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Synthesis, characterization of N-, S-, O-substituted naphtho- and benzoquinones and a structural study

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Abstract. The new series of N-, S-, O-substituted 1,4-naphthoquinone and S-, O-substituted 1,4-benzoquinone compounds were synthesized via vinylic substitution. Compounds **3** and **4** were synthesized from the reaction of **1** with **2**. Compounds **6**, **7** and **8** were synthesized from reaction of **1** with **5**. Compounds **10** and **11** were obtained from the reaction of **1** with **9**. Compounds **13** and **14** were synthesized from the reaction of **1** with **12**. Compounds **16** and **17** were obtained from the reaction of **15** with **2**. Photochemical and electrochemical properties of N-, S-, O-substituted quninone compounds were determined by using fluorescence spectroscopy and cyclic voltammetry. Crystal structure of 2-(7-sulphanyl-4-methyl-coumarinyl)-3-(1-ethoxy)-1,4-naphthoquinone **13** was determined by X-ray diffraction method.

Keywords. 1,4-Naphthoquinone; *p*-chloranil; fluorescence spectroscopy; cyclic voltametry; X-ray diffraction.

1. Introduction

Quinones are naturally occurring compounds with specific characteristics that have a great impact on the living cell. The ability to carry electrons makes them an important component of photosynthetic and respiratory electron transfer chain.[1] They are considered as components of biological electron transfer chains located in the membranes of mitochondria, bacteria and chloroplasts. Quinones are good electron acceptors and are known to be efficient quenchers of singlet state donor fluorescence of various fluorophores.[2] The current data are consistent with an electron transfer mechanism,[3] and the quenching efficiency is dependent on the redox potentials of the corresponding quinone–hydroquinone system. From the perspectives of designing magnetic materials[4] and understanding photo-physical properties,[5] the co-ordination chemistry of quinones is also very important. The quinones also find application as electrode material.[6]

Depending on the molecular structure, some quinones can be used as vitamin sor drugs.[7] It is recognized that the quinone nucleus and the substituents are both essential to develop specific biochemical functions. So, when the quinonic ring is substituted by an appropriate alkylchain, these compounds can exhibit anticancer and antitumour activity.[8] Naphthoquinone derivatives are an important class of naturally occurring compounds as they have favourable antimicrobial, antiparasitic, and phytotoxic activities.[9,10] The biological activity of quinones results from their ability to accept one or two electrons to form the corresponding radical anion or dianion species, and also their acid-base properties. Electron-attracting or -donating substituents modulate the redox properties of quinones, i.e., their variable ability to accept electrons. The molecular basis of quinone toxicity is the enzyme-catalysed reduction to semiquinone radicals, which then reduce oxygen to superoxide anion radicals thereby regenerating the quinone.[11] Further need for a study of the aryl amino-1,4-naphthoquinones is illustrated by the observation that the ortho-amino quinoid unit is present in many antitumour antibiotics such as actinomycins, mitomycin C, porfiromycin, and streptonigrin.[12]

It has been reported that some N-, S-, O-subsituted naphtho- and benzoquinone compounds were synthesized from 2,3-dichloro-1,4-naphthoquinone or *p*-chloranil.[13–15] In an earlier study by Prescott *et al.* the antitumour activity of 2,2-Hydrazobis(3-chloro-1,4-naphthoquinone) were investigated.[16] Novel vitamin K_3 analogues were synthesized and evaluated for their anticancer activity by Chen *et al.*[17] N-substituted enaminones were synthesized from 1,4-naphthoquinones by Parr *et al.*[18] We describe here the synthesis of some naphtho-

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and benzoquinone compounds and characterization of their structures by using micro analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, MS, UV-Vis. Photo- and electrochemical properties of N-, S-, O-substituted naphtho- and benzoquinone compounds were investigated by using fluorescence spectroscopy and cyclic voltammetry method. The single crystal structure of compound **13** was determined by X-ray diffraction method.

2. Experimental

2.1 *General*

Melting points were measured on a Buchi B-540 melting point apparatus. Elemental analyses were performed on a Thermo Finnigan Flash EA 1112 Elemental analyser. Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Perkin Elmer Precisely Spectrum One FTIR spectrometry. UV spectra in $CHCl_3$, THF and MetOH were recorded on Perkin Elmer Lambda 35 UV/VIS Spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on VarianUNITYINOVA operating at 500 MHz. Mass spectra were obtained on a Thermo Finnigan LCQ Advantage MAX LC/MS/MS spectrometer according to ESI probe. Products were isolated by column chromatography on Silica gel (Fluka Silica gel 60, particle size 63–200 μm). TLC plates silica $60F_{254}$ (Merck, Darmstadt), detection with ultraviolet light (254 nm). All chemicals were reagent grade and used without further purification. Moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes. Solvents, unless otherwise specified, were of reagent grade and distilled once prior to use.

2.2 *Fluorescence measurements*

Fluorescence spectra were run on a VARIAN Cary Eclipse Fluorescence Spectrophotometer. Excitation and emission spectra were measured for 10^{-4} M solutions for all compounds in MetOH/$CHCl_3$ (1:1) at room temperature. Excitation and emission slit widths were set at 10 nm.

2.3 *Crystal structure determination and refinement*

Red crystals of compound suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethylacetate solution at room temperature. A red crystal of compound **13**, $C_{22}H_{16}O_5S_1$, having approximate dimensions of 0.50 × 0.30 × 0.10 mm was mounted on a glass fibre. All measurements were made on a Rigaku R-Axis Rapid-S imaging plate area detector with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å). The data were collected at room temperature to a maximum 2θ value of 60.3°. Experimental conditions were summarized in table 1. The structure was solved

Table 1. Crystal data and refinement parameters for compound **13**.

CCDC deposit number	CCDC 724897
Empirical formula	$C_{22}H_{16}O_5S$
Crystal colour, habit	Red, block
Formula weight	392.43
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P–1
Cell dimensions	a = 8.4474(2) Å, b = 9.1257(1) Å c = 11.9197(2) Å, α = 84.474(4)° β = 84.506(4)°, γ = 80.473(4)°
Volume	899.00(3) Å^3
Z	2
Density (calculated)	1.450 mg/m^3
Absorption coefficient	0.213 mm^{-1}
F_{000}	408.00
Index ranges	$-10 \le h \le 11$, $-12 \le k \le 12$ $-16 \le l \le 16$
Reflections collected	71430
Independent reflections	5254 [R_{int} = 0.042]
Data/restraints/parameters	4958/0/253
Goodness of fit indicator	1.095
Final R indices [$I > 2\sigma$(I)]	R_1 = 0.056, wR_2 = 0.098
Largest diff. peak and hole	0.47 and −0.46 e.Å^{-3}

by SIR 92[19] and refined with CRYSTALS.[20] The non-hydrogen atoms were refined anisotropically. H atoms were located in geometrically idealized positions C-H = 0.95(6) Å and treated as riding and U_{iso}(H) = 1.2U_{eq}(C). The selected bond distances, bond and torsion angles for compound **13** were listed in tables 2 and 3, respectively. Drawings were performed with the program ORTEP-III[21] with 50% probability displacement elipsoide for compound **13** in figure 1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-724897 for **13**.[22]

Table 3. Selected bond and torsion angles (°) for compound **13**.

Atom	Bond angle	Atom	Torsion angle
C1-C2-C3	121.4(2)	C3-C2-C1-C10	−5.7(3)
C2-C3-C4	117.1(1)	O1-C10-C1-C2	−176.1(2)
C2-C3-O2	121.2(2)	O2-C3-C2-O3	3.2(3)
C1-C10-O1	120.8(2)	C10-C1-S1-C11	134.4(1)
S1-C1-C10	115.3(1)	C15-C17-C18-O5	173.3(2)
C1-S1-C11	104.0(8)	C18-O4-C19-C20	176.5(1)
C18-O4-C19	121.7(2)	C15-17-C18-O4	−5.3(3)
O4-C18-O5	116.6(2)	C11-S1-C1-C2	−49.4(2)
C2-O3-C21	124.5(2)	C1-C2-C3-O2	−171.3(2)

2.4 *Cyclic voltammetry measurements*

Electrochemical cyclic voltammetry measurements were performed at room temperature in an airtight three-electrode cell by using a glassy carbon electrode (GCE) with a 0.071 cm^2 surface area as the working electrode, a platinum wire served as the counter electrode and a Ag/AgCl (in a saturated KCl solution) reference electrode. The cell was driven with a computer controlled system of a Gamry Reference 600 Model potentiostat/galvanostat. The solutions were deoxygenated by bubbling nitrogen through them for approximately 5 min. The surface of the working electrode was polished with deagglomerated alumina (a particle size of 0.05 micron) before each run. The electrochemical reaction vessel was charged with 10 mL an DMF solution of **1**, **3**, **4**, **6**, **7**, **8**, **10**, **11**, **13**, **14**, **15**, **16** and **17** (1×10^{-4} M) and tetrabutyl ammonium perchlorate (0.1 M) as the electrolyte. Measurements were made over a potential range between 0 and −2 V for **1**, **3**, **4**, **6**, **8**, **10**, **11**, **15**, +1.0 and −2.5 V for **7**, 0 and −2.5 V for **13**, 0 and −1.8 V for **14**, **16**, **17** with a scan rate of 0.1 V s^{-1}. Voltammetric parameters for all compounds are summarized in table 6.

2.5 *Synthesis procedures*

Method 1: Sodium carbonate (1.52 g) was dissolved (60 mL) in ethanol. 2,3-dichloro-1,4-naphthoquinone or p-chloranil and nucleophile compounds were added slowly to this solution for synthesis of compounds **3**, **4**, **6**, **7**, **8**, **10**, **11**, **16** and **17**. Without heating, the mixture was stirred for 24 h. In addition, 2,3-dichloro-1,4-naphthoquinone and thiols were stirred for 12 h in a mixture solution of ethanol (25 mL) with triethlyamine (1 mL) for the synthesis of compounds **13** and **14**. The colour of the solution quickly changed and the extent of the reaction was monitored by TLC. Chloroform (30 mL) was added to the reaction mixture. The organic layer was washed with water (4 × 30 mL), and dried with Na_2SO_4. After the solvent was evaporated the residue was purified by column chromatography on silica gel (scheme 1).

Table 2. Selected bond distances (Å) for compound **13**.

Atom	Distance	Atom	Distance
C1-C2	1.354(2)	C3-O2	1.212(2)
C2-C3	1.495(3)	C10-O1	1.220(2)
C1-S1	1.762(2)	C2-O3	1.338(3)
C11-S1	1.765(2)	C18-O5	1.209(3)
C15-C16	1.509(3)	C18-O4	1.376(2)
C21-C22	1.505(4)	C19-O4	1.375(2)

2.5a *2-(11-Sulphanyl-1-undecanol)-3-ethoxy-1,4-naphthoquinone (3)*: Compound **3** was synthesized from the reaction of **1** (1 g, 4.4 mmol) with **2** (0.9 g, 4.4 mmol) according to method 1. Red oil, Yield: 0.6 g (34%). R_f: 0.50 [CH_2Cl_2/EtAc (4:1)]. IR (KBr pellet, cm^{-1}): 3410 (OH), 3070 (Ar-H), 2925, 2851 (C-H), 1661 (C=O), 1591, 1543 (C=C). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 1.2 (t, J = 6.84 Hz, 3H, CH_3), 1.3–1.4 (m, 14H, CH_2), 1.45–1.6 (m, 2H, S-CH_2-CH_2), 1.7 (m, 2H, CH_2-CH_2-OH), 3.1 (t, J = 7.32 Hz, 2H, S-CH_2), 3.6 (t, J = 6.83 Hz, 2H, CH_2-OH), 3.7 (s, 1H, OH), 4.4 (q, 2H, O-CH_2), 7.60 (t,J = 6.34 Hz, 1H, H_{arom}), 7.65 (t, J = 5.37 Hz, 1H, H_{arom}), 7.95 (dd, J = 6.34 Hz, J = 6.83 Hz, 1H, H_{arom}), 8.05 ppm (dd, J = 5.37 Hz, J = 5.37 Hz, 1H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 14.89 (CH_3), 24.73, 27.60, 27.67, 28.04, 28.10, 28.38, 28.40 (CH_2), 28.52 (S-CH_2-CH_2), 29.41 (CH_2-CH_2-OH), 33.33 (S-CH_2), 61.97 (CH_2-OH), 68.88 (O-CH_2), 125.35, 125.56, 132.49, 132.54 (CH_{arom}), 126.16, 132.75 (C_{arom}), 133.07 (=C-S), 156.75 (=C-O), 178.85, 181.85 ppm (C=O). MS[+ESI]: m/z 405 $[M]^+$, 359 $[M-45]^+$. Anal. Calcd. for $C_{23}H_{32}O_4S_1$ (M, 404.57): C, 68.28; H, 7.97; S, 7.92. Found: C, 68.30; H, 6.88; S, 7.98.

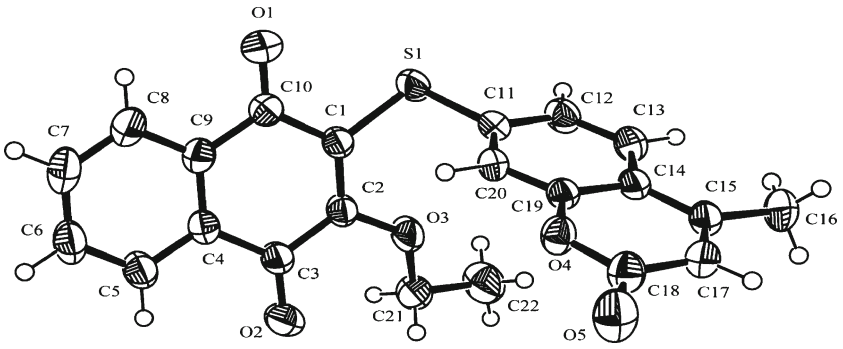
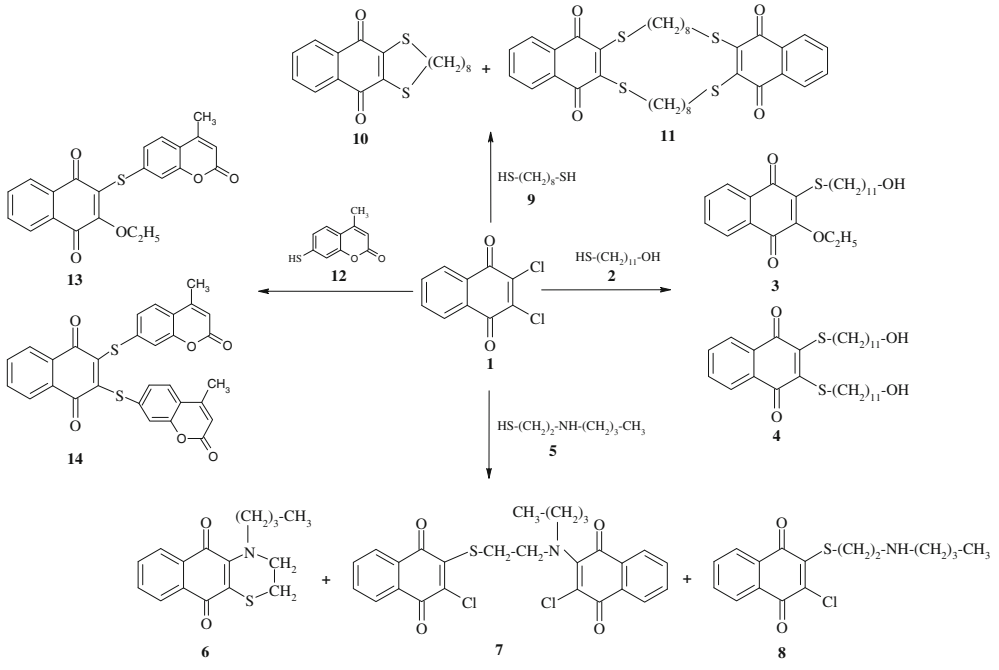


Figure 1. The crystal structure of **13**. Displacement ellipsoids are plotted at the 50% probability level (symmetry transformations used to generate equivalent atoms: (i)- x, -y, -z).

2.5b *2,3-Bis(11-sulphanyl-1-undecanol)-1,4-naphthoquinone (**4**)*: Compound **4** was synthesized from the reaction of **1** (1 g, 4.4 mmol) with **2** (0.9 g, 4.4 mmol) according to method 1. Orange solid. M.p.: 76–77°C. Yield: 1.3 g (53%). R_f: 0.32 [CH_2Cl_2/EtAc (4:1)]. IR (KBr pellet, cm^{-1}): 3314 (OH), 3062 (Ar-H), 2913, 2847 (C-H), 1665 (C=O), 1588, 1512 (C=C). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 1.1–1.3 (m, 28H, CH_2), 1.3–1.4 (m, 4H, S-CH_2-CH_2), 1.5–1.6 (m, 4H, CH_2-CH_2-OH), 3.2 (t, J = 7.32 Hz, 4H, S-CH_2), 3.6 (t, J = 6.35 Hz, 4H, CH_2-OH), 3.8 (s, 2H, OH), 7.60 (dd, J = 5.86 Hz, J = 5.85 Hz, 2H, H_{arom}), 7.97 ppm (dd, J = 5.36 Hz, J = 5.86 Hz, 2H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 24.74, 27.69, 28.10, 28.39, 28.43, 28.46, 28.54 (CH_2), 29.44 (S-CH_2-CH_2), 31.79 (CH_2-CH_2-OH), 33.96 (S-CH_2), 62.01 (CH_2-OH), 125.82, 132.38 (CH_{arom}), 132.06 (C_{arom}), 146.89 (=C-S), 178.01 ppm (C=O). MS[+ESI]: m/z 563 $[M]^+$, 546 $[M-17]^+$. Anal. Calcd. for $C_{32}H_{50}O_4S_2$ (M, 562.88): C, 68.28; H, 8.95; S, 11.39. Found: C, 68.40; H, 9.08; S, 11.28.

2.5c *[2,3-Cyclo-(2-butylamino)ethanesulphanyl]-1,4-naphthoquinone (**6**)*: Compound **6** was synthesized from the reaction of **1** (1 g, 4.4 mmol) with **5** (0.58 g, 4.4 mmol) according to method 1. Purple solid. M.p.: 125–126°C. Yield: 0.4 g (31%). R_f: 0.60 (CH_2Cl_2). IR (KBr pellet, cm^{-1}): 3069 (Ar-H), 2955, 2928, 2860 (C-H), 1657, 1624 (C=O), 1587, 1532 (C=C). ^{1}H NMR



Scheme 1. Synthesis of compounds **3**, **4**, **6**, **7**, **8**, **10**, **11**, **13** and **14**.

(499.74 MHz, $CDCl_3$): δ = 0.8 (t, *J* = 7.32 Hz, 3H, CH_3), 1.2–1.4 (m, 2H, CH_2), 1.6–1.7 (m, 2H, N-CH_2-CH_2), 2.9 (t, *J* = 6.81 Hz, 2H, N-CH_2-CH_2), 3.3 (t, *J* = 7.81 Hz, 2H, S-CH_2), 3.5 (t, *J* = 6.84 Hz, 2H, N-CH_2), 7.50 (t, *J* = 7.32 Hz, 1H, H_{arom}), 7.55 (t, *J* = 7.81 Hz, 1H, H_{arom}), 7.85 (dd, *J* = 6.84 Hz, *J* = 6.85 Hz, 1H, H_{arom}), 7.95 ppm (dd, *J* = 7.32 Hz, *J* = 6.84 Hz, 1H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 12.89 (CH_3), 19.08 (CH_2), 23.45 (N-CH_2-*C*H_2), 30.28 (S-CH_2), 49.17 (N-*C*H_2-CH_2), 54.22 (N-CH_2), 120.38, 124.57, 125.52, 131.18, 131.30, 131.56 (CH_{arom}, C_{arom}), 132.26 (=C-S), 145.13 (=C-N), 176.80, 178.82 ppm (C=O). MS[+ESI]: m/z 288 $[M]^+$, 232 $[M-56]^+$. Anal. Calcd. for $C_{16}H_{17}O_2S_1N_1$ (M, 287.38): C, 66.87; H, 5.96; N, 4.87; S, 11.15. Found: C, 64.40; H, 5.88; N, 4.85; S, 11.18.

2.5d *[2-(Butylamino)ethanesulphanyl][2,2′]-dichloro[3,3′]-bis(1,4-naphthoquinone) (**7**)*: Compound **7** was synthesized from the reaction of **1** (1 g, 4.4 mmol) with **5** (0.58 g, 4.4 mmol) according to method 1. Black solid. M.p.: 97–98°C. Yield: 1.1 g (48%). R_f: 0.40 (EtAc). IR (KBr pellet, cm^{-1}): 3069 (Ar-H), 2957, 2928, 2871 (C-H), 1662 (C=O), 1592, 1556 (C=C). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 0.9 (t, *J* = 7.32 Hz, 3H, CH_3), 1.1–1.4 (m, 2H, CH_2), 1.6–1.7 (m, 2H, N-CH_2-CH_2), 3.0 (t, *J* = 6.81 Hz, 2H, N-CH_2-CH_2), 3.8 (t, *J* = 7.32 Hz, 2H, S-CH_2), 4.1 (t, *J* = 6.84 Hz, 2H, N-CH_2), 7.50 (t, *J* = 5.84 Hz, 1H, H_{arom}), 7.65 (t, *J* = 6.83 Hz, 1H, H_{arom}), 7.95 (dd, *J* = 5.32 Hz, *J* = 5.85 Hz, 1H, H_{arom}), 8.10 ppm (dd, *J* = 5.32 Hz, *J* = 5.84 Hz, 1H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 12.70 (CH_3), 18.81 (CH_2), 22.78 (N-CH_2-*C*H_2), 29.39 (S-CH_2), 43.72 (N-*C*H_2-CH_2), 67.18 (N-CH_2), 125.77, 125.84, 127.80, 131.33, 131.51, 131.87 (CH_{arom}, C_{arom}), 133.90 (=C-S), 143.29 (=C–Cl), 148.89 (=C-N), 179.60, 183.43 ppm (C=O). MS[+ESI]: m/z 478 $[M-37]^+$, 441 $[M-73]^+$. Anal. Calcd. for $C_{26}H_{21}O_4S_2N_1Cl_2$ (M, 514.43): C, 60.70; H, 4.11; N, 2.72; S, 12.46 Found: C, 60.68; H, 4.08; N, 2.65, S, 12.28.

2.5e *2-[2-(Butylamino)ethanesulphanyl]-3-chloro-1,4-naphthoquinone (**8**)*: Compound **8** was synthesized from the reaction of **1** (1 g, 4.4 mmol) with **5** (0.58 g, 4.4 mmol) according to method 1. Black solid. M.p.: 110–111°C. Yield: 0.3 g (21%). R_f: 0.45 (CH_2Cl_2). IR (KBr pellet, cm^{-1}): 3344 (NH), 3068 (Ar-H), 2956, 2929, 2870 (C-H), 1659 (C=O), 1591, 1557 (C=C). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 0.8 (t, *J* = 7.32 Hz, 3H, CH_3), 1.1–1.5 (m, 2H, CH_2), 1.6–1.7 (m, 2H, N-CH_2-CH_2), 3.1 (t, *J* = 7.81 Hz, 2H, N-CH_2-CH_2), 3.3 (t, *J* = 6.84 Hz, 2H, S-CH_2), 3.7 (t,*J* = 6.84 Hz, 2H, N-CH_2), 3.8 (m, 1H, NH), 7.55 (t, *J* = 5.86 Hz, 1H, H_{arom}), 7.60 (t, *J* = 5.79 Hz, 1H, H_{arom}), 7.85 (dd, *J* = 5.85 Hz, *J* = 5.37 Hz, 1H, H_{arom}), 7.96 ppm (dd, *J* = 5.86 Hz, *J* = 5.37 Hz, 1H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 12.89 (CH_3), 19.37 (CH_2), 28.68 (NH-CH_2-*C*H_2), 31.83 (S-CH_2), 48.38 (NH-*C*H_2-CH_2), 51.63 (NH-CH_2), 124.80, 125.94, 126.00, 131.51, 131.84, 132.64 (CH_{arom}, C_{arom}), 139.07 (=C-S), 145.32 (=C-Cl), 179.24, 182.21 ppm (C=O). MS[+ESI]: m/z 325 $[M]^+$ Anal. Calcd. for $C_{16}H_{18}O_2S_1N_1Cl_1$ (M, 323.84): C, 59.34; H, 5.60; N, 4.32; S, 9.90. Found: C, 59.40; H, 5.48; N, 4.55, S, 9.78.

2.5f *2,3,4,5,6,7,8,9-Octahydronaphtho[2,3-e][1,10]dithionine-11,16-dione (**10**)*: Compound **10** was obtained from the reaction of **1** (1 g, 4.4 mmol) with **9** (0.78 g, 4.4 mmol) according to method 1. Orange solid. M.p.: 170–171°C. Yield: 0.52 g (35%). R_f: 0.65 ($CHCl_3$). IR (KBr pellet, cm^{-1}): 3068 (Ar-H), 2930, 2897, 2850 (C-H), 1665 (C=O), 1594 (C=C). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 1.1–1.2 (m, 8H, CH_2), 1.6 (m, 4H, S-CH_2-CH_2), 3.2 (t, *J* = 5.86 Hz, 4H, S-CH_2), 7.65 (dd, *J* = 5.37 Hz, *J* = 6.84 Hz, 2H, H_{arom}), 8.05 ppm (dd, *J* = 7.32 Hz, *J* = 6.84 Hz, 2H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 21.96, 24.19 (CH_2), 26.62 (S-CH_2-*C*H_2), 35.41 (S-CH_2), 126.21, 132.09, 132.60 (CH_{arom}, C_{arom}), 149.99 (=C-S), 177.63 ppm (C=O). MS [+ESI]: m/z 333 $[M]^+$. Anal. Calcd. for $C_{18}H_{20}O_2S_2$ (M, 332.48): C, 65.02; H, 6.06; S, 19.28. Found: C, 65.10; H, 6.36; S, 19.13.

2.5g *7,8,9,10,11,12,13,14,23,24,25,26,27,28,29,30-Hexadecahydrodinaphtho[2,3-e:2′,3′-n] [1,10,13,22]tetrathiacyclotetracosine-5,16,21,32-tetrone (**11**)*: Compound **11** was obtained from the reaction of **1** (1 g, 4.4 mmol) with **9** (0.78 g, 4.4 mmol) according to method 1. Red solid. M.p.: 134–135°C. Yield: 1.4 g (48%). R_f: 0.48 ($CHCl_3$). IR (KBr pellet, cm^{-1}): 3069 (Ar-H), 2923, 2851 (C-H), 1654 (C=O), 1590, 1454 (C=C). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 1.2–1.40 (m, 16H, CH_2), 1.4–1.6 (m, 8H, S-CH_2-*C*H_2), 3.2 (t, *J* = 7.32 Hz, 8H, S-CH_2), 7.60 (dd, *J* = 5.85 Hz, *J* = 5.37 Hz, 4H, H_{arom}), 7.95 ppm (dd, *J* = 5.85 Hz, *J* = 5.86 Hz, 4H, H_{arom}). ^{13}C NMR (125.66 Hz, $CDCl_3$): δ 27.36, 27.82 (CH_2), 29.27 (S-CH_2-*C*H_2), 34.00 (S-CH_2), 125.85, 132.05, 132.41 (CH_{arom}, C_{arom}), 147.00 (=C-S), 177.95 ppm (C=O). MS [+ESI]: m/z 665 $[M]^+$. Anal. Calcd. for $C_{36}H_{40}S_4O_4$ (M, 664.97): C, 65.02; H, 6.06; S, 19.28. Found: C, 65.05; H, 6.10; S, 19.25.

2.5h *2-(7-Sulphanyl-4-methyl-coumarinyl)-3-(1-ethoxy)-1,4-naphthoquinone (**13**)*: Compound **13** was synthesized from the reaction of **1** (0.5 g, 2.2 mmol) with **12** (0.42 g, 2.2 mmol) according to method 1. Red crystal. M.p.: 194–195 °C. Yield: 0.35 g (40%). R_f: 0.65 (CH_2Cl_2). IR (KBr pellet, cm^{-1}): 3071 (Ar-H), 2918, 2849 (C-H), 1720, 1667 (C=O), 1600, 1551 (C=C). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 1.2 (t, J = 6.83 Hz, 3H, O-CH_2-CH_3), 2.3 (s, 3H, CH_3), 4.5 (q, 2H, O-CH_2-CH_3), 6.1 (s, 1H, CH), 7.1 (t, J = 5.60 Hz, 1H, H_{arom}), 7.2 (t, J = 6.84 Hz, 2H, H_{arom}), 7.4 (dd, J = 7.84 Hz, J = 7.32 Hz, 1H, H_{arom}), 7.65 (dd, J = 6.34 Hz, J = 5.83 Hz, 2H, H_{arom}), 8.00 (dd, J = 7.32 Hz, J = 6.84 Hz, 1H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 14.81 (O-CH_2-CH_3), 17.54 (CH_3), 69.82 (O-CH_2), 117.31, 123.69, 123.80 125.79, 125.98, 126.52, 130.37, 131.03, 132.78, 133.30 (CH_{arom}, C_{arom}), 113.57 (CH), 115.79 (=C-CH_3), 139.21 (=C-S), 150.93 (S-C_{arom}), 152.59 (=C-O), 159.79 (C=O), 178.62, 180.18 ppm (C=O). MS[+ESI]: m/z 393 $[M]^+$, 365 $[M-28]^+$. Anal. Calcd. for $C_{22}H_{16}O_5S_1$ (M, 392.43): C, 67.33; H, 4.11; S, 8.17. Found: C, 67.41; H, 4.08; S, 8.25.

2.5i *2,3-Bis(7-sulphanyl-4-methyl-coumarinyl)-1,4-naphthoquinone (**14**)*: Compound **14** was synthesized from the reaction of **1** (0.5 g, 2.2 mmol) with **12** (0.42 g, 2.2 mmol) according to method 1. Dark brown solid. M.p.: 270–271°C. Yield: 0.6 g (51%). R_f: 0.45 (CH_2Cl_2). IR (KBr pellet, cm^{-1}): 3080 (Ar-H), 2972, 2950 (C-H), 1733, 1660 (C=O), 1601, 1546 (C=C). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 2.3 (s, 6H, CH_3), 6.2 (s, 2H, CH), 7.2 (dd, J = 7.81 Hz, J = 8.3 Hz, 2H, H_{arom}), 7.4 (d, J = 8.3 Hz, 4H, H_{arom}) ,7.7 (dd, J = 5.86 Hz, J = 5.85 Hz, 2H, H_{arom}) 7.95 ppm (dd, J = 5.85 Hz, J = 5.37 Hz, 2H, H_{arom}). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 17.57 (CH_3), 114.32 (CH), 117.27 (=C-CH_3), 118.36, 124.20, 124.88, 126.58, 131.45, 133.37, 137.22, 147.38 (CH_{arom}, C_{arom}), 150.74 (=C-S), 152.59 (S-C=), 159.00 (C=O), 177.13 ppm (C=O). MS[−ESI]: m/z 538 $[M]^+$. Anal. Calcd. for $C_{30}H_{18}O_6S_2$ (M, 538.601): C, 66.90; H, 3.36; S, 11.90. Found: C, 66.71; H, 3.18; S, 11.85.

2.5j *2,3,6-Tris(11-sulphanyl-1-undecanol)-5-ethoxy-1,4-benzoquinone (**16**)*: Compound **16** was synthesized from the reaction of **15** (0.6 g, 2.4 mmol) with **2** (1.96 g, 9.5 mmol) according to method 1. Yellow-brown solid. M.p.: 60–61°C. Yield: 0.5 g (27%). R_f: 0.65 [EtAc/CH_2Cl_2 (2:1)]. IR (KBr pellet, cm^{-1}): 3311 (OH), 2917, 2849 (C-H), 1659 (C=O), 1567 (C=C). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 1.1 (t, J = 7.32 Hz, 3H, CH_3), 1.2–1.3 (m, 42H, CH_2), 1.4–1.5 (m, 6H, S-CH_2-CH_2), 1.7 (s, 3H, OH), 3.0 (t, J = 7.32 Hz, 6H, S-CH_2), 3.6 (t, J = 6.83 Hz, 6H, HO-CH_2), 4.2 ppm (q, 2H, O-CH_2-CH_3). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 14.77 (CH_3), 24.74, 24.76, 24.77, 27.66, 27.68, 27.71, 28.14, 28.39, 28.15, 28.42, 28.43, 28.46, 28.48, 28.51, 28.54, 28.56, 28.58, 29.21, 29.44, 29.49 (CH_2), 31.79 (S-CH_2-CH_2), 31.93 (HO-CH_2-CH_2), 32.01, 33.55, 33.88 (S-CH_2), 61.96 (HO-CH_2), 68.76 (O-CH_2), 130.67, 141.37, 146.18 (=C-S), 155.68 (=C-O), 173.99, 177.72 ppm (C=O). MS [−ESI]: m/z 758 $[M]^+$, 712 $[M-45]^+$. Anal. Calcd. for $C_{41}H_{74}O_6S_3$ (M, 759.23): C, 64.86; H, 9.82; S, 12.66. Found: C, 64.90; H, 9.76; S, 12.43.

2.5k *2,3,5,6-Tetrakis(11-sulphanyl-1-undecanol)-1,4-benzoquinone (**17**)*: Compound **17** was synthesized from the reaction of **15** (0.6 g, 2.4 mmol) with **2** (1.96 g, 9.5 mmol) according to method 1. Yellow-green solid. M.p.: 85–86°C. Yield: 1.4 g (63%). R_f: 0.45 [EtAc/CH_2Cl_2 (2:1)]. IR (KBr pellet, cm^{-1}): 3279 (OH), 2917, 2848 (C-H), 1656 (C=O), 1484 (C=C). ^{1}H NMR (499.74 MHz, $CDCl_3$): δ = 1.1–1.3 (m, 56H, CH_2), 1.3–1.4 (m, 8H, S-CH_2-CH_2), 1.52 (s, 4H, OH), 3.0 (t, J = 7.32 Hz, 8H, S-CH_2), 3.6 (t, J = 6.34 Hz, 8H, HO-CH_2). ^{13}C NMR (125.66 MHz, $CDCl_3$): δ = 24.76, 27.74, 28.18, 28.43, 28.51, 28.52, 28.59 (CH_2), 29.54 (S-CH_2-CH_2), 31.80 (HO-CH_2-CH_2), 33.38 (S-CH_2), 62.02 (HO-CH_2), 145.07 (=C-S), 173.35 ppm (C=O). MS [+ESI]: m/z 918 $[M]^+$. Anal. Calcd. for $C_{50}H_{92}O_6S_4$ (M, 917.54): C, 65.45; H, 10.10; S, 13.97. Found: C, 65.50; H, 10.26; S, 13.23.

3. Results and discussion

The reaction of 2,3-dichloro-1,4-naphthoquinone **1** with 11-mercapto-1-undecanol **2** in ethanol in the presence of Na_2CO_3 gave S, O-substituted-1,4-naphthoquinone **3** and S, S-substituted-1,4-naphthoquinone **4**. Ethoxy substituted mono(thio)-1,4-naphthoquinone **13** and bis(thio)substituted-1,4-naphthoquinone **14** were obtained from the reaction of **1** with **12** in EtOH/Na_2CO_3. In these reactions, mono(thio)-substituted compounds containing chlorine atom derivatives were not observed potentially due to the decreased thiol amount in the medium of the reaction, while the ethoxy derivatives of mono(thio)-substituted compounds were obtained successfully. While compounds **3** and **13** were formed, one chloro atom was replaced with ethoxy groups, which acted as a nucleophilic compound.

Compounds **6**, **7** and **8** were obtained from the reaction of **1** with 2-(butylamino)ethanethiol **5**. For compounds **6** and **7**, no bands were observed in the region 3200–3450 cm^{-1} attributable to the streching vibration of the bonded NH group, indicating that the formation of cyclization reaction had taken place yielding the compounds **6**. It was shown that interesting heterocylic compounds **10** and **11** could be obtained from the reaction of 2,3-dichloro-1,4-naphthoquinone **1** with long alkyl chain dithiol **9**. Isolation and identification proved that a cyclization reaction had taken place, yielding the compound **10** and intramolecular cyclization to yield heterocyclic diquinone **11** (scheme 1). The ethoxy substituted-tris(thio)-1,4-benzoquinone **16** and tetrakis(thio)-substituted-1,4-benzoquinone **17** compounds were obtained from the reaction of p-chloranil **15** with 11-mercapto-1-undecanol **2** via vinilic substitution (scheme 2).

FT-IR spectrum in KBr showed the following important absorption bands. In the IR spectra of synthesized compounds two typical strong quinonic carbonyl absorptions were observed between at 1654 and 1667 cm^{-1}. Compounds **13** and **14** gave strong and sharp carbonyl bands at 1667, 1660 cm^{-1} and at 1720, 1733 cm^{-1} which were due to coumarine ring. The NH absorption appeared at 3344 cm^{-1} for compound **8**. The IR spectra of compounds **3**, **4**, **16** and **17** showed broad bands at 3410, 3314, 3312 and 3279 cm^{-1} for the -OH streching, respectively.

The ^{1}H spectrum of the products in $CDCl_3$ displayed distinct signals with appropriate multiplets. ^{1}H NMR signal of the hydrogen atoms of the methylene group (S-CH_2) adjacent to the sulphur atom in compound **11** was shifted to a higher field and displayed triplet at 3.2 ppm (J = 7.32 Hz). The ^{13}C NMR spectra of compound **13** gave two carbonyl signals at 178.62 and 180.18 ppm (C=O) while compound **14** showed one carbonyl signal at 177.3 ppm (C=O) in naphthoquinone unit.

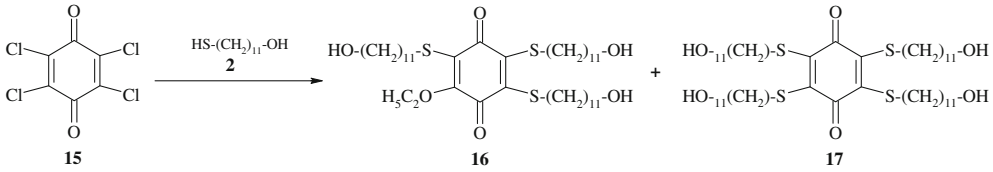
The positive ion mode of ESI mass spectrum of the compound **3** and the respective molecular ion peak was observed at m/z (%) 405 (100) $[M]^+$. The cleavage of ethoxy group from compound **3** of the molecular ion gave to rise fragment F_1 at m/z (%) 359 (100) which was the base peak. The respective molecular ion peak was observed at m/z (%) 918 (100) for compound **17** in the mode of ESI.

3.1 *Absorption and fluorescence spectroscopy*

The absorption parameters of compounds **3**, **4**, **6**, **7**, **8**, **10**, **11**, **13**, **14**, **16** and **17** in different solutions were reported in table 4. The electronic absorption spectra of **6**, **7**, **8** showed the expected naphthoquinone bands in the UV region around 240–248 nm and 300–347 nm (π–π^* electronic transitions) in chloroform. In addition, a third energy transition appeared as a broad band in the visible region between 451 and 554 nm (see table 4). This absorption was typical of amino-substituted benzoquinones, naphthoquinones and anthraquinones and is assigned to charge transfer (CT) transitions and weak n–π^* transitions of the carbonyl group in the quinone.[23] A broad band in the visible region at 535 nm in tetrahydrofurane, 554 nm in chloroform and 549 nm in methanol for compound **6** show strong bathochromic shift relative to compounds **7** and **8**. This bathochromic shift was due to N,S-substituted cyclo group in quinone unit of compound **6**. The absorption spectra of **13** and **14** display the intense bands having maxima between 278 and 331 nm and a shoulder of lower intensity between 451 and 463 nm. Ethoxy substituted naphthoquinone compound **13** was considerably red-shifted at 243 and 329 nm in the UV region relative to compound **14** which absorbs around at 237 and 326 nm, respectively in THF.

The fluorescence excitation and emission maxima of compounds **3**, **4**, **6**, **7**, **8**, **10**, **11**, **13**, **14**, **16** and **17** in $CHCl_3$/MetOH (1:1) solution were summarized in table 5. Fluorescence is an important property of quinone compounds for the use of organic materials.[24,25] The spectrum was composed of two broad bands and comparable to those of the similar compounds.[26,27]

Figure 2 shows the excitation and the emission of **13** in $CHCl_3$/MetOH (1:1). The first band at 327 nm was the fluorescence characteristic of the coumarin ring substituted naphthoquinone assigned to the excited band and the second band at 398 nm was emission band at room temperature.



15 **16** **17**

Scheme 2. Synthesis of compounds **16** and **17**.

Table 4. UV-Vis data of compounds **3**, **4**, **6**, **7**, **8**, **10**, **11**, **13**, **14**, **16** and **17** in different solvents.

Compound	λ^a (logε)	λ^b (logε)	λ^c (logε)
3	241(4.2), 266(4.2) 335(3.5), 443(3.5)	241(4.2), 273(4.2) 338(3.5), 457(3.4)	238(3.7), 264(3.8) 333(3.1), 444(2.9)
4	241(4.5), 281(4.5) 335(4.0), 467(3.9)	242(4.2), 281(4.2) 344(3.6), 471(3.6)	241(3.9), 276(3.9) 343(3.3), 460(3.3)
6	239(4.2), 298(4.3) 535(3.4)	240(3.5), 300(3.7) 554(2.9)	236(3.6), 298(3.8) 549(2.9)
7	236(3.9), 339(3.3) 471(2.9)	241(4.2), 345(3.6) 483(3.2)	223(3.8), 267(3.6) 341(3.1), 460(2.7)
8	246(3.8), 342(2.9) 451(2.8)	248(3.4), 347(3.3) 451(2.9)	–
10	245(3.0), 266(2.9) 312(2.5), 449(2.3)	248(3.7), 269(3.7) 315(3.2), 453(3.1)	247(3.8), 266(3.7) 313(3.2), 445(3.1)
11	241(3.6), 270(2.7) 343(3.0), 462(3.0)	257(3.8), 279(4.0) 344(3.4), 467(3.4)	-
13	243(3.6), 281(3.5) 329(3.5), 451(2.6)	244(4.5), 282(4.5) 331(4.5), 463(3.6)	241(3.7), 278(3.7) 330(3.7), 450(2.7)
14	237(4.0), 326(4.0) 451(3.1)	240(3.5), 267(3.4) 326(3.5), 462(2.6)	222(4.3), 279(3.6) 326(3.7)
16	225(3.7), 245(3.9) 396(3.5)	229(4.4), 244(4.4) 401(3.9)	210(4.0), 245(4.0) 396(3.7)
17	223(3.2), 241(3.1) 401(2.8)	225(3.5), 240(3.7) 405(3.5)	210(3.6), 240(3.7) 401(3.5)

[a]THF; [b] $CHCl_3$; [c]MetOH.
(–); **8** and **11** were dissolved in MetOH

3.2 *X-ray study*

The compound **13** was crystallized in the triclinic crystal system (space group P-1) with the unit cell parameters a = 8.4474(2) Å, b = 9.1257(1) Å, c = 11.9197(2) Å, α = 84.474(4)°, β = 84.506(4)°, γ = 80.473(4)°, V = 899.00(3) Å^3, Z = 2. The structure was solved by direct methods (SIR92) and refined to the residual index R_1 = 0.056. Drawings were prepared with the program ORTEP-III[21] with 50% probability displacement elipsoide for compound **13** in figure 1.

Table 5. Fluorescence data of the compounds **3**, **4**, **6**, **7**, **8**, **10**, **11**, **13**, **14**, **16** and **17**.

Compound	Solvent (1:1)	λ_{max}(ex.) (nm)	λ_{max}(em.) (nm)
3	$CHCl_3$/MetOH	221	455
4	$CHCl_3$/MetOH	220	456
6	$CHCl_3$/MetOH	226, 268	453, 535
7	$CHCl_3$/MetOH	246	494
8	$CHCl_3$/MetOH	249	497
10	$CHCl_3$/MetOH	261	417
11	$CHCl_3$/MetOH	245	494
13	$CHCl_3$/MetOH	327	398
14	$CHCl_3$/MetOH	327	390
16	$CHCl_3$/MetOH	221	457
17	$CHCl_3$/MetOH	222	458

The standard average C–C bond distance in a flat six carbon atom containing aromatic ring is 1.395(1) Å. The double bond distance of C1–C2 was 1.354(2) Å in **13**, which was smaller than expected due to substituents such as =O. The double bond length of the quinone moiety agreed well with corresponding distance in a similar compound.[28] Crystal data and refinement parameters for compound **13** were summarized in table 1. The selected bond distances, bond and torsion angles for compound **13** are listed in tables 2 and 3, respectively. The bond lengths of C3-O2, C10-O1 and C18-O5 were 1.212(2) Å, 1.220(2) Å, and 1.209(1) Å, respectively, typical of C=O bonds. In the compound **13**, C–C–C and C–C–O angles were very close to 120°, as expected for sp^2 hybridized atoms. In the structure of the compound, the U_{eq} values of the C atoms of the ethoxy chain generally increase on going

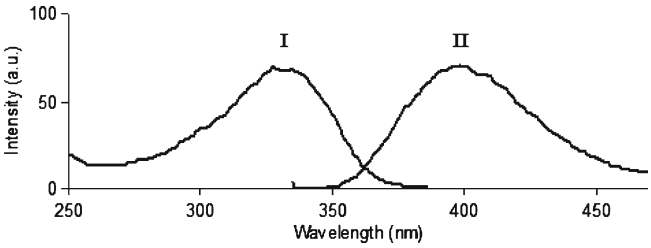


Figure 2. The excitation (**I**) and emission (**II**) spectra of **13** (2×10^{-4} M) in $CHCl_3$/MetOH (1:1) at room temperature.

from C21 to C22, reflecting libration of the chain. The both rings of naphthoquinone unit were planar with a maximum deviations of 0.0157(1) Å (plane 1 = C1-C2-C3-C4-C9-C10) and 0.0045(1) Å (plane 2 = C4-C5-C6-C7-C8-C9). The substituted coumarine ring was planar with a maximum deviation of 0.0024(1) Å (plane 3 = C11-C12-C13-C14-C19-C20) and 0.0139(1) Å (plane 4 = C14-C15-C17-C18-O4-C19). Dihedral angles were 64.54(1)° between planes 1 and 3, 63.61(1)° between planes 2 and 4.

3.3 *Electrochemical study*

Cyclic voltammetry measurements of **1**, **3**, **4**, **6**, **7**, **8**, **10**, **11**, **13**, **14**, **15**, **16** and **17** were performed in DMF to explore the substituent effects on their redox potentials. The voltammetric data of these compounds; cathodic peak potentials (E_{pc}), anodic peak potentials (E_{pa}) *versus* glassy carbon electrode (GCE), half-wave peak potentials ($E_{1/2}$), the difference between the first oxidation and reduction processes (ΔE_p) and cathodic *vs*. anodic peak current ratio (i_{pc}/i_{pa}) were shown in table 6. Experiments using a glassy carbon electrode were performed in order to investigate the electrooxidizable groups and to complete the information in the presence of proton sources. Additional oxidation waves were discernible.

Electrochemical study, cyclic voltammetry was performed in aprotic medium and the unsubstituted quinones 2,3-dichloro-1,4-naphthoquinone **1** and *p*-chloranil **15** were used as standarts. Compounds **1** and

Table 6. Voltammetric parameters in DMF/TBAP 0.1 M, v = 0.1 V s^{-1}.

Compound	$-(E_{pc})^a$	$-(E_{pa})^a$	$-(E_{1/2})^a$	$(\Delta E_p)^b$	$(i_{pc}/i_{pa})^c$
2,3-Dichloro-1,4-naphthoquinone **1**	0.287[d]	0.189[d]	0.238	0.097	0.992
	1.074[d]	0.973[d]	1.023	0.099	2.034
p-chloranil **15**	0.730[d]	0.644[d]	0.687	0.085	1.659
3	0.408[d]	0.353[d]	0.381	0.055	1.141
	0.592[d]	0.536[d]	0.564	0.055	1.624
	1.349	–	–	–	–
4	0.540[d]	0.465[d]	0.498	0.075	1.254
	1.187	–	–	–	–
6	0.804[d]	0.726[d]	0.765	0.077	1.028
	1.367	–	–	–	–
7	0.815[d]	0.502[d]	0.658	0.313	1.058
	1.277	1.796	–	–	–
	1.916	–	–	–	–
	2.258	–	–	–	–
8	0.550[d]	0.255[d]	0.403	0.295	1.055
	0.872	0.594	–	–	–
10	0.506[d]	0.433[d]	0.470	0.073	1.238
	1.213	–	–	–	–
11	0.564[d]	0.463[d]	0.513	0.102	1.109
	0.848	–	–	–	–
13	0.473[d]	0.403[d]	0.438	0.069	1.057
	1.088	–	–	–	–
	1.898	–	–	–	–
	2.185	–	–	–	–
14	0.283[d]	0.209[d]	0.246	0.073	0.946
	0.909	–	–	–	–
	1.271	–	–	–	–
16	0.403[d]	0.325[d]	0.364	0.077	1.004
	1.129	–	–	–	–
17	0.374[d]	0.301[d]	0.337	0.073	1.085
	1.039	–	–	–	–

[a]Peak potential (V *vs*. Ag/AgCl) at room temperature as determined by cyclic voltammetry at a GC electrode and given without *i*R drop correction, $E_{1/2}$ (approximated by $(E_{pa} + E_{pc})/2$) in V *vs*. Ag/AgCl; supporting electrolyte tetrabutyl ammonium perchlorate (0.1 M) in DMF, scan rate 0.1 V s^{-1} concentration of compounds 10^{-4} M. [b]$(E_{pa} - E_{pc})$ in V. [c]Cathodic *vs*. anodic peak current ratio. [d]Reversible wave

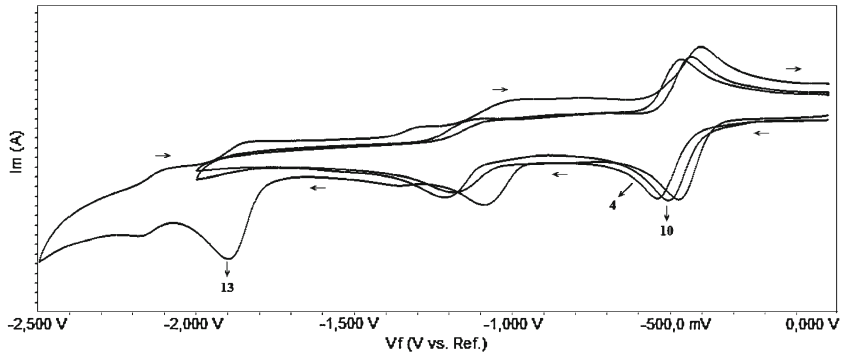


Figure 3. Cyclic voltammogram of compounds **4**, **10** and **13** in DMF obtained by using tetrabutyl ammonium perchlorate (0.1 M) as the supporting electrolyte at scan rate of v = 0.1 V s^{-1}.

15 showed behaviour typical of quinones in aprotic medium.[29,30] Two reversible one-electron waves were observed. The first reversible reduction wave was, for **1**, −0.287 V *vs*. Ag/AgCl, represented the addition of one electron to the quinone core to form a semiquinone anion radical. Furthermore, if we consider that the ratio of the cathodic to anodic peak current was near 1 (i_{pc}/i_{pa} = 0.99 for compound **1**), it could be proposed that 2,3-dichloro-1,4-naphthoquinone **1** is transformed to a stable semiquinone anion radical ($Q^{\cdot -}$). In the case of more negative reduction process (second cathodic and first anodic peak), the largest difference between the cathodic and anodic peak potential (E_{pa}–E_{pc} = 99.7 mV) (see in table 6) suggests that the reduction of the semiquinone anion radical (Q^-) to the dianion (Q^{2-}) was partially controlled by the electronic transference and by diffusion. These oxidation-reduction reactions could be represented by the following equations:[31]

$$Q + e^- \rightleftharpoons Q^{\cdot -} \text{ (reversible)}$$
$$Q^{\cdot -} + e^- \rightleftharpoons Q^{-2} \text{ (quasi} - \text{reversible)}.$$

For this electrochemical reaction, the standard potential was also estimated from the difference between both the anodic and cathodic peak potential: $E_{1/2}$ = −1.027 V (*vs*. SCE),[31] in our study, $E_{1/2}$ = −1.024 V (*vs*. GCE) in table 6 for **1**. The cyclic voltammogram of *p*-chloranil **15** exhibits an anodic peak related to the oxidation of HQ^-, presents a cathodic peak related to reduction of *p*-chloranil (Q) to reduced *p*-chloranil (HQ^-).

The reversibility of this redox couple ($I_{pc} \approx I_{pa}$) suggests that the dianion was also stable in the time scale of the voltammetric experiments. The ratio of the cathodic to anodic peak current was near 1 for compounds **3**, **4**, **6**, **7**, **8**, **10**, **11**, **13**, **14**, **16** and **17**. Two reduction waves representing in table 6, were observed at a scan rate 0.1 Vs^{-1} for compounds **4**, **6**, **8**, **10**, **11**, **16** and **17**. The redox behaviour of compounds **3**, **7**, **13** and **14** was very different. Three reduction waves were observed for **3** and **14**, and four reduction waves were observed for **7** and **13**. Cyclic voltammogram of compounds **4**, **10** and **13** in DMF was given in figure 3. The intensity of the two quinone reduction waves has decreased, the quasi-reversible character of the second wave has almost disappeared for **3**, **7**, **13** and **14**. The potentials for reductions were more negative for **3**, **4**, **6**, **7**, **8**, **10**, **11**, **13** and **14** according to 2,3-dichloro-1,4-naphthoquinone **1**.

4. Conclusions

The aim of this study was to synthesize and characterize some naphthoquinone and benzoquinone **3**, **4**, **6**, **7**, **8**, **10**, **11**, **13**, **14**, **16** and **17** compounds. Their structures were determined by using micro analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, MS, UV-Vis. Photo- and electrochemical properties of N-, S-, O-substituted naphthoquninone and S-, O-substituted benzoquinone compounds were investigated by using fluorescence spectroscopy and electrochemical method (cyclic voltammetry). The crystal structure of compound **13** was determined by X-ray diffraction method. These compounds possess high solubility in various organic solvents such as chloroform, dichloromethane, tetrahydrofurane and are insoluble in water.

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