Without heating, the colour of the solution quickly changed and the extent of the reaction was monitored by TLC. The reaction mixture was concentrated in vacuum and the residue extracted with dichloromethane. After solvent recovery, the crude product was purified by chromatography.

3.3. Synthesis

*3.3.1. Synthesis of 9,10-dichloro-2,3,5,6-tetrahydrobenzo-[b][1,4,7]trithionine-8,11-dione (**3**), 2,3,5,6,10,11,13,14-octahydrobenzo[1,2-b:4,5-b′]bis[1,4,7]trithionine-8,16-dione (**4**)*

Compounds **3** and **4** were synthesized by the reaction of 1 g (4.067 mmol) *p*-chloranil (**1**) with 1.06 ml (8.174 mmol) bis(2-mercaptoethyl) sulfide (**2**) using Method B.

*3.3.1.1. Compound **3***. Dark blue crystals, yield: 15% (0.20 g). M.p. 239–241 °C. $R_f = 0.59$ (petroleum ether/CH_2Cl_2 (1:1)). UV/vis ($CHCl_3$): λ_{max} (nm) = 245, 318, 555. IR (KBr): $\nu = 2900$ (C–H), 1660 (C=O), 1530 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$): $\delta = 2.8$–2.9 (t, 4H, *CH$_2$*), 3.6–3.7 (t, 4H, *CH$_2$*). MS: *m/z* (%) = 326.87. $C_{10}H_8Cl_2O_2S_3$ (327.27): calcd. C 36.7, H 2.46, S 29.39; found C 37.04, H 2.17, S 28.61.

*3.3.1.2. Compound **4***. Black-yellow crystals, yield: 24% (0.40 g). M.p. 169–182 °C. $R_f = 0.26$ (petroleum ether/CH_2Cl_2 (1:1)). UV/vis ($CHCl_3$): λ_{max} (nm) = 248, 421. IR (KBr): $\nu = 2850$ (C–H), 1620 (C=O), 1530 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$): $\delta = 2.8$–2.9 (m, 8H, *CH$_2$*), 3.6–3.7 (m, 8H, *CH$_2$*). ^{13}C NMR ($CDCl_3$): $\delta = 34.53$ (=C–S–*CH$_2$*–CH$_2$–S), 37.83 (S–CH$_2$–*CH$_2$*–S–CH$_2$), 144.78 (O=C–*C*–S), 178.77 (S–C–*CO*–C–S). MS: *m/z* (%) = 408.88 [M$^+$], 380.82 [M$^+$–*CH$_2$*–*CH$_2$*], 348.84 [M$^+$–S], 320.81 [M$^+$–CH$_2$–CH$_2$], 292.81 [M$^+$–CH$_2$–CH$_2$], 258.95 [M$^+$–S], 230.88 [M$^+$–CH$_2$–CH$_2$]. $C_{14}H_{16}O_2S_6$ (408.67): calcd. C 41.15, H 3.95, S 47.08; found C 40.56, H 3.16, S 46.16.

*3.3.2. Synthesis of 2,3,7,8-tetrahydrobenzo[1,2-b:4′,5′-b′]-bis(1-oxo,4-thiacyclohexano)-5,10-dione (**6**), 2,3,7,8-tetrahydrobenzo[1,2-b:4,5-b′]bis(1-oxo,4-thiacyclohexano)-5,10-dione (**7**)*

Compounds **6** [1] and **7** were synthesized from the reaction of 1 g (4.067 mmol) *p*-chloranil (**1**) with 1.14 ml (16.342 mmol) 2-mercaptoethanol (**5**) using Method A.

*3.3.2.1. Compound **6***. Brown crystals, yield: 5.1% (50 mg). M.p. 328–330 °C [Lit. [1]: 325–330 °C]. $R_f = 0.34$ (CH_2Cl_2). UV/vis ($CHCl_3$): λ_{max} (nm) = 251, 378 [Lit. [1]: 379, 552]. IR (KBr): $\nu = 2970$ (C–H), 1630 (C=O), 1560 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$): $\delta = 3$–3.1 [Lit. [1]: 3.15] (t, 4H, *CH$_2$*), 4.4–4.5 [Lit. [1]: 4.39] (t, 4H, *CH$_2$*). ^{13}C NMR (DMSO): $\delta = 24.77$ (S–*CH$_2$*–CH$_2$), 66.67 (O–*CH$_2$*–CH$_2$), 118.43 (S–*C*–C=O), 149.91 (O–*C*–C=O), 176.20 (O–C–*CO*–C–S). MS: *m/z* (%) = 257.04 [M$^+$] [Lit. [1]: 255], 228.69 [M$^+$–O–CH$_2$], 200.99 [M$^+$–O–CH$_2$]. $C_{10}H_8O_4S_2$ (256.3): calcd. C 46.86, H 3.15, S 25.02; found C 47.2, H 2.93, S 24.65 [Lit. [1]: C 46.64, H 3.12].

*3.3.2.2. Compound **7***. Dark blue crystals, yield: 4.32% (45 mg). M.p. 337–338 °C. $R_f = 0.31$ (CH_2Cl_2). UV/vis ($CHCl_3$): λ_{max} (nm) = 244, 379, 565. IR (KBr): $\nu = 2970$ (C–H), 1620, 1650 (C=O), 1560 cm^{-1} (C=C). ^{1}H NMR ($CDCl_3$): $\delta = 3.0$–3.1 (t, 4H, *CH$_2$*), 4.4–4.5 (t, 4H, *CH$_2$*). ^{13}C NMR ($CDCl_3$): $\delta = 25.12$ (S–*CH$_2$*–CH$_2$), 66.48 (O–*CH$_2$*–CH$_2$), 120.80 (S–*C*–C=O), 148.29 (O–*C*–C=O), 170.65 (S–C–*CO*–C–S), 180.35 (O–C–*CO*–C–O). MS: *m/z* (%) = 257.04 [M$^+$]. $C_{10}H_8O_4S_2$ (256.3): calcd. C 46.86, H 3.15, S 25.02; found C 47.05, H 3.04, S 24.13.

*3.3.3. Synthesis of 2,7-dimethyl-3,8-dihydrobenzo[1,2-b:4′,5′-b′]bis(1-oxo,4-thiacyclohexano)-5,10-dione (**9**), 2,7-dimethyl-3,8-dihydrobenzo[1,2-b:4,5-b′]bis(1-oxo,4-thiacyclohexano)-5,10-dione (**10**)*

Compounds **9** and **10** were synthesized from the reaction of 1 g (4.067 mmol) *p*-chloranil (**1**) with 1.43 ml (16.29 mmol) 1-mercapto-2-propanol (**8**) using Method A.

*3.3.3.1. Compound **9***. Light brown crystals, yield: 5.3% (61 mg). M.p. 180.2–183.4 °C. $R_f = 0.25$ (petroleum ether/CH_2Cl_2 (1:3)). IR (KBr): $\nu = 2980$ (C–H), 1650 (C=O), 1570 (C=C). ^{1}H NMR (DMSO): $\delta = 1.37$–1.41 (m, 6H, *CH$_3$*), 2.86–2.92 and 3.16–3.22 (m, 4H, *CH$_2$*), 4.4–4.5 (m, 2H, *CH*).^{13}C NMR (DMSO): $\delta = 20.54$ (O–CH–*CH$_3$*), 29.84 (S–*CH$_2$*–CH), 38.2 (O–*CH*–CH$_3$), 117.78 (S–*C*–C=O), 149.43 (O–*C*–C=O), 176.32 (O–C–*CO*–C–S). MS: *m/z* (%) = 284.99 [M$^+$]. $C_{12}H_{12}O_4S_2$ (284.36): calcd. C 50.69, H 4.25, S 22.55; found C 50.53, H 4.17, S 21.46.

*3.3.3.2. Compound **10***. Dark blue crystals, yield: 5.7% (66 mg). M.p. 166.6–168.3 °C. $R_f = 0.23$ (petroleum ether/CH_2Cl_2 (1:3)). IR (KBr): $\nu = 2980$ (C–H), 1630, 1660

(C=O), 1560 cm^{-1} (C=C). ^1H NMR ($CDCl_3$): $\delta = 1.48$–1.52 (m, 6H, *CH_3*), 2.76–2.82 and 2.98–3.04 (m, 4H, *CH_2*), 4.42–4.52 (m, 2H, *CH*). ^{13}C NMR ($CDCl_3$): $\delta = 20.32$ (O–CH–*CH_3*), 30.31 (S–*CH_2*–CH_2), 71.99 (O–*CH_2*–CH_2), 119.49 (S–*C*–C=O), 147.78 (O–*C*–C=O), 170.71 (S–C–*CO*–C–S), 180.24 (O–C–*CO*–C–O). MS: *m/z* (%) = 284.99 [M^+]. $C_{12}H_{12}O_4S_2$ (284.36): calcd. C 50.69, H 4.25, S 22.55; found C 50.15, H 4.59, S 21.58.

*3.3.4. Synthesis of 2,3,5,6-tetrakis(naphalen-1-ylthio)-cyclohexa-2,5-diene-1,4-dione (**12**)*

Compound **12** was synthesized from the reaction of 0.5 g (2.033 mmol) *p*-chloranil (**1**) with 1.303 g (8.131 mmol) naphthalene-2-thiol (**11**) using Method A.

*3.3.4.1. Compound **12***. Dark brown crystals, yield: 2.4% (36 mg). M.p. 214–216 °C. $R_f = 0.$ 65 (petroleum ether/CH_2Cl_2 (1:1)). UV/vis ($CHCl_3$): λ_{max} (nm) = 242, 295, 371. IR (KBr): $\nu = 3040$ (C–H), 1650 (C=O), 1540 cm^{-1} (C=C). ^1H NMR ($CHCl_3$): $\delta = 7$–8 (m, 28H, *CH*). MS: *m/z* (%) = 740.90 [M^+]. $C_{46}H_{28}O_2S_4$ (740.99): calcd. C 74.56, H 3.81, S 17.31; found C 74.02, H 3.48, S 17.26.

*3.3.5. Synthesis of 2-chloro-3,5 6-tris[(6-hydroxyhexyl)-thio]benzo-1,4-guinone (**14**), 2,3,5,6-tetrakis [(6-hydroxyhexyl)thio]benzo-1,4-guinone (**15**)*

Compounds **14** and **15** were synthesized from the reaction of 1 g (4.067 mmol) *p*-chloranil (**1**) with 2.22 ml (16.29 mmol) 6-mercapto-1-hexanol (**13**) using Method B.

*3.3.5.1. Compound **14***. Dark oil, yield: 26% (0.58 g). $R_f = 0.33$ ($CHCl_3$/EtAc (1:2)). IR (Film): $\nu = 3370$ (CH_2–OH), 2975, 2988 (C–H), 1660 (C=O), 1570 cm^{-1} (C=C). ^1H NMR ($CDCl_3$): $\delta = 3.60$–3.63 (t, 6H, O–CH_2), 3.10–3.23 (m, 6H, S–CH_2), 2.02 (s, 3H, OH), 1.37–1.63 (m, 24, CH_2). MS: *m/z* (%) = 538.1 [M^+], 437.04 [M^+–$(CH_2)_6$–OH], 335.95 [M^+–$(CH_2)_6$–OH], 302.99 [M^+–S]. $C_{24}H_{39}ClO_5S_3$ (539.2): calcd. C 53.46, H 7.29, S 17.84; found C 54.06, H 7.05, S 18.25.

*3.3.5.2. Compound **15***. Dark brown crystals, yield: 38% (0.97 g). M.p. 76.8–77.2 °C. $R_f = 0.23$ ($CHCl_3$/EtAc (1:2)). IR (KBr): $\nu = 3410$ (CH_2–OH), 2970, 2980 (C–H), 1640 (C=O), 1530 cm^{-1} (C=C). ^1H NMR ($CDCl_3$): $\delta = 3.60$–3.62 (t, $J = 6.35$ Hz, 8H, O–CH_2), 3.07–3.10 (t, $J = 7.32$ Hz, 8H, S–CH_2), 2.2 (s, 4H, OH), 1.36–1.61 (m, 32, CH_2). ^{13}C NMR ($CDCl_3$): $\delta = 24.56$, 27.48 (*CH_2*), 29.69 (S–CH_2–*CH_2*), 31.56 (S–*CH_2*), 33.27 (HO–CH_2–*CH_2*), 61.64 (HO–*CH_2*), 145.31 (*C*–C=O), 173.04 (*C=O*). MS: *m/z* (%) = 637.07 [M^+], 535.12 [M^+–$(CH_2)_6$–OH], 433.97 [M^+–$(CH_2)_6$–OH]. $C_{30}H_{52}O_6S_4$ (637): calcd. C 56.57, H 8.23, S 20.13; found C 56.41, H 7.18, S 20.95.

4. Conclusions

The novel 9,10-dichloro-2,3,5,6-tetrahydrobenzo[*b*] [1,4,7]-trithionine-8,11-dione (**3**) and 2,3,5,6,10,11,13,14-octahydro-benzo[1,2-*b*:4,5-*b′*]bis[1,4,7]trithionine-8,16-dione (**4**) were synthesized from the reaction of *p*-chloranil with bis(2-mercaptoethyl) sulfide. Compounds **6** and **7** were obtained from *p*-chloranil with 2-mercaptoethanol, while *p*-chloranil reacted with 1-mercapto-2-propanol gave new unknown compounds **9** and **10** and the novel compound **12** was prepared from *p*-chloranil with naphthalene-2-thiol. Finally the reaction of *p*-chloranil with 6-mercapto-1-hexanol yielded unknown compounds **14** and **15**. The structures of these novel compounds were characterized by elemental analysis, UV/vis, FT-IR, ^1H NMR, ^{13}C NMR and mass spectroscopies.

Acknowledgements

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