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Structural characterization and electrochemical properties of the 3,3′-5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone

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Abstract

Crystals of the 3,3′-5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (TTBDQ) in the reaction mixture DCM/MeOH (1:1, v/v) were obtained as a result of C–C coupling reaction of the sterically hindered phenol (2,6-di-*tert*-butylphenol, DTBP) using the binuclear Co(II) complexes. The oxidation product (TTBDQ), $C_{28}H_{40}O_2$, crystallizes in the space group $P\bar{1}$ with one-half molecule in the asymmetric unit and the other half generated by an inversion centre. The diphenoquinone moiety is planar within ±0.016(3) Å. The crystal structure is stabilized by intramolecular C–H···O hydrogen bonds. The spectroscopic and electrochemical properties of the TTBDQ also have been studied.

Keywords: Oxidation product; X-ray; Electrochemical

1. Introduction

The oxidation of organic substrates with molecular oxygen under mild conditions is of great interest for industrial and synthetic processes from an economical and environmental point of view [1]. Although the reaction of organic substances with dioxygen is thermodynamically favored, it is kinetically hindered due to the triplet ground state of O_2. In biological systems, this problem is overcome by the use of copper or iron containing metalloproteins which serve as highly efficient oxidation catalysts [2]. The propensity of cobalt complexes to bind with molecular oxygen [3,4] and the use of such dioxygen–cobalt complexes as catalysts in various oxidation reactions have been a subject of intensive research in the recent years [5,6]. The dioxygen–cobalt complexes formed from cobalt complexes in presence of oxygen are known to catalyze a variety of organic reactions like oxidation of thiols [7], phenols [8,9], aldehydes [10,11] and hydrocarbons [12] involving hydrogen abstraction or one electron transfer.

The C–C coupling reaction of the 2,6-di-*tert*-butylphenol has been performed using the Co(II) complexes [13]. The oxidation product (TTBDQ) has been characterized by single-crystal X-ray and spectroscopic tecniques. The electrochemical property of TTBDQ was investigated at different scan rates.

2. Experimental

2.1. Materials and physical measurements

2,6-Di-*tert*-butylphenol was purchased from Fluka and used without any purification. All solvents were pure and obtained from Merck. Elemental analyses (C, H and N) were performed using a LECO CHNS 932 elemental analyser. IR spectra were obtained using KBr discs (4000–400 cm^{-1}) on a Shimadzu 8300 FT-IR spectrophotometer. The electronic spectra in the 200–1100 nm range were obtained on a Shimadzu UV-160 A spectrophotometer. ^1H NMR spectra were recorded on a Varian XL-300 instrument. TMS was used as internal standard and deuteriated CD_3OD as solvent. Catalysis experiments were monitored on a Shimadzu 160-A UV–vis spectrophotometer. The compound 2,6-di-*tert*-butylphenol (DTBP) was oxidized by aerial oxygen quantitatively to the TTBDQ by using the cobalt(II) complex as a catalyst. The changes in the concentration of the TTBDQ were monitored by optical spectroscopy.

Electrochemical studies were carried out with an Iviumstat Electrochemical workstation equipped with a low current mod-

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ule (BAS PA-1) at a platinum disk electrode and a platinum microelectrode of 10 μm diameter (BAS). Cyclic voltammetric measurements were made at room temperature in an undivided cell (BAS model C-3 cell stand) with a platinum counter electrode (BAS). All potentials are reported with respect to Ag/AgCl. The solutions were deoxygenated by passing dry nitrogen through the solution for 30 min prior to the experiments, and during the experiments the flow was maintained over the solution. The ferrocene/ferrocinium (Fc/Fc) redox couple was used as internal standard: under the experimental conditions used, $E_{1/2}$ for the Fc/Fc$^+$ couple was 0.48 and 0.45 V in DMF and $(CH_3)_2SO$, respectively. Prior to use, the Pt working electrode was polished with an aqueous suspension of 0.05-mm alumina (Buehler) on a Master-Tex (Buehler) polishing pad, then rinsed with water and acetone and dried in an oven. Digital simulations were performed using DigiSim 3.0 for windows (BAS Inc.). Experimental cyclic voltammograms used for the fitting process had the background subtracted and were corrected electronically for ohmic drop.

2.2. *Catalytic oxidation of 2,6-di-tert-butylphenol*

In a dichloromethane/methanol solvent mixture (1:1, 50 cm^3), the cobalt(II) complexes were dissolved. To it 2,6-di-*tert*-butylphenol was added and the solution was stirred for 48 h. The solution was then filtered and the filtrate was evaporated to dryness. Five cubic centimetres of methanol was added to dissolve the excess 2,6-di-*tert*-butylphenol. For measuring the progress of the reaction, 50 μL from the aliquot was passed through an Amberlyst cationic ion-exchanger and washed with 10 cm^3 (2 × 5) dichloromethane. The changes in the concentrations of the oxidation product TTBDQ were monitored by optical spectroscopy.

Electrochemical data for TTBDQ. Scan rate at 50 mV s^{-1}: −0.72, 0.27 (E_{pc}, V), scan rate at 100 mV s^{-1}: −0.15, 0.42 (E_{pc}, V), scan rate at 500 mV s^{-1}: −0.57, 0.48 (E_{pc}, V). Scan rate at 50 mV s^{-1}: 0.29, 0.20 (E_{pa}, V), scan rate at 100 mV s^{-1}: −0.19, 0.44 (E_{pa}, V), scan rate at 500 mV s^{-1}: −0.38, 0.20 (E_{pa}, V).

2.3. *Structure determination*

A needle pale yellow crystal with dimensions 0.2 mm × 0.2 mm × 0.2 mm was chosen for the structure determination. Diffraction experiment was carried out on a four-circle Rigaku R-AXIS RAPID-S diffractometer equipped with a two-dimensional area IP detector. The graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) and oscillation scans technique with $\Delta\omega = 5°$ for one image were used for data collection. Images for oxidation compound TTBDQ was taken successfully by varying ω with three sets of different χ and φ values. For each compounds the 108 images for six different runs covering about 99.7% of the Ewald spheres were performed. The lattice parameters were determined by the least-squares methods on the basis of all reflections with $F^2 > 2\sigma(F^2)$. Integration of the intensities, correction for Lorentz and polarization effects and cell refinement was performed using Crystal Clear software [14]. The structure was solved by SHELXS-97 [15] and refined by SHELXL-97 [16] software package. All H atoms were located in geometrically idealized positions, with C–H distance of 0.93 Å (aromatic H atoms), and 0.96 Å (methyl H atoms). The U_{iso}(H) values were set equal to 1.2–1.5 U_{eq}(C) for aromatic CH and methyl groups, respectively. The final cycle of the refinement included 142 variable parameters $R_1 = 0.0777$, $\omega R_2 = 0.1485$ where $\omega = 1/[\sigma^2(F_0^2) + (0.0409P)^2]$ were obtained. The details of the X-ray data collection, structure solution and refinement details were given in Table 1. Further experimental details have been deposited as supplemantary material at the Cambridge Crystallographic Data Centre CCDC 631500. Atomic scattering factors were taken from International Tables for X-ray crystallography [17].

Table 1
Crystal data and structure refinement for the title compound

Empirical formula	$C_{28}H_{40}O_2$
Formula weight	408.60
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Cell dimensions	$a = 6.096(4)$ Å; $b = 10.431(8)$ Å; $c = 10.535(5)$ Å; $\alpha = 81.410(2)°$; $\beta = 75.950(2)°$; $\gamma = 81.490(2)°$
Cell volume	638.2(7) Å^3
Z	1
Density (calculated)	1.1063 mg/m^3
Absorption coefficient	0.228 mm^{-1}
F_{000}	224
Crystal size	0.2 mm × 0.2 mm × 0.2 mm
θ (°) range for data collection	3.47–30.86
Index ranges	$-8 \le h \le 8$; $-15 \le k \le 14$; $-15 \le l \le 15$
Reflections collected/unique	16490/3571 [R(int) = 0.2136]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3571/0/142
Goodness-of-fit on F^2	0.932
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0777$, $\omega R_2 = 0.1485$
Largest diff. peak and hole	0.114 and −0.101 e Å^{-3}

3. Results and discussion

In this study, we used the binuclear cobalt(II) complexes as a catalyst for the C–C coupling reaction of the DTBP [13].

The ^{1}H(^{13}C) NMR spectra of the TTBDQ were recorded using CD_3OD as a solvent. In the ^{1}H NMR spectrum of the TTBDQ, the sharp singlets in the range 1.49–1.62 ppm can be attributed to the protons of the *t*-butyl groups. The aromatic ring protons are equivalent and seen in the 6.18–6.95 ppm range. In the ^{13}C NMR spectrum, the signal at 195.89 ppm may be due to the carbon atom of the C=O group on the aromatic ring. The aromatic ring carbon atoms are seen in the range 114.67–156.43 ppm. The methyl carbon atoms of the *t*-butyl groups were seen in the range 31.85–32.10 ppm. In the infrared spectrum of the TTBDQ, the vibration at 1685 cm^{-1} can be attributed to the ν(C=O). The aliphatic ν(C–H) stretchings of the *t*-butyl groups were seen at 1945 cm^{-1} as a sharp peak.

Benzoquinone, diphenoquinones and their derivatives are important intermediates for industrial synthesis of a wide vari-

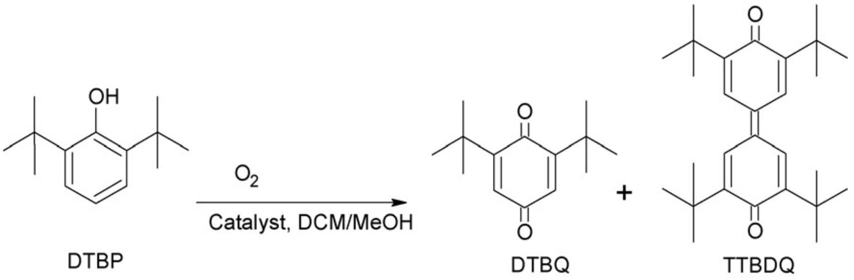

Fig. 1. C–C coupling reaction of the DTBP by the metal catalyzed.

ety of special chemicals, such as pharmaceuticals, dyes and agricultural chemicals. Development of processes that utilize heterogeneous catalysis in environmentally beneficial media is of fundamental and practical importance. The oxidation reactions of DTBP to the DTBQ and TTBDQ have been investigated to evaluate the factors necessary to achieve high product conversion and selectivity in various media (Fig. 1). The oxidative coupling reactions of the DTBP with molecular oxygen were performed by using a series of the binuclear cobalt(II) chelate complexes as a catalyst. The oxidation product of the DTBP has been investigated at λ 425 nm using the UV–vis. As the reaction times proceed, the concentration of the fenol compound decreases and at the end of the reaction finishes. This situation shows that the oxidation reaction occurs. Under the applied reaction conditions, the reaction product of the DTBP was only TTBDQ (C–C coupling product).

The title compound, $C_{28}H_{40}O_2$, has been originally described in 1986 [18], and 4 years later this structure has also been solved by X-ray diffraction [19]. Both two structural determinations on crystal data and refinement results confirm good agreements. Eventhough some structural refinement results of our determination are not better than the previous records, our findings indicate that the redetermination of X-ray crystal structure of the compound is necessary to gain additional information on the molecular conformation, packing of the molecules and the hydrogen bonding in the structure. A number of intramolecular hydrogen bonds were identified and listed in this study, which were not mentioned in the earlier studies. Therefore we report here a redetermination of X-ray crystal structure of (I) from crystals were grown by C–C coupling oxidation reactions of the sterically hindered phenol in the DCM/MeOH solvent mixture.

The ORTEP [20,21] diagram of the molecule indicating atom numbering scheme with thermal ellipsoids at 30% probability is illustrated in Fig. 2. The space group and unit cell dimensions in (I) show that there are no significant differences between present structure and previously reported structures [18,19], except for the unit cell volume increased by 2 Å^3. The molecule of the title compound consists of a diphenoquinone and four *tert*-butyl groups. The asymmetric unit of (I) contains one-half molecule with other half generated by a centre

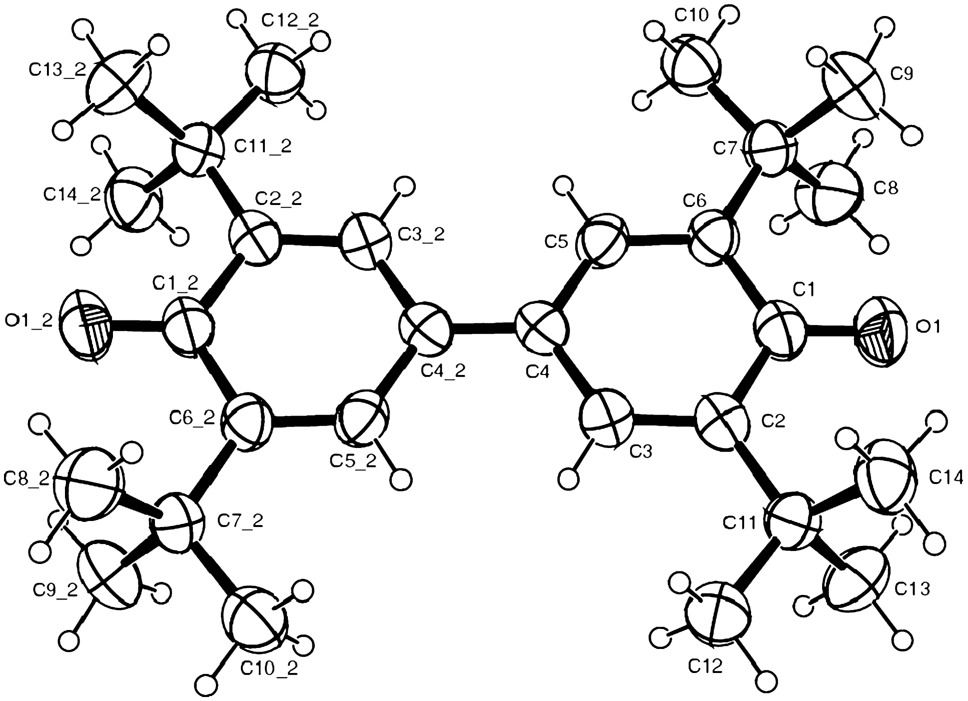

Fig. 2. Molecular structure of the oxidation compound TTBDQ with atom numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

Table 2
Selected bond lengths (Å), bond angles (°) and torsion angels (Å)

C1–O1	1.222(3)	C2–C11	1.5222(4)
C14–C11	1.555(4)	C1–C6	1.497(4)
C7–C9	1.555(4)	C6–C7	1.515(4)
C2–C3	1.353(4)	C4–C4_2^{I}	1.395(5)
C1–C2–C3	118(4)	C1–C6–C7	119.1(3)
C3–C2–C11	122.4(3)	C5–C4–C4_2^{I}	121.7(3)
C1–C2–C11	119.1(3)	C3–C4–C4_2^{I}	121.8(3)
C4–C5–C6	124.4(3)	C5–C4–C3	116.5(3)
C2–C11–C12	112.5(3)	O1–C1–C2	121.1(3)
C5–C6–C1	117.7(3)	C5–C6–C7	123.0(3)
C3–C2–C11–C12	−1.4(4)	C11–C2–C1–O1	1.8(4)
C6–C5–C4–C4_2^{I}	−177.0(3)	C7–C6–C1–O1	−1.9(4)
C3–C2–C1–C6	3.2(4)	C2–C3–C4–C4_2^{I}	178.6(3)
C11–C2–C1–C6	−177.6(2)	C1–C2–C3–C4	−2.9(4)
C3–C2–C1–O1	−177.4(3)	C5–C6–C1–C2	−1.8(4)

Note. Symmetry transformations used to generate equivalent atoms (symmetry code: $-x+1$, $-y+2$, $-z+2$).

of inversion; the centre of inversion lies at the midpoint of the C4–C4_2 bond [symmetry code: $-x+1$, $-y+2$, $-z+2$]. The bond distance C4–C4_2 of 1.395(4) Å confirms its double-bond character which is comparable with the earlier report as 1.402(4) Å [18]. In the diphenoquinone system, there is an electron delocalization causing bond lengths shortening; C4–C5 and C4–C3 [1.437(4), 1.439(4) Å] bond lengths are relatively shorter than the C1–C2 and C1–C6 [1.485(4),1.497(4) Å] bond lengths. The same feature of the crystal structure was seen and discussed in detail in earlier report [18]. The diphenoquinone system adopts almost planar conformation within ±0.016(3) Å while the *tert*-butyl groups deviate from the planarity. The deviations of the C9, C13, C8 and C14 atoms from the plane of the compound moiety are 1.271(3), −1.276(3), 1.247(3) and 1.231(4) Å, respectively. The dihedral angle between the diphenoquinone and whole compound system is 1.55(5)°. The C–O bond can have a double-bond character [1.222(3) Å] which is comparable with the value of 1.228(2) Å [18] and all C–C bond lengths of the *tert*-butyl groups show single bond character (Table 2).

In the diphenoquinone system, the C3–C4–C5 angle is narrowed to 116.5(3)°, and C4–C5–C6 and C2–C3–C4 angles are widened to 124.4(4) and 124.1(3)° from the normal value of 120°. These angles were reported, respectively, as 116.0(2), 124.2(2) and 124.2(2)° [18]. The largest torsion angles causing slight distortion of the crystal structure are the C3–C2–C1–C6, C6–C5–C4–C4_2 and C1–C2–C3–C4 of 3.2(4), −177.0(3) and −2.9(4) Å, respectively. The rest of the bond lengths and angles have the normal values and well agreement with the earlier study [18]. Selected bond lengths, bond angles and torsion angles are listed in Table 2.

Although the original reports on compound (I) [18,19] gave no intramolecular hydrogen-bonding interactions which support to stabilize the molecular structure, our findings by PARST [22] and PLATON [23] analysis of (I) identified four strong short intramolecular C–H···O contacts, which can be recognized as hydrogen bonds. All O atoms participate in intramolecular short contacts and these interactions in molecular packing were shown in Fig. 3. Besides one weak intermolecular short C–H···O contact was found [$C9\cdots O1^{*} = 3.435$ Å; (*; $-x$, $-y+1$, $-z+2$)] which is comparable with the shortest contact found [C···O = 3.413 Å] in earlier report. The hydrogen bonding geometry is listed in Table 3.

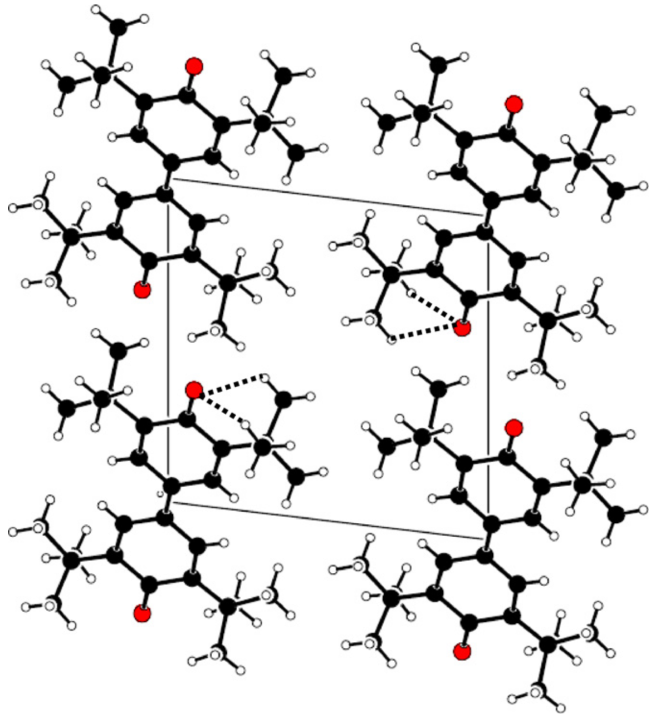

Fig. 3. The crystal packing arrangement for (I). Dashed lines indicate the intramolecular hydrogen bonds.

The electrochemical properties of the oxidation product TTBDQ at 50, 100 and 500 mV s^{-1} scan rates over a potential range from −2.0 to +2.0 V were studied by using DMF as solvent and tetrabutylammonium tetrafluoroborat ($[CH_3(CH_2)_3]_4NBF_4$, 0.1 M) as supporting electrolyte (in nitrogen atmosphere). A typical voltammogram of the oxidation product is shown in Fig. 4. As this compound is diquinone, there are oxidation and reduction processes. Two reversible processes can be observed in the voltammograms. One of them is an oxidative process that appears between 0.20 and −0.38 V which we assign to the oxidation of the 3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-4,4′-diol (TTBDPOH) to the TTBDQ. The second process is a reductive one, assigned to the reduction of the TTBDQ to the TTBDPOH and it is observed at −0.72 and 0.48 V potentials (Fig. 5 a and b).

Table 3
Hydrogen bonding geometry (Å, °)

D–H···A	D–H	H···A	D···A	D–H···A
C8–H8A···O1	0.96	2.350	2.98(5)	124
C9–H9A···O1	0.96	2.390	3.001(4)	121
C13–H13C···O1	0.96	2.360	2.98(5)	124
C14–H14A···O1	0.96	2.360	2.99(5)	123

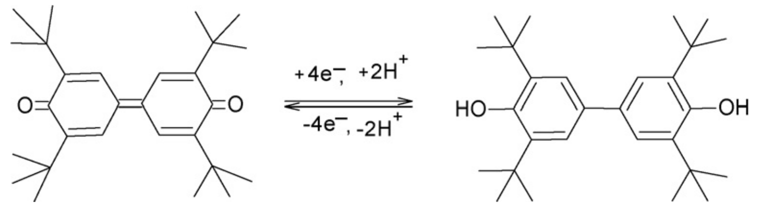

Fig. 4. The reduction process of the 3,3′-5,5′-tetra-*tert*-butyl-4,4′-di-phenoquinone (TTBD) to the 3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-4,4′-diol in DMF solution in the presence of tetrabutylammonium hexafluoroborate (0.1 M).

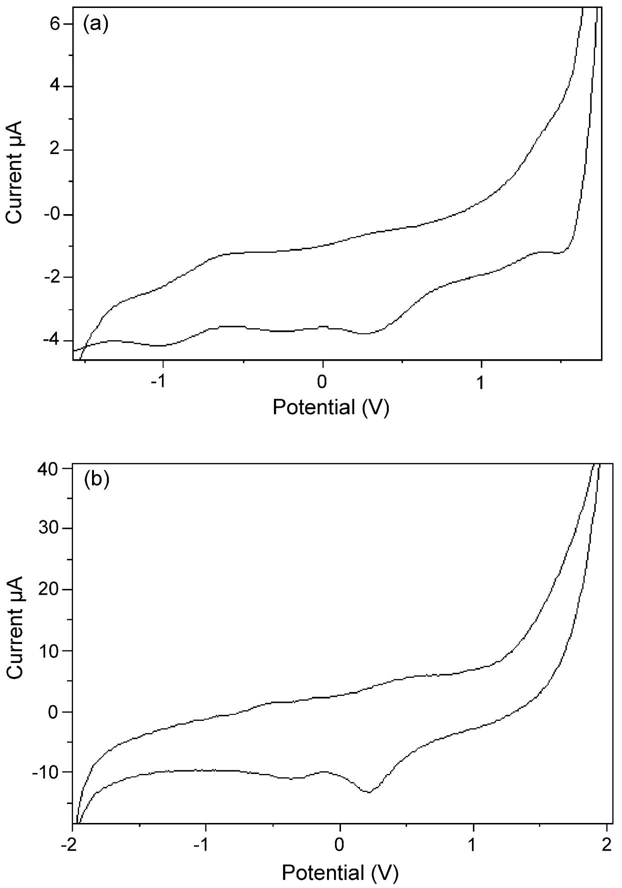

Fig. 5. Cyclic voltammetry of the 3,3′-5,5′-tetra-*tert*-butyl-4,4′-di-phenoquinone (TTBDQ) in DMF in the presence of tetrabutylammonium tetrafluoroborate (0.1 M). (a) Scan rate: 50 mV s^{-1}; (b) scan rate: 500 mV s^{-1}.

4. Conclusion

Sterically hindered quinone compound (TTBDQ) as a single crystal from the oxidation reaction were obtained. The compound was characterized by the spectroscopic methods. The electrochemical properties of the compound were studied at different scan rates. The current is directly proportional to the rate of electrolysis at the electrode surface. Electrolysis occurs at the electrode surface in response to a change in potential in order to try and maintain the surface concentrations of the oxidized and reduced species at the values required by the Nernst equation. Therefore, for example, increasing the scan rate can decrease the effect of a coupled chemical reaction, since the reaction has less time to occur. Reversibility can also vary with temperature.

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