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# Synthesis, electrochemistry, *in-situ* spectroelectrochemistry and molecular structures of 1,4-naphthoquinone derivatives

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ABSTRACT

A novel series of 1,4-naphthoquinones substituted containing sulfur, nitrogen, oxygen atoms were synthesized. The structures of the novel products were characterized by using the various spectroscopic techniques such as $^{1}$H nuclear magnetic resonance (NMR), $^{13}$C NMR, mass spectrometry (MS), Fourier transform infrared spectroscopy (FT-IR) and microanalysis. The crystal structures of 2,3-bis(benzylsulfanyl)-1,4-napthoquinone **4** and 2,3-bis(ethylsulfanyl)-1,4-naphthoquinone **7** were determined by using X-ray single crystal diffraction method. Electrochemical behaviors of some 1,4-naphthoquinone (NQ) derivatives **3, 4, 7, 8, 9, 10, 12, 13, 15, 16, 17, 19** and **20** were studied by using cyclic voltammetry, square wave voltammetry and in-situ UV-Vis spectroelectrochemistry. The substituents of the NQ derivatives significantly altered the redox mechanism. In-situ UV-Vis spectroelectrochemical analyses of NQs supported the proposed redox mechanism.



## 1. Introduction

Naphthoquinone derivatives occur naturally as plant constituents, and many of these have found use as colorant in the past. The color of the naphthoquinone compounds can be produced in the 1,4-naphthoquinone chromogen by introducing amino and hydroxyl groups into the quinoid ring, into the benzenoid ring, or into both rings. The advantage of the naphthoquinone dyes is their strong and stable coloring ability [1], so they are extensively used in the cosmetics industry in the production of cosmetic dyes, especially hair dyes. Heterocyclic naphthoquinone derivatives have been gaining importance in the manufacturing of dyes and pigments because of their substantivity to cellulosic and hydrophobic fibers [2]. Moreover, particularly 1,4-naphthoquinones are widely distributed phenolic compounds in nature such as naphthoquinones are reported to exhibit diverse pharmacological properties like antibacterial [3], antifungal, antiviral, anti-inflammatory antipyretic and anticancer activity [4]. These 1,4-naphthoquinones have the ability to induce oxidative stress which is responsible for initiation of tissue damage selectively in tumor cells and this seems to be a promising approach for targeting cancer cells [5].

Because of their biological importance, the redox reactions of the 1,4-naphthoquinone derivatives have been investigated to their usage in various biological and electrochemical fields such as corrosion inhibitor, antimicrobials and sensors [6–9]. Thus, it becomes necessary to understand the factors which regulate the potentials and reaction pathways of these 1,4-naphthoquinone species. While the quinone derivatives undergo a two-step reduction with two-step hydrogenation in aqueous media, they are first reduced to its radical anion and then to the dianion in aprotic solvents. While the ideal reduction reactions are the two identical reduction couples with similar peak currents and peak to peak separation, substituent environments of the quinone derivatives frequently cause deviation significantly from those expected for a simple two-step reaction [10–16]. It has been observed that most of their activities are associated with their redox behavior. Thus, electrochemical examinations of synthesized 1,4-naphthoquinone derivatives (**3, 4, 7, 8, 9, 10, 12, 13, 15, 16, 17, 19, 20**) were carried out in this study in order to use these moieties for the practical applications in electrochemical technologies in the future.

## 2. Materials and methods

### 2.1. Experimental section

Melting points were measured on a Buchi B-540 melting point apparatus. TLC plates silica $60F_{254}$ (Merck, Darmstadt), detection

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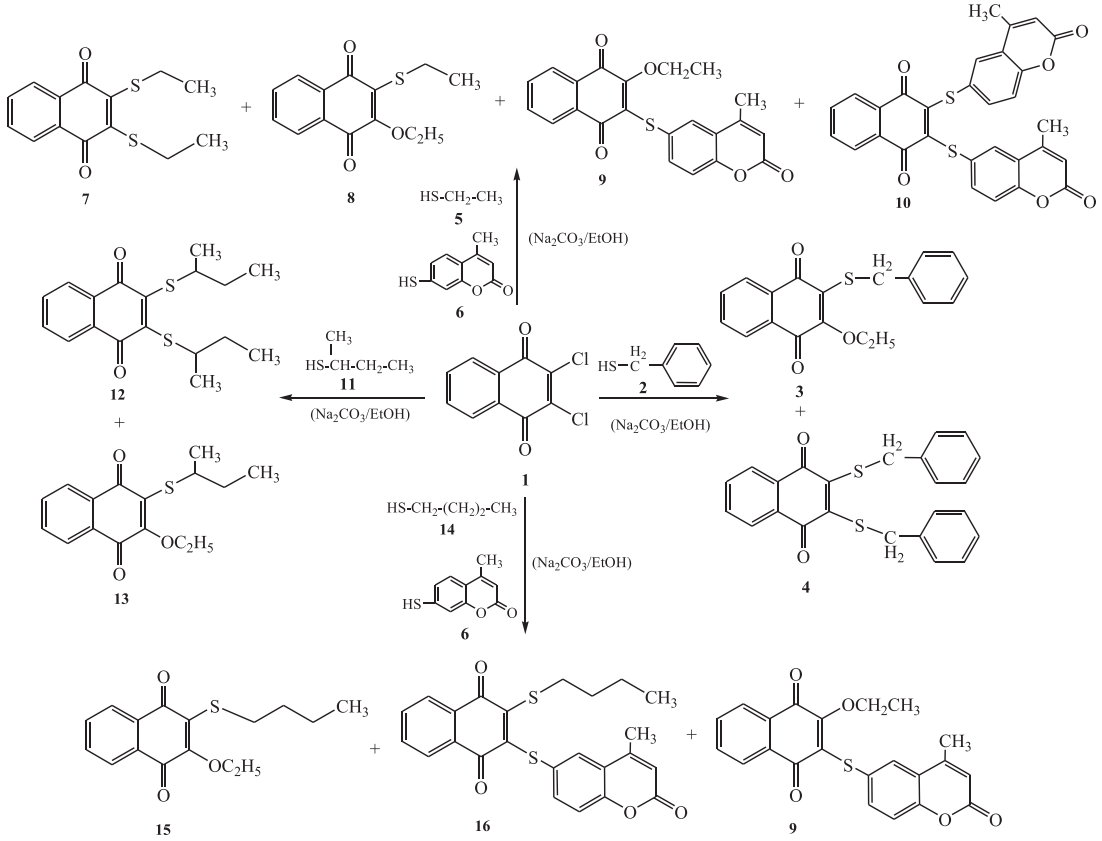
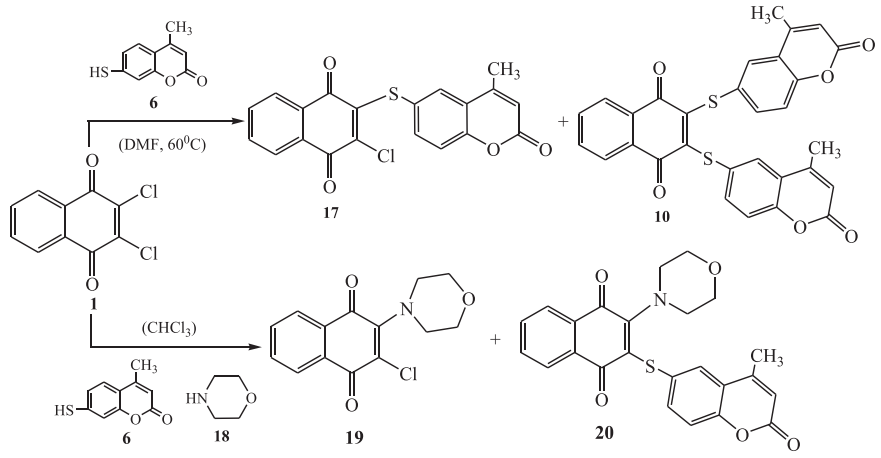


**Scheme 1.** The synthesis of S,S- and S,O-substituted-1,4-naphthoquinones in the presence of ethanol.



**Scheme 2.** The synthesis of S-, S,S-, N- and N,S-substituted-1,4-naphthoquinones in the presence of DMF or chloroform.

with ultraviolet light (254 nm). Elemental analyses were performed on a Thermo Finnigan Flash EA 1112 Elemental analyzer. Infrared (IR) spectra were recorded in KBr pellets in Nujol mulls on a Perkin Elmer Precisely Spectrum One FTIR spectrometry. $^{1}$H and $^{13}$C NMR spectra were recorded on Varian UNITYINOVA 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). 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. Synthesis procedures

The heteroatom substituted-1,4-naphthoquinone compounds **3, 4** [21], **7** [21], **8, 9** [16], **10** [16], **12** [22], **13, 15, 16, 17, 19** [23] and **20** were synthesized acourding to method 1, 2, 3 and illustrated in Schemes 1, 2 and 3. The synthesized 1,4-naphthoquinone derivatives **3, 8, 13, 15, 16, 17** and **20** were fully new compounds. All spectroscopic data ($^{1}$H NMR, $^{13}$C NMR, FTIR, MS) and results of micro analysis were given in the experimental section for characterization of these new 1,4-naphthoquinone compounds **3, 8, 13, 15, 16, 17** and **20**. In addition to, some known 1,4-naphthoquinone compounds (**4, 7, 9, 10, 12, 19**) were yielded from these reactions. The synthesis method and spectral characterizations of these

known quinone compounds **4, 7, 9, 10, 12** and **19** were previously reported in the related literature [16,21–23]. The both study of crystal structure determination of compounds **4, 7** and their electrochemical properties of compounds (**4, 7, 9, 10, 12, 19)** were firstly investigated in this study. The electrochemical properties of all synthesized compounds were investigated in this study.

Method 1: Sodium carbonate (1.52 g) was dissolved (60 mL) in ethanol. 2,3-Dichloro-1,4-naphthoquinone 1 and nucleophiles 2 or (5, 6) or 11 or (6, 14) were added slowly to this solution. Without heating, the mixture was stirred for 6 hours. The color 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 Na2SO4. After the solvent was evaporated the residue was purified by column chromatography on silica gel.

Method 2: 2,3-Dichloro-1,4-naphthoquinone 1 and nucleophile compound 6 in the presence of dimethylformamide (DMF) (50 mL) were stirred and heated at 60°C for 6 hours. The extent of the reaction was monitored by Thin-Layer Chromatography (TLC). Chloroform (30 mL) was added to the reaction mixture. The organic layer was washed with water (4 × 30 mL) and dried with Na2SO4. After the solvent was evaporated the residue was purified by column chromatography on silica gel.

Method 3: 2,3-Dichloro-1,4-naphthoquinone 1 and nucleophiles 6 and 18 in the presence of chloroform (50 mL) were stirred without heating for 8 hours. 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 Na2SO4. After the solvent was evaporated the residue was purified by column chromatography on silica gel.

*2-Benzylsulfanyl-3-ethoxy-1,4-naphthoquinone* (**3**):

Compound **3** was synthesized from reaction of **1** (1.0 g, 4.40 mmol) with **2** (0.54 g, 4.40 mmol) according to the method 1. Yield: 0.78 g (52%); Red oil; $R_f$ = 0.40 ($CHCl_3$); FT-IR (KBr pellet, $cm^{-1}$): 3063 ($CH_{arom}$), 2923, 2852 (C-H), 1661 (C=O), 1600 (C=C); $^1$H NMR (499.74 MHz, $CDCl_3$): $\delta$ = 1.18 (t, J = 6.84 Hz, 3H, $CH_3$), 4.4 (q, 2H, O-$CH_2$), 6.1 (s, 2H, S-$CH_2$-Ph), 7.0-8.2 ppm (m, 9H, $H_{arom}$); $^{13}$C NMR (125.66 MHz, $CDCl_3$): $\delta$ = 12.41 ($CH_3$), 28.67 (S-$CH_2$), 65.17 (-$OCH_2$), 113.91, 117.70, 123.93, 126.19, 126.29, 127.70, 131.94, 132.81, 133.07, 135.88 (**C**$H_{arom,}$ **C**$_{arom}$), 138.42 (=C-S), 153.07 (=C-O), 176.39, 178.69 ppm (C=O); MS [+ESI]: m/z 348 $[M+Na]^+$; $C_{19}H_{16}O_3S_1$ (M = 324.402 g/mol). Calculated: C, 70.34; H, 4.97; S, 9.88%. Found: C, 70.33; H, 4.95; S, 9.89%.

*2-Etylsulfanyl-3-ethoxy-1,4-naphthoquinone* (**8**):

Compound **8** was synthesized from reaction of **1** (1.0 g, 4.40 mmol) with **5** (0.27 g, 4.40 mmol) and **6** (0.84 g, 4.40 mmol) according to the method 1. Yield: 0.47 g (41%); Red oil; $R_f$ = 0.50 ($CHCl_3$); FT-IR (KBr pellet, $cm^{-1}$): 3071 ($CH_{arom}$), 2975, 2927, 2869 (C-H), 1659 (C=O), 1591 (C=C); $^1$H NMR (499.74 MHz, $CDCl_3$): $\delta$ = 1.2 (t, $J$ = 8.34 Hz, 3H, $CH_3$), 1.4 (t, $J$ = 7.32 Hz, 3H, $CH_3$), 3.2 (q, 2H, S-$CH_2$), 4.4 (q, 2H, O-$CH_2$), 7.65 (t, $J$ = 7.32 Hz, 1H, $H_{arom}$), 7.55 (d, 1H, $H_{arom}$), 7.92 (dd, $J$ = 7.81 Hz, $J$ = 6.35 Hz, 1H, $H_{arom}$), 7.95 ppm (dd, $J$ = 6.84 Hz, $J$ = 5.32 Hz, 1H, $H_{arom}$); $^{13}$C NMR (125.66 MHz, $CDCl_3$): $\delta$ = 14.25, 14.87 ($CH_3$), 28.67 (S-$CH_2$), 68.91 (-$OCH_2$), 125.38, 125.71, 130.46, 131.37, 132.52, 132.58 (**C**$H_{arom,}$ **C**$_{arom}$), 133.42 (=C-S), 156.72 (=C-O), 177.91, 181.91 ppm (C=O); MS [+ESI]: m/z 262 $[M]^+$, 235 $[M-(CH_2-CH_3)]^+$; $C_{14}H_{14}O_3S_1$ (M = 262.332 g/mol). Calculated: C, 61.10; H, 5.37; S, 12.22%. Found: C, 61.03; H, 5.35; S, 12.25%.

*2-(Isopropylsulfanyl)-3-etoxy-1,4-naphthoquinone* (**13**):

Compound **13** was synthesized from reaction of **1** (1.0 g, 4.40 mmol) with **11** (0.39 g, 4.40 mmol) according to the method 1. Yield: 0.57 g (45%); Red oil; $R_f$ = 0.40 ($CHCl_3$); FT-IR (KBr pellet, $cm^{-1}$): 3071 ($CH_{arom}$), 2968, 2927, 2874 (C-H), 1663 (C=O), 1593 (C=C); $^1$H NMR (499.74 MHz, $CDCl_3$): $\delta$ = 0.9 (t, $J$ = 8.34 Hz, 3H, $CH_3$), 1.1 (t, $J$ = 7.32 Hz, 3H, $CH_3$), 1.4 (d, 3H, $CH_3$), 1.45-1.6 (m, 2H, $CH_2$), 3.8 (m, 1H, S-CH), 4.4-4.5 (q, 2H, O-$CH_2$), 7.55 (t, $J$ = 7.32 Hz, 1H, $H_{arom}$), 7.65 (d, 1H, $H_{arom}$), 7.95 (dd, $J$ = 7.81 Hz, $J$ = 6.35 Hz, 1H, $H_{arom}$), 8.0 ppm (dd, $J$ = 6.84 Hz, $J$ = 5.32 Hz, 1H, $H_{arom}$); $^{13}$C NMR (125.66 MHz, $CDCl_3$): $\delta$ = 14.93, 14.99, 17.35 ($CH_3$), 20.02 ($CH_2$), 29.34 (S-CH), 68.92 (-$OCH_2$), 125.80, 125.87, 131.37, 132.47, 132.60, 132.85 (**C**$H_{arom,}$ **C**$_{arom}$), 133.23 (=C-S), 157.53 (=C-O), 178.68, 181.86 ppm (C=O); MS [+ESI]: m/z 290 $[M]^+$, $C_{16}H_{18}O_3S_1$ (M = 290.383 g/mol). Calculated: C, 66.18; H, 6.24; S, 11.04%. Found: C, 66.19; H, 6.25; S, 11.04%.

*2-(Butylsulfanyl)-3-etoxy-1,4-naphthoquinone* (**15**):

Compound **15** was synthesized from reaction of **1** (1.0 g, 4.40 mmol) with **6** (0.84 g, 4.40 mmol) and **14** (0.39 g, 4.40 mmol) according to the method 1. Yield: 0.47 g (37%); Red oil; $R_f$ = 0.40 ($CHCl_3$); FT-IR (KBr pellet, $cm^{-1}$): 3071 ($CH_{arom}$), 2959, 2929, 2872 (C-H), 1662 (C=O), 1593 (C=C); $^1$H NMR (499.74 MHz, $CDCl_3$): $\delta$ = 0.95 (t, $J$ = 8.34 Hz, 3H, $CH_3$), 1.2 (t, $J$ = 7.32 Hz, 3H, $CH_3$), 1.4 (m, 2H, 6.84 Hz, 1H, $H_{arom}$), 7.60 (d, 1H, $H_{arom}$), 7.68 (dd, $J$ = 7.81 Hz, $J$ = 6.85 Hz, 1H, $H_{arom}$), 7.95 (dd, $J$ = 6.84 Hz, $J$ = 5.32 Hz, 1H, $H_{arom}$), 8.2 (dd, $J$ = 5.84 Hz, $J$ = 6.84 Hz, 1H, $H_{arom}$); $^{13}$C NMR (125.66 MHz, $CDCl_3$): $\delta$ = 14.88, 15.00 ($CH_3$), 20.84, 28.67 ($CH_2$), 31.26 (S-$CH_2$), 68.89 (-$OCH_2$), 125.36, 125.57, 125.85, 125.95, 132.50, 132.56 (**C**$H_{arom,}$ **C**$_{arom}$), 133.26 (=C-S), 156.77 (=C-O), 177.90, 181.89 ppm (C=O); MS [+ESI]: m/z 290 $[M]^+$, 275 $[M-(CH_3)]^+$; $C_{16}H_{18}O_3S_1$ (M = 290.383 g/mol). Calculated: C, 66.18; H, 6.24; S, 11.04%. Found: C, 66.17; H, 6.25; S, 11.05%.

*2-(Butylsulfanyl)-3-(7-sulphanyl-4-methyl-coumarinyl)-1,4-naphthoquinone* (**16**):

Compound **16** was synthesized from reaction of **1** (1.0 g, 4.40 mmol) with **6** (0.84 g, 4.40 mmol) and **14** (0.39 g, 4.40 mmol) according to the method 1. Yield: 0.48 g (25%); Black oil; $R_f$ = 0.50 ($CHCl_3$); FT-IR (KBr pellet, $cm^{-1}$): 3062 ($CH_{arom}$), 2959, 2928, 2871 (C-H), 1621 (C=O), 1600 (C=C); $^1$H NMR (499.74 MHz, $CDCl_3$): $\delta$ = 0.84 (t, $J$ = 8.34 Hz, 3H, $CH_3$), 1.3-1.4 (m, 2H, $CH_2$), 1.6 (m, 2H, S-$CH_2$-*C*$H_2$), 2.3 (s, 3H, $CH_3$), 3.3 (t, $J$ = 7.32 Hz, 2H, S-$CH_2$), 6.1 (s, 1H, CH), 7.1-8.1 (m, 7H, $H_{arom}$); $^{13}$C NMR (125.66 MHz, $CDCl_3$): $\delta$ = 12.57, 17.58 ($CH_3$), 20.81 ($CH_2$), 31.45 (S-$CH_2$-***C***$H_2$), 34.0 (S-$CH_2$), 113.69 (CH), 115.83, 117.56, 123.75, 123.99, 126.24, 131.38, 131.99, 132.72, 133.11, 138.54, 139.08 (**C**$H_{arom,}$ **C**$_{arom}$), 150.95, 152.63 (=C-S), 159.27 (C=O), 176.30, 178.75 ppm (C=O); MS [+ESI]: m/z 437 $[M]^+$. $C_{24}H_{20}O_4S_2$ (M = 436.54 g/mol). Calculated: C, 66.03; H, 4.62; S, 14.69%. Found: C, 66.04; H, 4.65; S, 14.65%.

*2-(7-Sulphanyl-4-methyl-coumarinyl)-3-chloro-1,4-naphthoquinone* (**17**):

Compound **17** was synthesized from reaction of **1** (1.0 g, 4.40 mmol) with **6** (0.84 g, 4.40 mmol) according to the method 2. Yield: 0.72 g (43%); Orange oil; $R_f$ = 0.50 ($CHCl_3$); FT-IR (KBr pellet, $cm^{-1}$): 3019 ($CH_{arom}$), 2400 (C-H), 1670 (C=O), 1600 (C=C); $^1$H NMR (499.74 MHz, $CDCl_3$): $\delta$ = 2.3 (s, $CH_3$), 6.2 (s, 1H, CH), 7.1-8.2 (m, 7H, $H_{arom}$); $^{13}$C NMR (125.66 MHz, $CDCl_3$): $\delta$ = 17.60 ($CH_3$), 114.46 (CH), 117.98 (=C-$CH_3$), 118.57, 124.11, 125.54, 126.64, 126.71, 130.18, 131.10, 133.45, 133.49, 136.09, 144.17 (**C**$H_{arom,}$ **C**$_{arom}$), 144.72 (=C-S), 150.69 (S-C=), 152.53 (=C-Cl), 159.03 (=C-O), 174.62, 177.35 ppm (C=O); MS [+ESI]: m/z 383 $[M]^+$, MS/MS [+ESI]: m/z 347 [M-Cl]+, 319 $[M-(Cl+CH+CH_3)]^+$; $C_{20}H_{11}O_4S_1Cl_1$ (M = 382.77 g/mol). Calculated: C, 62.75; H, 2.89; S, 8.37%. Found: C, 62.73; H, 5.85; S, 8.35%.

*2-Morpholinyl-3-(7-sulphanyl-4-methyl-coumarinyl)-1,4-naphthoquinone* (**20**):

Compound **20** was synthesized from reaction of **1** (1.0 g, 4.40 mmol) with **6** (0.84 g, 4.40 mmol) and **18** (0.84 g, 4.40 mmol) ac-

**Table 1**
Voltammetric data of the NQ derivatives.

| Compounds | $NQ/NQ^{\cdot-}$ reduction couple | | | $NQ^{\cdot-}/NQ^{2-}$ reduction couple | | | $NQ_2^{\cdot-}/NQ_2^{2-}$ reduction couple | | |
|---|---|---|---|---|---|---|---|---|---|
| | [a]$E_{1/2}$ vs. SCE (V) | [b]$\Delta E_p$ | $I_{pa}/I_{pc}$ | [a]$E_{1/2}$ vs. SCE (V) | [b]$\Delta E_p$ | $I_{pa}/I_{pc}$ | [a]$E_{1/2}$ vs. SCE (V) | [b]$\Delta E_p$ | $I_{pa}/I_{pc}$ |
| **3** | -0.42 | 70 | 0.98 | -0.96 | 75 | 0.96 | | | - |
| **4** | -0.43 | 67 | 1.00 | -1.06 | 64 | 0.97 | | | - |
| **7** | -0.46 | 62 | 0.97 | -1.08 | 60 | 0.95 | | | - |
| **8** | -0.48 | 69 | 0.92 | -1.12 | 65 | 0.93 | | | |
| **9** | -0.42 | 63 | 0.93 | -1.06 | 61 | 0.96 | -1.90 | - | - |
| **10** | -0.22 | 67 | 0.90 | -0.78 | 65 | 0.92 | -1.87 | - | - |
| **12** | -0.47 | 85 | 0.98 | -1.16 | 70 | 0.97 | | | |
| **13** | -0.45 | 85 | 0.92 | -1.15 | 82 | 0.90 | | | |
| **15** | -0.42 | 67 | 0.90 | -1.35 | 64 | 0.92 | -1.93 | - | - |
| **16** | -0.33 | 64 | 0.86 | -0.96 | 61 | 0.42 | -1.93 | - | - |
| **17** | -0.20 | 63 | 0.98 | -0.78 | 64 | 0.96 | -1.82 | 100 | 0.34 |
| **19** | -0.58 | 87 | 0.90 | -1.08 | 68 | 0.88 | -1.88 | - | - |
| **20** | -0.53 | 76 | 0.89 | -1.30 | 67 | 0.93 | -1.85 | - | - |

[a] $E_{1/2}$ values were given for reversible processes. $E_{pc}$ values were given for irreversible reduction processes.
[b] $\Delta E_p = | E_{pa} - E_{pc}|$.

cording to the method 3. Yield: 0.72 g (38%); Red oil; $R_f$ = 0.40 ($CHCl_3$); FT-IR (KBr pellet, $cm^{-1}$): 3014 ($CH_{arom}$), 2963, 2922, 2862 (C-H), 1621 (C=O), 1600 (C=C); $^1H$ NMR (499.74 MHz, $CDCl_3$): $\delta$ = 2.3 (s, $CH_3$), 3.5, 3.7 (t, $J$ = 9.27 Hz, $J$ = 9.27 Hz, 8H, $H_{morp}$), 6.1 (s, 1H, CH), 7.1-8.0 (m, 7H, $H_{arom}$); $^{13}C$ NMR (125.66 MHz, $CDCl_3$): $\delta$ = 17.57($CH_3$), 51.57, 66.41 ($C_{morp}$), 114.24 (CH), 117.19 (=C-$CH_3$), 116.76, 121.50, 123.95, 124.23, 125.70, 126.05, 131.02, 131.34, 132.23, 133.36, 141.33 (**C**$H_{arom}$, **C**$_{arom}$), 141.33 (=C-S), 151.09 (S-$C_{arom}$), 154.77 (=C-N), 159.40 (=C-O), 177.12, 180.00 ppm (C=O); MS [+ESI]: m/z 434 $[M]^+$; $C_{24}H_{19}O_5S_1N_1$ (M = 433.487 g/mol). Calculated: C, 66.49; H, 4.41; N, 3.23; S, 7.39%. Found: C, 66.50; H, 4.45; S, 7.35%.

### 2.3. Electrochemical and spectroelectrochemical studies

Electrochemical and spectroelectrochemical measurements were carried out with a Gamry Reference 600 potentiostat/galvanostat utilizing a three-electrode configuration at 25°C. For cyclic voltammetry (CV), and square wave voltammetry (SWV) measurements, the working electrode was a Pt disc with a surface area of 0.071 $cm^2$. The surface of the working electrode was polished with a diamond suspension before each run. A Pt wire served as the counter electrode. Ag/AgCl electrode was employed as the reference electrode and separated from the bulk of the solution by a double bridge. Ferrocene was used as an internal reference. Tetrabuthylammonium perchlorate (TBAP) in dimethylsulfoxide (DMSO) was employed as the supporting electrolyte at a concentration of 0.10 $moldm^{-3}$. High purity $N_2$ was used to remove dissolved $O_2$ at least 15 minutes prior to each run and to maintain a nitrogen blanket during the measurements. Voltammetric data of the compounds were illustrated in the Table 1. IR compensation was applied to the CV and SWV scans to minimize the potential control error. UV/Vis absorption spectra were measured by an OceanOptics QE65000 diode array spectrophotometer. *In-situ* spectroelectrochemical measurements were carried out by utilizing a three-electrode configuration of thin-layer quartz spectroelectrochemical cell at 25°C. The working electrode was a semitransparent Pt tulle. A Pt wire counter electrode and a SCE reference electrode separated from the bulk of the solution by a double bridge were used. CV responses of compounds **4, 7, 12, 9, 15** and **17** at various scan rates on GCE in DMSO/TBAP were illustrated in Figs. 1–6, respectively. UV-vis spectral changes of compounds **4, 15, 12** and **9** were given in Figs. 7–10, respectively.

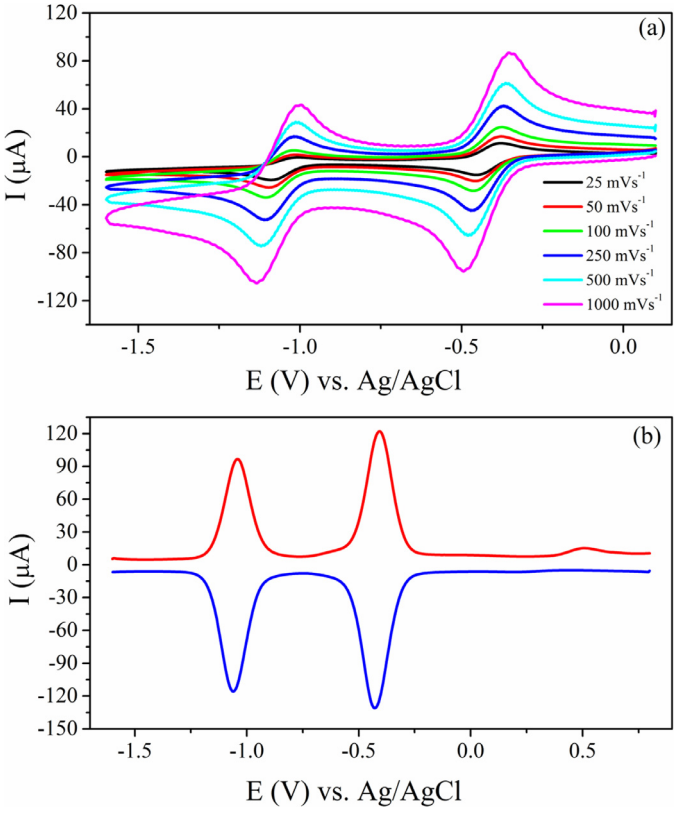



**Fig. 1.** CV responses of compound **4** at various scan rates on GCE in DMSO/TBAP.

### 2.4. X-ray crystallography

Red and black crystals of compounds **4** and **7** suitable for X-ray diffraction analysis were obtained by slow evaporation of an ethanol solution at room temperature. A red crystal of compound **4**, $C_{24}H_{18}O_2S_2$, a black crystal of compound **7,** $C_{14}H_{14}O_2S_2$, having approximate dimensions of 0.30 × 0.20 × 0.10 and 0.60 × 0.30 × 0.10 mm, respectively, were mounted on a glass fiber. All measurements were made on a Rigaku R-Axis Rapid-S imaging plate area detector with graphite monochromatic Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Experimental conditions were sum-

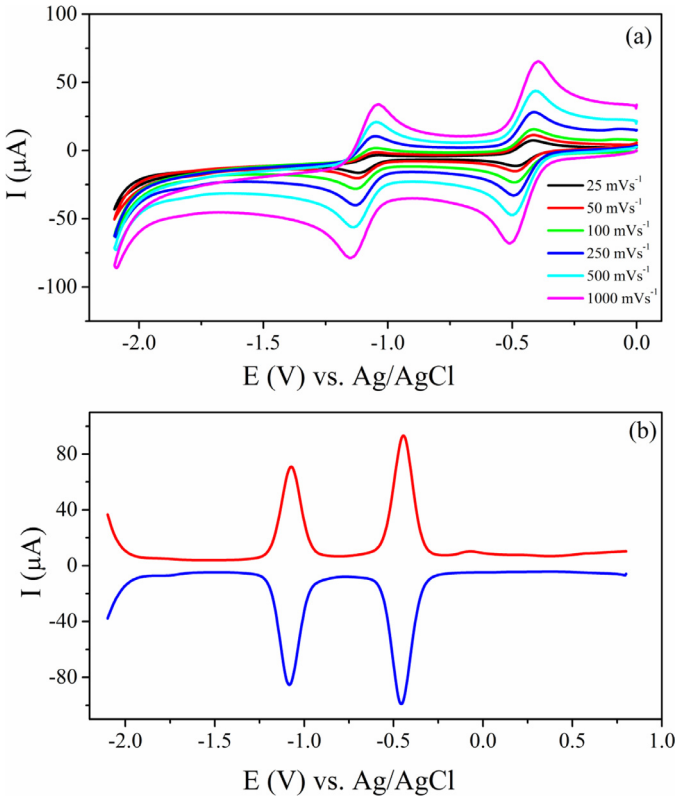



**Fig. 2.** CV responses of compound **7** at various scan rates on GCE in DMSO/TBAP.

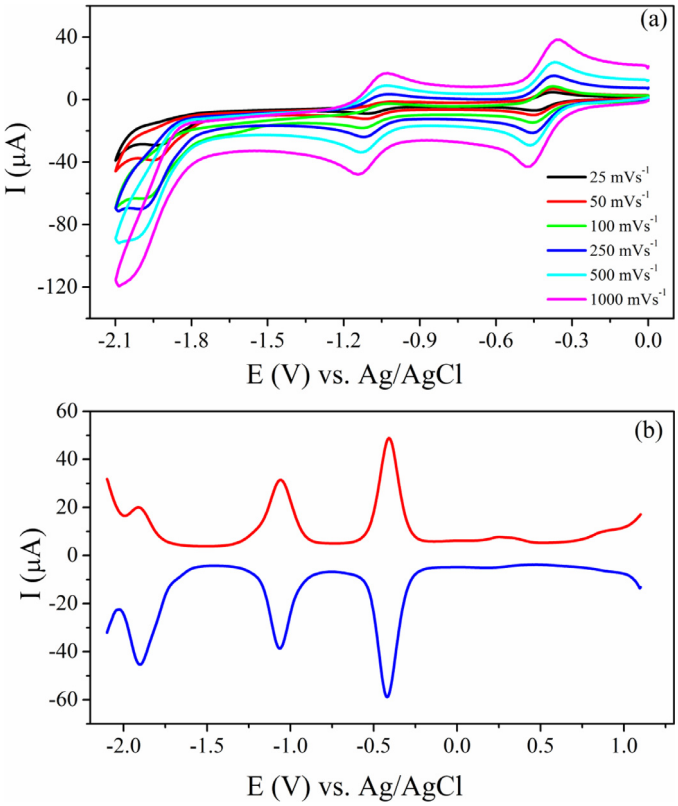



**Fig. 4.** CV responses of compound **9** at various scan rates on GCE in DMSO/TBAP.

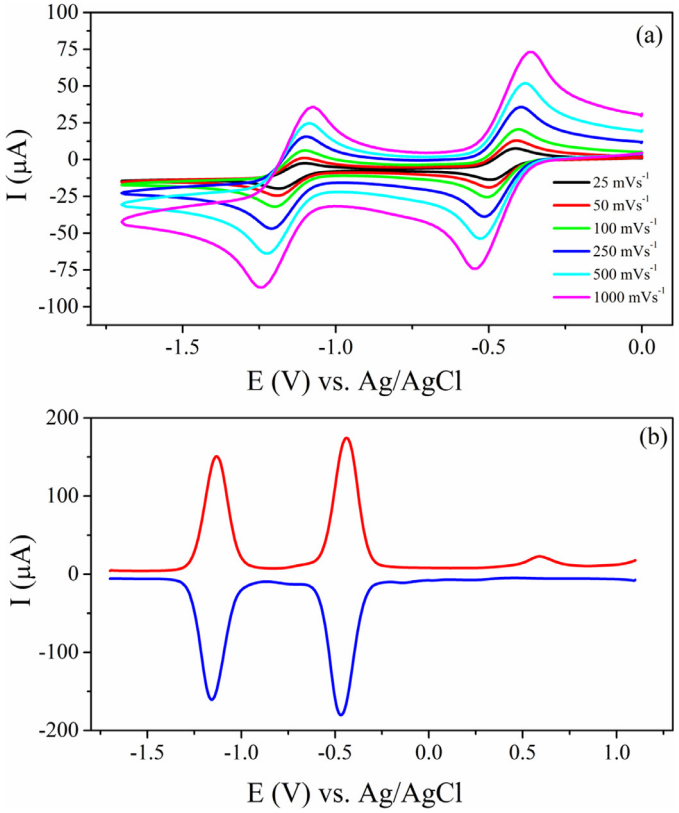



**Fig. 3.** CV responses of compound **12** at various scan rates on GCE in DMSO/TBAP.

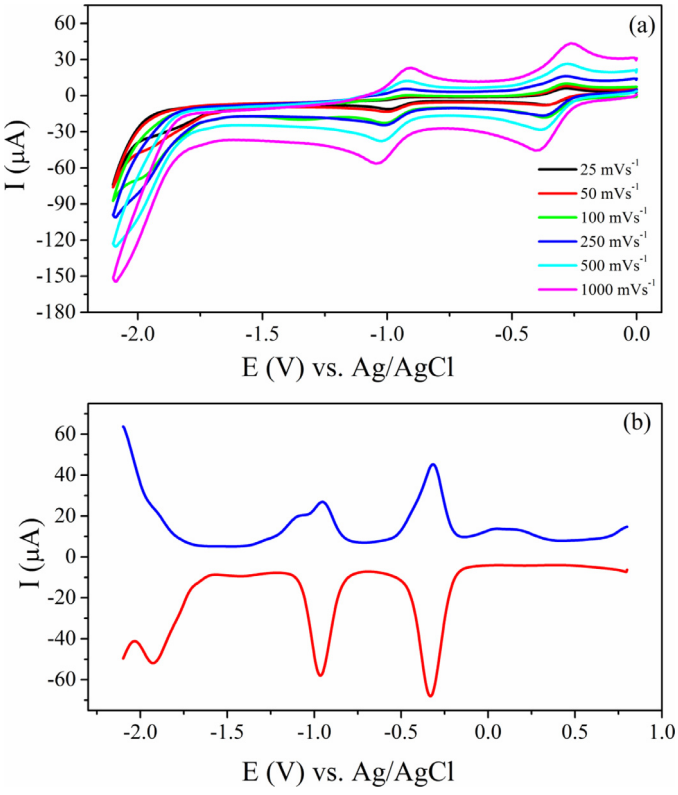



**Fig. 5.** CV responses of compound **15** at various scan rates on GCE in DMSO/TBAP.

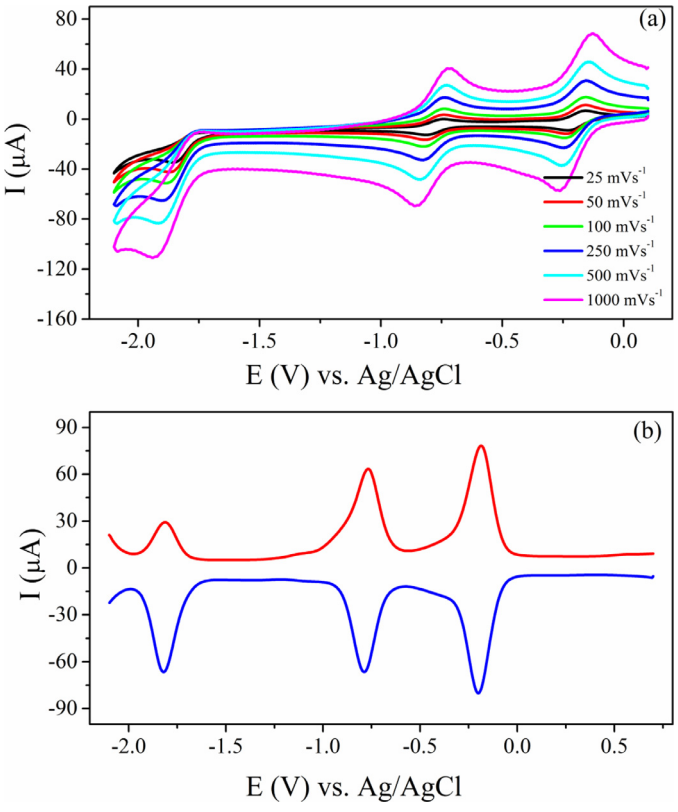



**Fig. 6.** CV responses of compound **17** at various scan rates on GCE in DMSO/TBAP.

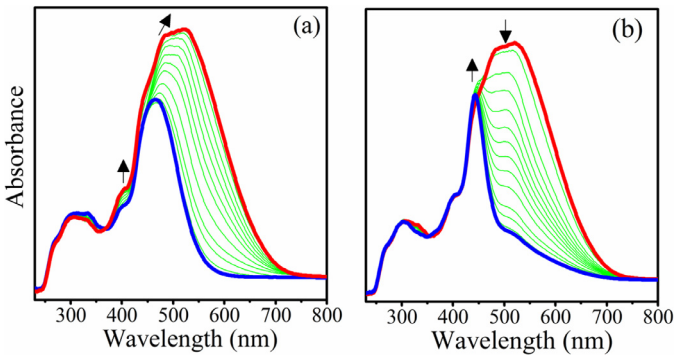



**Fig. 7.** UV-vis spectral changes of compound **4** recorded during *in-situ* spectroelectrochemical measurements at applied potentials of a) $E_{app}$= -0.75 V, and b) $E_{app}$= 1.25 V in DMSO/TBAP electrolyte system (changing of the spectrum during the redox reactions were represented with the arrow directions).

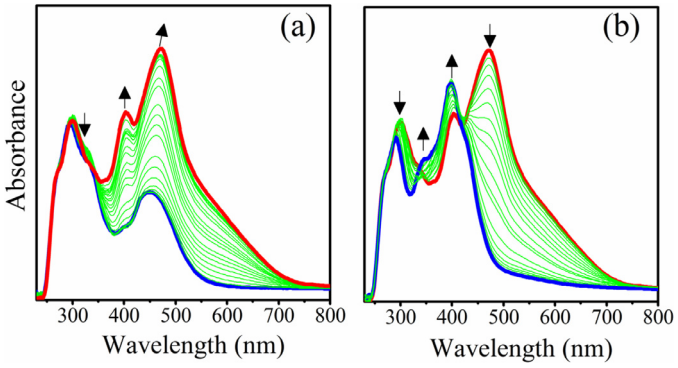



**Fig. 8.** UV-vis spectral changes of compound **15** recorded during *in-situ* spectroelectrochemical measurements at applied potentials of a) $E_{app}$= -0.75 V, and b) $E_{app}$= 1.25 V in DMSO/TBAP electrolyte system. (changing of the spectrum during the redox reactions were represented with the arrow directions).

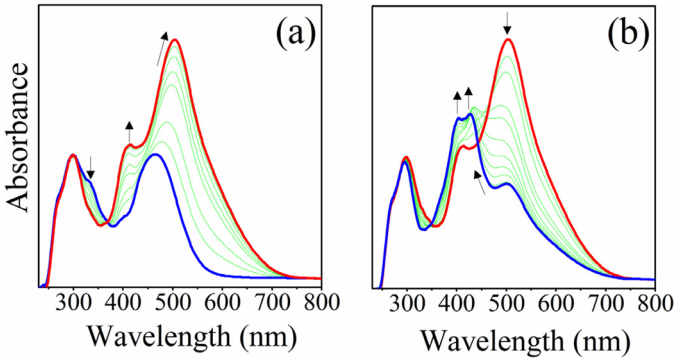



**Fig. 9.** UV-vis spectral changes of compound **12** recorded during *in-situ* spectroelectrochemical measurements at applied potentials of a) $E_{app}$= -0.75 V, and b) $E_{app}$= -1.25 V in DMSO/TBAP electrolyte system. (changing of the spectrum during the redox reactions were represented with the arrow directions).

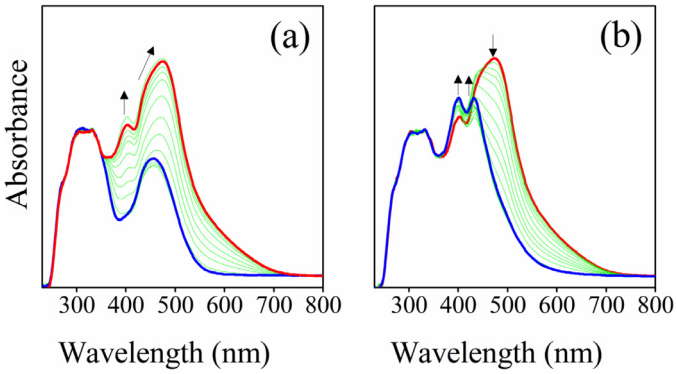



**Fig. 10.** UV-vis spectral changes of compound **9** recorded during *in-situ* spectroelectrochemical measurements at applied potentials of a) $E_{app}$= -0.75 V, and b) $E_{app}$= -1.25 V in DMSO/TBAP electrolyte system. (changing of the spectrum during the redox reactions were represented with the arrow directions).

marized in Table 2. The crystal structures were solved by SIR 92 [17] and refined with CRYSTALS [18]. 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 (Å), bond and torsion angels (°) for compounds **4** and **7** were listed in Table 3, respectively. The hydrogen bond parameters for compounds **4** and **7** were given in Table 4. Drawing was performed with the program ORTEP-III [19] with 50% probability displacement ellipsoid. ORTEP and unit cell packing diagrams for compounds **4** and **7** were given in Figs. 11–15. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers. CCDC-1041226, 1041225 for compounds **4** and **7**, respectively [20].

## 3. Result and discussion

### 3.1. Chemistry

The heteroatom substituted 1,4-naphthoquninone compounds **3, 4, 7, 8, 9, 10, 12, 13, 15, 16, 17, 19** and **20** were synthesized as outlined in Schemes 1 and 2. Detailed synthetic procedures (methods 1-3) for all compounds are described in the experimental section. All spectroscopic data ($^1$H NMR, $^{13}$C NMR, FTIR, MS) and results of micro analysis were given for unknown quinone derivatives **3, 8, 13, 15, 16, 17** and **20** in the experimental section. In addition to, some known 1,4-naphthoquinone compounds (**4, 7, 9, 10, 12, 19**) were yielded from these reactions. The synthesis and spectral

**Table 2**
The main crystallographic parameters of compounds **4** and **7.**

| | Compound 4 | Compound 7 |
|---|---|---|
| Empirical formula | $C_{24}H_{18}O_2S_2$ | $C_{14}H_{14}O_2S_2$ |
| Crystal colour, habit | Red, block | Black, prism |
| Crystal size (mm) | 0.30 × 0.20 × 0.10 | 0.60 × 0.30 × 0.10 |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | $P2_12_12_1$ | Cc |
| Cell dimensions | $a$ = 5.7143(2) Å | $a$ = 4.0389(3) Å |
| | $b$ = 16.5246(5) Å | $b$ = 19.2923(9) Å |
| | $c$ = 20.6520(6) Å | $c$ = 17.1209(9) Å |
| Cell volume (Å$^3$) | 1950.10(11) | 1325.2(1) |
| Cell Formula units (Z) | 4 | 4 |
| Density (g.cm$^{-3}$) | 1.371 | 1.395 |
| $\mu$ [cm$^{-1}$] | 0.290 | 0.392 |
| $F_{000}$ | 840.00 | 584.00 |
| h,k,l ranges | -6≤h≤6, -19≤k≤19 | -5≤h≤5, -26≤k≤26 |
| | -24≤l≤24 | -24≤l≤23 |
| Reflections collected | 75388 | 38346 |
| Indepenent reflections | 3455 [$R_{int}$ = 0.081] | 3945[$R_{int}$ = 0.027] |
| Data/restraints/parameters | 265/0 271 | 1979 /0/ 177 |
| Goodness of fit indicator | 1.101 | 1.041 |
| Final R indices [$I$>2$\sigma$(I)] | $R_1$ = 0.045 | $R_1$ = 0.075 |
| | $wR_2$ = 0.083 | $wR_2$ = 0.096 |
| Largest diff. peak and hole | 0.56 and −0.56 e.Å$^{-3}$ | 0.67 and −0.67e.Å$^{-3}$ |
| CCDC deposition number | 1041226 | 1041225 |

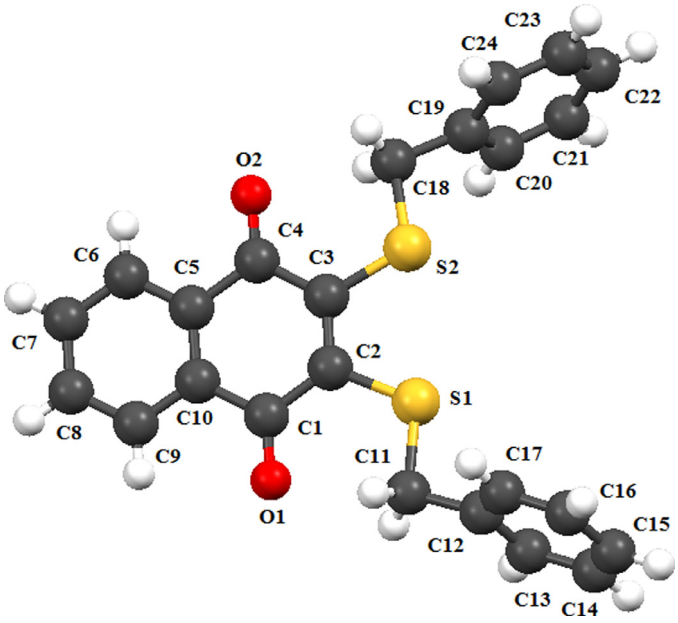



**Fig. 11.** The molecular structure of compound **4**. Displacement ellipsoids are plotted at the 50% probability level.

**Table 3**
Selected bond distances (Å), bond and torsion angels (°) for compounds **4** and **7.**

Bond distances (Å)

| 4 | | 7 | |
|---|---|---|---|
| C2-C3 | 1.365(9) | C1-C2 | 1.381(1) |
| C5-C10 | 1.379(9) | C8-C9 | 1.352(1) |
| C1-O1 | 1.215(9) | C7-O1 | 1.170(1) |
| C4-O2 | 1.222(9) | C10-O2 | 1.291(1) |
| C2-S1 | 1.759(5) | C8-S1 | 1.753(8) |
| C3-S2 | 1.757(5) | C9-S2 | 1.729(9) |
| S1-C11 | 1.833(7) | S1-C11 | 1.783(9) |
| S2-C18 | 1.828(6) | S2-C13 | 1.901(1) |

Bond angles (°)

| 4 | | 7 | |
|---|---|---|---|
| C1-C2-C3 | 121.6(5) | C8-C9-C10 | 120.6(7) |
| C3-C4-C5 | 117.2(6) | C1-C7-C8 | 116.7(8) |
| C2-C1-C10 | 117.1(6) | C2-C10-C9 | 119.4(6) |
| O1-C1-C2 | 121.9(5) | O1-C7-C8 | 124.8(9) |
| O2-C4-C3 | 122.6(5) | O2-C10-C9 | 117.4(7) |

Torsion angles (°)

| 4 | | 7 | |
|---|---|---|---|
| C1-C2-C3-C4 | 9.6(9) | C7-C8-C9-C10 | -13.0(1) |
| S1-C2-C3-S2 | 0.01(7) | S1-C8-C9-S2 | 1.0(1) |
| C2-S1-C11-C12 | -170.2(4) | C8-S1-C11-C12 | 164.2(5) |
| C3-S2-C18-C19 | -163.8(4) | C9-S2-C13-C14 | 156.0(1) |

**Table 4**
The hydrogen bond parameters for compounds **4** and **7**.

| **D**−**H**···**A** | **D**−**H** (Å) | **H**···**A** (Å) | **D**···**A** (Å) | < **D**−**H**···**A** (°) |
|---|---|---|---|---|
| **Compound 4** | | | | |
| C20-H14···C18 | 0.95(2) | 2.66(1)$^{i}$ | 3.61(1) | 139.97(1) |
| **Compound 7** | | | | |
| C11-H5···O2 | 0.95(1) | 2.69(1)$^{ii}$ | 3.64(1) | 161.30(1) |
| C14-H14···C6 | 0.95(2) | 2.89(2)$^{iii}$ | 3.84(1) | 147.60(2) |
| C4-H2···S2 | 0.95(1) | 2.99(2)$^{iv}$ | 3.94(1) | 128.98(1) |

(i) ½+$x$, 1.5−$y$, 2−$z$, (ii) -1+$x$, −$y$, −½+$z$, (iii) $x$, −$y$, ½+$z$, (iv) ½+$x$, −½+$y$, $z$

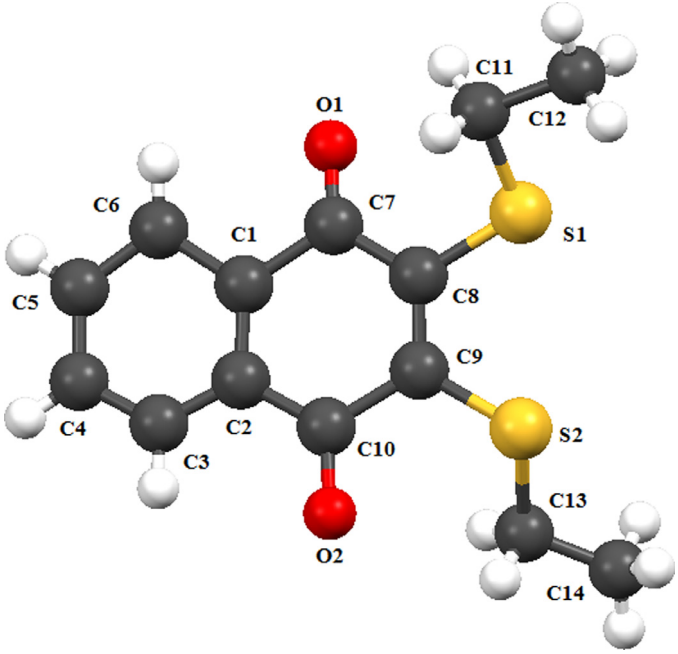



**Fig. 12.** The molecular structure of compound **7**. Displacement ellipsoids are plotted at the 50% probability level.

characterization of compounds **4, 7, 9, 10, 12** and **19** were previously reported in the related literature [16,21–23]. The both study of crystal structure determination of compounds **4, 7** and their electrochemical properties of compounds (**4, 7, 9, 10, 12, 19**) were firstly investigated in this study.

S, S- and S, O-substituted-1,4-naphthoquinones (**3, 4**) and (**12, 13**) were synthesized from reactions of 2,3-dichloro-1,4-naphthoquinone **1** with nucleopiles **2** or **11** according to general method 1 (Scheme 1). Compound 2,3-bis(benzylsulfanyl)-1,4-naphthoquinone **4** was crystallized from ethanol by slow evaporation as red block crystals. The solid-state molecular structure of 2,3-bis(benzylsulfanyl)-1,4-naphthoquinone **4** was determined by using X-ray single crystal diffractometer method. The

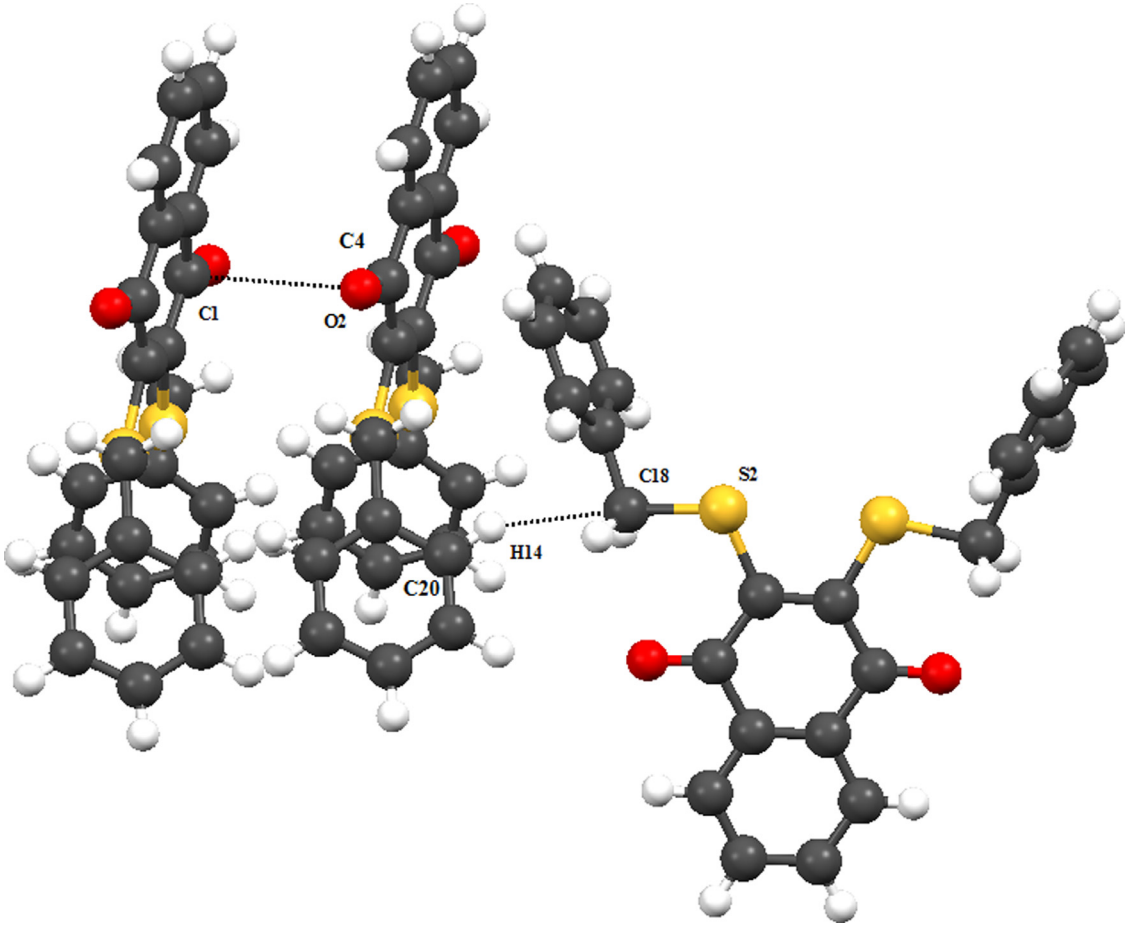



**Fig. 13.** The hydrogen and intermolecular bonds of compound **4**.

four compounds **7** [21], **8, 9** [16] and **10** [16] were synthesized from one reaction of **1** with nucleophile **6** according to general method 1 (Scheme 1). The black prisms single crystals of compound **7** were determined by using X-ray single crystal diffractometer method. New mono S-coumarinyl ring substituted 1,4-naphthoquinone compound **17** as a main target compound and known **10** [16] as a side product were synthesized in the presence of DMF and high temperature at 60°C according to general method 2 (Scheme 2).

In this study, we used the technique of one-pot multicomponent reactions to obtain the compounds **16** (in Scheme 1) and **20** (in Scheme 2) containing substantial elements of all the reactants. As shown in Schemes 1 and 2, starting compound **1** reacted in a single reaction vessel with an equimolar amount of two nucleophiles (**6, 14**) or (**6, 18**), respectively. These one-pot multicomponent reactions occurred according to methods 1 and 3. Multicomponent reactions are one-pot processes in which three or more reactants come together in a single reaction vessel to give a final product containing substantial elements for all the reactants. Moreover, compounds **9** [16] and **15** in Scheme 1 and compound **19** [23] in Scheme 2 were synthesized from these multicomponent reactions as side products. We have published previously some naphthoquinone derivatives which obtained by the one-pot multicomponent processes [24].

### 3.2. Electrochemical studies

In order to investigate the redox mechanism of some 1,4-naphthoquinone (NQ) derivatives (**3, 4, 7, 8, 9, 10, 12, 13, 15, 16, 17, 19, 20**), Voltammetric and *in-situ* UV-vis spectroelectrochemical characterizations were performed in aprotic dimethyl sulfoxide (DMSO) solvent. It is reported in the literature that, while the ideal redox response of NQ is two well-defined voltammetric peaks, substituent environment and electrolyte type may alter the redox mechanism of these species [25–29]. Therefore, more than two sets of reduction couples could be observed due to the formation of different dimeric species. It is very important to determine redox responses of newly synthesized NQ based functional materials in order to decide their possible usage in different electrochemical technologies. Especially determination of the dimerization mechanism and, if it is possible, preventing dimerization is the proposed route for these complexes. Therefore, here we reported electrochemical mechanism of synthesized NQ compounds (**3-4, 7-10, 12-13, 15-17, 19-20**). Redox parameters of all compounds derived from the analyses of the CV and SWVs of the compounds are listed in Table 1 for comparison. As shown in Table 1, the NQ compounds studied here can be classified in two categories with respect to their CV and SWV responses. The first category (**3-4, 7-8, 12-13, 15**) which have S,S- and S,O-substituents, shows ideal two sets of reduction couples. However, the second category (**9-10, 16-17, 19-20**) which bear morpholinyl and/or coumarinyl substituents, shows complication of two sets of reduction couples with the redox waves of dimeric species.

CV and SWV responses of compounds **4, 7** and **12** are represented in Figs. 1–3 as examples for the compounds having two sets of reduction couples. It is easily seen in these figures that while the compounds of the first category (**3-4, 7-8, 12-13, 15**) generally

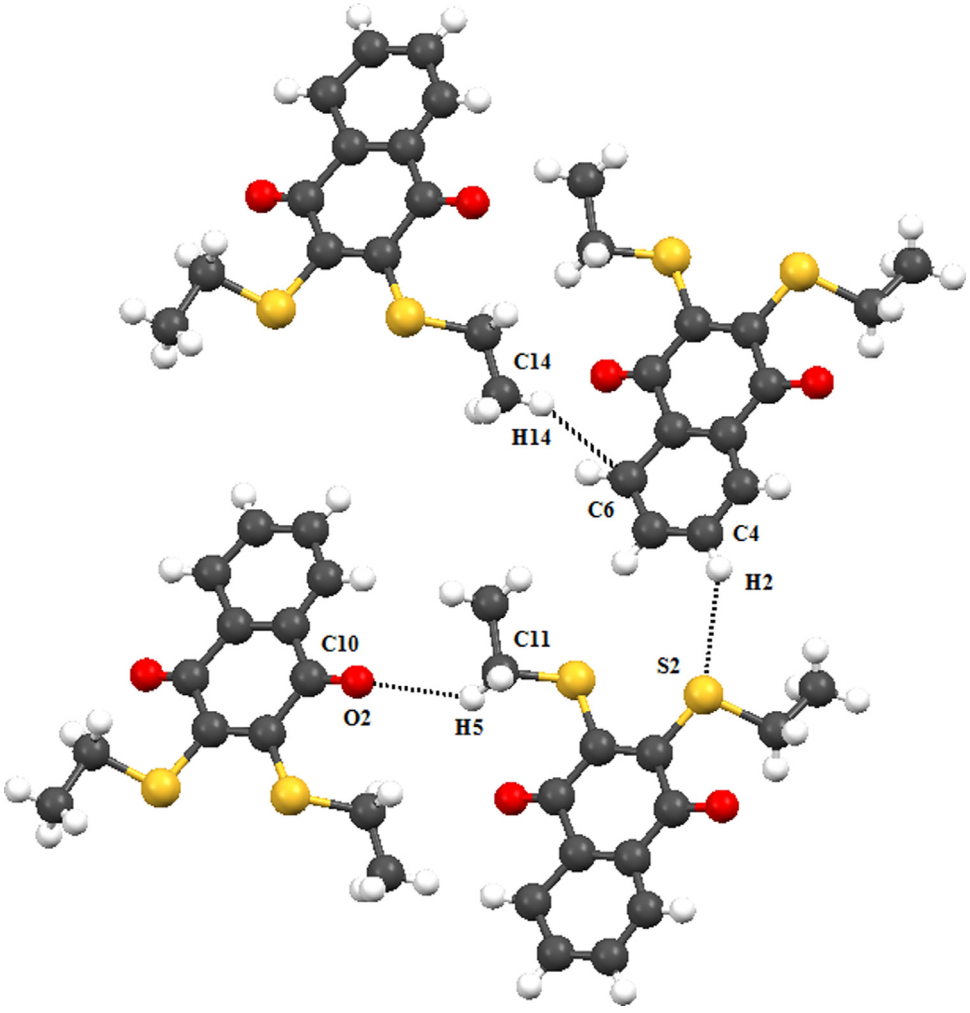



**Fig. 14.** The hydrogen and intermolecular bonds of compound **7**.

illustrate very similar reversible reduction couples, the substituent environment of these compounds only alters the reversibility and peak potentials of these redox processes. For instance, the compound **4** (2,3-bis(benzylsulfanyl)-1,4-naphthoquinone) gives two reduction couples at -0.43 V ($\Delta E_p$ = 67 mV and $I_{pa}/I_{pc}$ = 1.00) and -1.06 V ($\Delta E_p$ = 64 mV and $I_{pa}/I_{pc}$ = 0.97) respectively. These processes shift to -0.47 V ($\Delta E_p$ = 85 mV and $I_{pa}/I_{pc}$ = 0.98) and -1.16 V ($\Delta E_p$ = 70 mV and $I_{pa}/I_{pc}$ = 0.97) for the compound **12** (2,3-bis(isopropylsulfanyl)-1,4-naphthoquinone). Due to the presence of oxy or sulfonyl bridge between 1,4-naphthoquinone and the substituents, electronic structure of the substituents does not significantly alter the redox activity and mechanism of 1,4-naphthoquinone.

Figs. 4–6 show CV and SWV responses of compounds **9, 15** and **17** as examples for the second category (**9-10, 16-17, 19-20**) compounds. The main differences between the CV responses of these compounds from the compounds in the first category is the observation of a third reduction reaction at more negative potentials and decreasing the peak currents of the second reduction couple with respect to the peak current of the first reduction couple. These different electrochemical responses most probably resulted from the formation of dimeric $NQ_2^{\cdot -}$ radical and reduction of $NQ_2^{\cdot -}$ to $NQ_2^{2-}$ species. It is well documented that dimeric $NQ_2^{\cdot -}$ species reduce at more negative potential than that of monomeric $NQ^{\cdot -}$ radical species. Analysis of the CV and SWV responses of these compounds give the following proposed mechanism for these compounds:

$$NQ + e^- \leftrightarrow NQ^{\bullet -}$$

$$NQ^{\bullet -} + e^- \leftrightarrow NQ^{2-}$$

$$NQ + NQ^{\bullet -} \leftrightarrow NQ_2^{\bullet -}$$

$$NQ_2^{\bullet -} + e^- \leftrightarrow NQ_2^{2-}$$

Decreasing of the peak currents of the second reduction processes are due to the conversion of $NQ^{\cdot -}$ radical species to $NQ_2^{\cdot -}$ species and decreasing the concentration of $NQ^{\cdot -}$ radical species with this fast chemical reaction. When we compared the electrochemical responses of these compounds, we could conclude that electron transfer abilities of the NQ, and $NQ^{\cdot -}$ radical species could be easily modulated by the electron-withdrawing or -donating substituents of the electroactive NQ core. Therefore, the first reduction reactions of these compounds change from -0.20 V to -0.58 V by changing the substituents of the compounds. While the most easily reduced one is the compound **17** (*2-(7-Sulphanyl-4-methyl-coumarinyl)-3-chloro-1,4-naphthoquinone*), the most difficultly reduced one is the compound **19** (*2-Morpholinyl-3-chloro-1,4-naphthoquinone*). These data indicated that the electron releasing

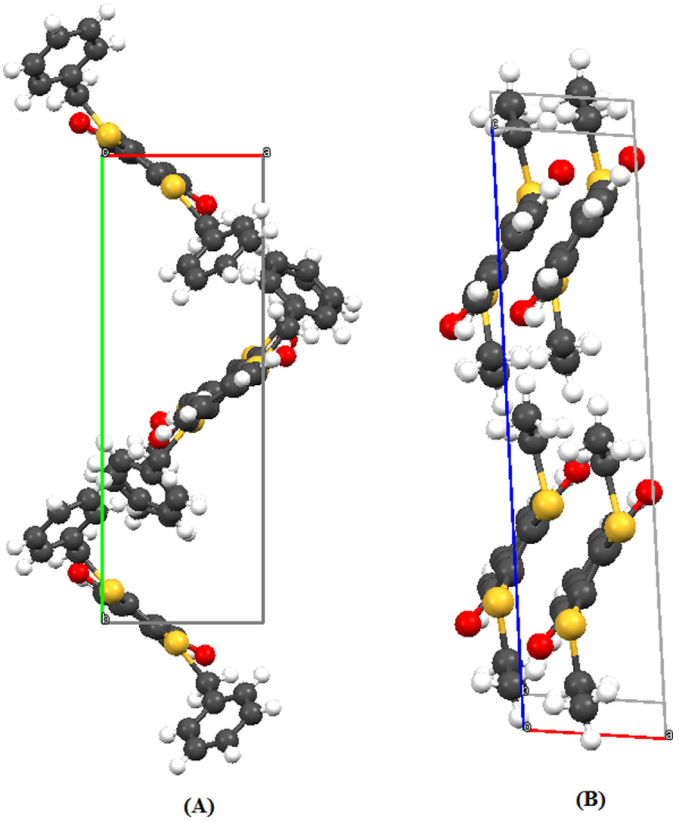



**Fig. 15.** Unit cell packing diagrams of the compounds **4** (A) and **7** (B).

groups cause to the shifting of the reduction processes towards more negative potentials. Morpholinyl group on compound 19 behave the most like electron releasing group and the substituents of the compound 17 behave the most like electron withdrawing group among the compounds studied here.

*In-situ* UV-Vis spectroelectrochemical studies were carried out to perform assignments of the redox reactions and to determine the spectra of the electrogenerated species of the compounds. Although *in-situ* FT-IR spectroelectrochemical studies of these type compounds were frequently reported in the literature, this is the first study for the *in-situ* UV-Vis spectroelectrochemical studies of NQ compounds in the literature [30–32]. There is only one paper in the literature, which reports the spectra of the neutral, monoanionic and dianionic NQ species [33]. However, we represented spectral changes recorded during the reduction reactions in order to clarify the redox reactions and demonstrate optical responses of the redox species of NQ compounds. The initial spectra of all compounds are similar to each other, spectral changes during the reduction reactions of the first and second categories. Figs. 7 and 8 show *in-situ* UV-Vis spectral changes during the reduction reactions of compounds **4** and **15** as examples of the first category compounds. For example, for the compound **4** under open circuit potential, the compound gives a band at 466 nm due to the $\pi$ to $\pi^*$ electronic transition (Fig. 7). During the first reduction reaction, the bands at 466 nm increase in absorption with shifting to the longer wavelengths (521 nm). During the second reduction reaction, while the band at 521 nm decreases in intensity, a new band is observed at 443 nm. Observation of the well resolved isosbestic points (at 368 nm during the first reduction and at 358 nm during the second reduction reaction) illustrate formation of one type reduced species during these processes. These spectral changes support the electrochemical responses of the first category compounds, which illustrate only the ideal two sets of reduction reaction to monoanionic radical $NQ^{\cdot-}$ and dianionic $NQ^{2-}$.

The general trend of the spectral changes of the second category compounds are similar to those of the first category compounds. However, during the second reduction reaction, a split new band is observed as shown in Figs. 9 and 10. For example, the compound **12** shows new bands at 403 and 430 nm after the second reduction reaction as shown in Fig. 9. The band at 403 nm may be assigned to the dimeric $NQ_2^{\cdot-}$ and the band at 430 nm could be assigned to dianionic $NQ^{-2}$ species. The compound **9** gives very similar spectral changes for the formation of dimeric $NQ_2^{\cdot-}$ and monoanionic $NQ^{\cdot-}$ radicals (Fig. 10). The bands at 400 and 432 nm observed after the second reduction reaction characterize the formation of dimeric $NQ_2^{\cdot-}$ and dianionic $NQ^{-2}$ species for the compound **9**. Moreover, isosbestic points recorded during the second reduction reaction oscillate continuously. These spectral changes illustrate presence of two different redox species in the media. These species may be dimeric $NQ_2^{\cdot-}$ and dianionic $NQ^{2-}$. These spectral changes support the electrochemical responses of the second category compounds, which give redox responses of dimeric in addition to the monomeric NQ species.

### 3.3. X-ray study

The compounds 2,3-bis(benzylsulfanyl)-1,4-naphthoquinone **4** and 2,3-bis(ethylsulfanyl)-1,4-naphthoquinone **7** crystallized in the orthorhombic and monoclinic, space groups $P2_12_12_1$ and Cc with $Z = 4$ from ethanol as red block and black prisms, respectively. Displacement ellipsoids are plotted at the 50% probability level in Figs. 11 and 12. The crystal data and refinement parameters for compounds **4** and **7** were summarized in Table 2. The selected bond distances (Å), bond and torsion angels (°) for compounds **4** and **7** were listed in Table 3.

The double bonds length of the quinone moiety agreed well with corresponding distance in a similar compound [16,24]. The bond lengths of C1-O1/C4-O2 of compound **4** and C10-O2/C7-O1 of compound **7** were 1.215(9)/1.222(9) and 1.290(1)/1.170(1) Å, respectively, typical of C=O bonds. C-C-C and C-C-O angles were very close to 120°, as expected for $sp^2$ hybridized atoms in the compounds **4** and **7**. In the compound **7**, the both rings of naphthoquinone unit were planar with a maximum deviations of 0.0115(1) Å (plane 1 = C1-C2-C3-C4-C5-C6) and 0.0340(1) Å (plane 2 = C1-C7-C8-C9-C10-C2). Dihedral angle was 2.342(1)° between planes 1 and 2. In solid state the ethylsulphanyl group of the molecule is non planar with respect to the quinone ring. Unit cell packing diagrams for compounds **4** and **7** were drawn in Figs. 14 and 15. The whole packing diagrams exhibited a zigzag-shaped intermolecular chain along the b axis in the unit cells. The hydrogen bond distances and angles of compounds **4** and **7** were given in Table 4. Another intermolecular bond for compound **4** between C1-O2 had the following parameters; C4-O2···C1$^{(i)}$: 3.19(1)Å, 104.63(1)°, (i) $-1+x$, $y$, $z$, (Fig. 13).

## 4. Conclusion

The heteroatom substituted-1,4-naphthoquinone derivatives (**3, 4, 7, 8, 9, 10, 12, 13, 15, 16, 17, 19** and **20**) were synthesized acourding to method 1-3 and their structures were characterized by using micro analysis, UV-Vis, $^1$H-, $^{13}$C NMR and MS in this study. The six known 1,4-naphthoquinone compounds (**4, 7, 9, 10, 12, 19**) were yielded from these reactions. The synthesis method and spectral characterizations of these known quinone compounds **4, 7, 9, 10, 12** and **19** were previously reported in the related literature [16,21–23]. Altough these compounds (**4, 7, 9, 10, 12, 19**) were not new, the study of crystal structure determination of compounds **4, 7** and their electrochemical properties of compounds

were firstly investigated in this study. Crystal structures of 2,3-bis(benzylsulfanyl)-1,4-napthoquinone **4** and 2,3-bis(ethylsulfanyl)-1,4-naphthoquinone **7** were determined by using X-ray single crystal diffraction method.

Electrochemical behaviors of some 1,4-naphthoquinone (NQ) derivatives (**3, 4, 7, 8, 9, 10, 12, 13, 15, 16, 17, 19** and **20)** were studied using cyclic voltammetry, square wave voltammetry and *in-situ* UV-Vis spectroelectrochemistry. The different substituted groups of the NQ derivatives significantly alters the redox mechanism. The redox behavior of the 1,4-naphthoquinone (NQ) derivatives is strongly influenced by the chemical propertied of the ring substituents. When the NQ bearing morpholinyl and/or coumarinyl moieties shows redox processes for the dimeric NQ species in addition to the monomeric NQs, NQs carrying S,S- and S,O-substituents (**3, 4, 7, 8, 12, 13, 15**) showed ideal two sets of reduction couples. Morpholinyl and/or coumarinyl moieties also alters the redox potentials significantly. *In-situ* UV-Vis spectroelectrochemical analyses of NQs supported the proposed redox mechanism.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

**Nahide Gulsah Deniz:** Supervision, Visualization, Writing - review & editing. **Cigdem Sayil:** Methodology, Writing - original draft. **Duygu Akyüz:** Formal analysis. **Atif Koca:** Investigation, Methodology, Formal analysis.

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## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2020.129145.

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