

# Conversion of 1,4-naphthalenediol to 1,4-naphthoquinone by 1,4-benzoquinone

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## Abstract

1,4-Naphthalenediol gets converted to 1,4-naphthoquinone on reaction with 1,4-benzoquinone. In the reaction, 1,4-benzenediol is formed. The reaction passes through charge delocalisation in the equivalent *keto* and *enol* forms. The spectroscopic and electrochemical studies discern the role of equivalent charge transfer complex derived from 1,4-naphthoquinone with 1,4-benzenediol (**A**). The conversion of 1,4-naphthalenediol to 1,4-naphthoquinone in the presence of oxidants such as hydrogen peroxide and *t*-butylhydroperoxide are catalysed by 1,4-benzoquinone © 2002 Elsevier Science B.V. All rights reserved.

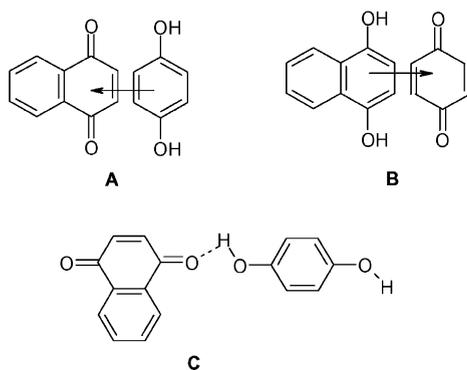
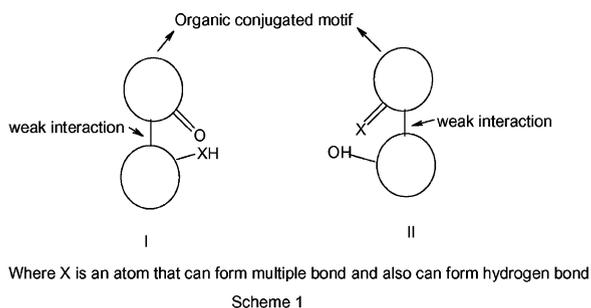
**Keywords:** Supramolecular isomerisation; Quinhydrone electrode system; Charge transfer complex

## 1. Introduction

The charge transfer complexes are important from their structural and material properties point of view [1,2]. Such complexes having mixed stacks of donor–acceptor molecules have interesting magnetic and electrical properties [3]. However, there is practically no attention put on comparative study of the properties of charge transfer complexes derived from isomeric pairs of donor and acceptor [4–7]. The understanding of the space isomers of charge transfer complexes would add more dimensions to the space interaction in supramolecular isomerisation [8–10]. If the donor and acceptor have provision of hydrogen bonding and also have the possibility to be in different equivalent structures on interchange of conjugation between the donor and acceptor (Scheme 1), they may have equivalent structures. These molecules could also probably help in designing equivalent

structures formed via proton transfer through space and also from exchange between two organic motifs shown in Scheme 1. One simple system for such study is the pairs derived from 1,4-naphthoquinone (NQ) with 1,4-benzenediol (BD) and 1,4-naphthalenediol (ND) with 1,4-benzoquinone (BQ). They should have structures **A** and **B**, respectively. While studying for such reactions it has been possible to prepare only **A**, the attempt to prepare **B** from ND and BQ yielded NQ and BD. The above system has direct relevance to the quinhydrone electrode that has been long used as redox electrode. As a secondary electrode system, quinhydrone has been of great importance and have found great utility in physical chemistry [11]. Interesting surface properties can be understood from the quinhydrone electrode system [12,13]. The electrode system has also been of great value in nanochemistry as well [14]. In addition to all these, the electrochemistry of quinone systems has been of great importance as they have interesting redox sequences when arranged in orderly manner. For example, a cyclic arrangement having multiple quinone units in

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a calix arene has generated profound interest due to the multiple stepwise electron transfer processes [15]. The quinonic units, separated by methylene linker attached at *ortho*-position of the ring, have been used to understand the electron transfer process [15]. The bis-quinone systems are also studied so as to separate the quinonic units in such a way to obtain the effect of the linker on the quinonic units [16,17]. As far as the above discussion on the electrochemical studies are concerned, they dealt with either a discrete unit of quinone or separated by a linker [18–20]. The emphasis to discern the redox behaviour of charge transfer complexes are limited to the surface phenomenon only [6]. This article describes the interconversion of ND to NQ by BQ.

## 2. Experimental

The compounds ND, NQ, BQ and BD were obtained from Sigma-Aldrich and were used as obtained. The purity of the chemicals were checked by recording their IR spectra and melting points, and recrystallised whenever necessary. The spectroscopic

(HPLC) grade acetonitrile was used for electrochemical studies. The UV–VIS spectroscopic studies were performed with a Hitachi 2000 spectrophotometer. For electrochemical studies, approximately 3–5 mg of substrates were dissolved in degassed acetonitrile (5 ml, HPLC grade dried and distilled over  $P_2O_5$ ) and to the solution, tetrabutylammoniumperchlorate (200 mg) was added and stirred well, so as to dissolve it and make a homogeneous solution. The electrochemical studies were performed under nitrogen environment with three electrodes system comprising of two platinum electrodes and an Ag/AgCl standard electrode in a CHI660A electrochemical workstation. The scan speed used was  $100 \text{ mV s}^{-1}$ .

### 2.1. Reaction of 1,4-naphthoquinone with 1,4-benzenediol

Saturated solutions of NQ (158 mg, 1 mmol) and BD (110 mg, 1 mmol) in acetone (10 ml) were prepared separately. These two solutions were mixed together and stirred for two hours at room temperature. The solvent was then removed under reduced pressure. Black solid was obtained (yield 265 mg). Elemental analysis calculated for  $C_{16}H_{12}O_4$ : C, 71.64, H, 4.47; found C, 71.14, H, 4.69. IR (KBr) 3250 (bs), 1653 (s), 1593 (s), 1520 (s), 1460 (s), 1348 (s), 1224 (s), 1208 (s), 1102 (s), 830 (s), 771 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 8.6 (s, 2H), 8 (m, 2H), 7.8 (m, 2H), 7.1 (s, 2H), 6.6 (s, 4H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) 185.7, 150.6, 139.6, 135.0, 132.4, 126.7, 116.5  $\delta$ .

### 2.2. Reaction of 1,4-naphthalenediol with 1,4-benzoquinone

Saturated solutions of ND (160 mg, 1 mmol) and BQ (108 mg, 1 mmol) were prepared separately in acetone (10 ml each) and were mixed together and stirred at room temperature for two hours. The solvent was removed under reduced pressure and a black solid was obtained (yield 268 mg). IR (KBr) 3257 (bs), 1659 (s), 1633 (s), 1586 (s), 1480 (s), 1367 (s), 1334 (s), 1301 (s), 1268 (s), 1222 (s), 877 (s), 784 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 8.6 (s, 2H), 8 (m, 4H), 7.8 (m, 4H), 7.1 (s, 4H), 6.9 (s, 4H), 6.6 (s, 4H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ) 188.5, 185.6, 150.6, 139.6, 137.4, 135.1, 132.4, 126.7, 116.5  $\delta$ . On the

basis of these results it is concluded to have a mixture of NQ, BD and BQ.

### 3. Results and discussion

The reaction of equimolar amounts of NQ with BD results in the formation of charge transfer complex **A**. The charge transfer interaction between the two counterparts can be seen in the UV-VIS spectrum. The intensity of absorption of original BD is enhanced with a minor increase in the intensity of absorption peak at 334 nm of NQ. This was observed either in the solution of the equimolar mixture of NQ and BD or from isolated adduct. In the proton NMR spectrum of **A**, there are two multiplets at 7.8 and 8.0 ppm from the two sets of non-equivalent protons at 5, 8 and 6, 7 positions of the naphthalenic ring. It has a singlet at 7.1 ppm from the protons located at 2 and 3 positions of the naphthalenic ring. These peaks are slightly different from the original NQ. The protons from the BD counterpart appear at 6.6 and 8.6 ppm. The free BD has NMR signals very close to signals at 6.5 and 8.5 ppm. Apparently, no new signal other than the original counterpart appeared in the spectrum. The signals of NQ appear at 7.0, 7.8 and 8.1 ppm, whereas these are obtained at 7.1, 7.8, and at 8.0 ppm in the crude product of NQ with BD. The proton NMR of the crude reaction mixture from the reaction of equimolar amount of NQ and BD as well as that of the ND with BQ are identical except that the later pair has an additional singlet at 6.9 ppm. The proton signals of BQ that appear in free state at 6.8 ppm, appeared at 6.9 ppm in the product. ND has proton signals at 6.45, 6.7, 8.2 and 9.35 ppm which were not observed in the case of the reaction product of ND with BQ. Since the products from the reaction of ND with BQ and NQ with BD were same, there must be an equilibrium between the two pairs. The small shift in the chemical shift and non-observation of strong charge transfer absorption at a higher wavelength than the original counterpart makes us to believe that in solution the charge transfer interaction is less prominent than a hydrogen bonding interaction as shown as **C** rather than truly  $\pi$ -interacting stacked structures. It is to be noted that the powder diffraction pattern of the two adducts are much different from each other confirming that the structures in solid state to be different

from the structures in solution. The two adducts also have clear non-overlapping pattern of diffraction suggesting them to have interaction between the diol and quinone in solid state.

The results are also supported by the  $^{13}\text{C}$  NMR of the products of the crude mixture in each case. In the case of the reaction of NQ with BD, the reaction mixture has seven signals in the aromatic region out of which one is due to carbonyl. Whereas, in the case of the reaction mixture of ND with BQ the reaction mixture has nine signals of which seven are common to the earlier case and two are from BQ (Fig. 1).

The proton NMR integration of the products of the reaction shows that only 50% of BQ is transformed from BD and ND completely got converted to NQ. These results support that the reaction must be passing through an incomplete equilibrium and an additional process in operation that oxidises the ND. Another possibility is that the reaction may proceed without a charge transfer interaction. To ascertain these, the visible spectra of the reactions were monitored with time at 1 min intervals and observed that the reaction of ND with BQ leads to initial increase in absorption at 334 nm. This absorption reaches a maximum value and then decays (Fig. 2). During this decay there is an increase in the absorbance at 294 nm that is due to the formation of BD. As mentioned earlier, there is an incomplete equilibrium between BQ and BD in the presence of ND. In this reaction all the ND got oxidized, but BD is partially reduced. The transformation of ND by an external agent or alternative way cannot be ruled out. To check such possibilities, to a solution of ND in acetonitrile, hydrogen peroxide was added in an independent experiment. This did not change the visible spectra of the solution. But on addition of a trace amount of BQ to this, the peak intensity at 324 nm was enhanced. After a lapse of few seconds the absorption at 324 nm started decreasing and growth at 294 nm (Fig. 3) took place. This supported the fact that BQ was causing a catalytic effect on oxidation of ND in the presence of oxidant. Similar results was also observed when tertiary-butylhydroperoxide was used as oxidant. These results also supported the fact that the ND oxidation by BQ accompanies a parallel process. The yield of BQ in the above reaction slightly increase when anhydrous solvent was used. Thus, the results can be explained by considering the proton transfer process in a highly hydrogen bonded network of the

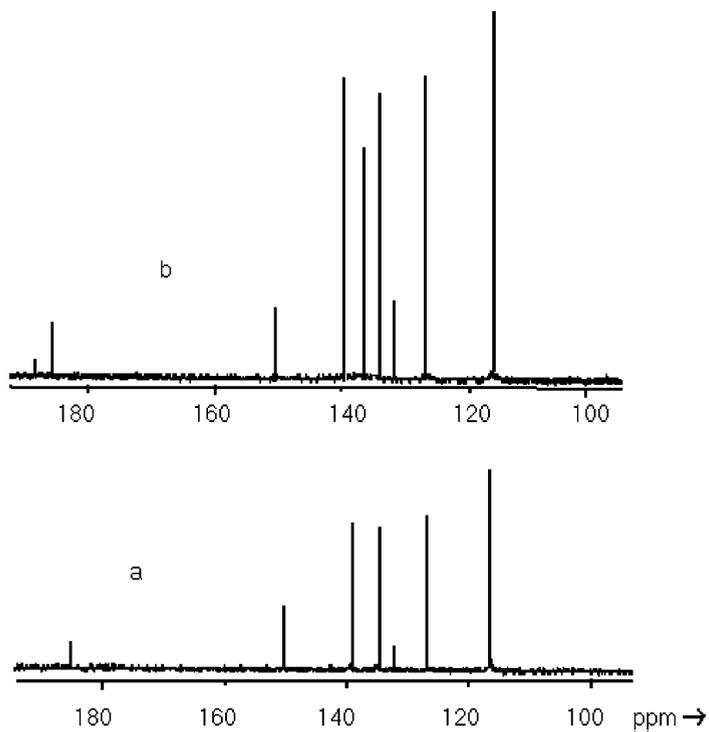


Fig. 1.  $^{13}\text{C}$  NMR (400MHz) of: (a) the adduct of NQ and BD (A); (b) the crude product mixture of equimolar ND with BQ.

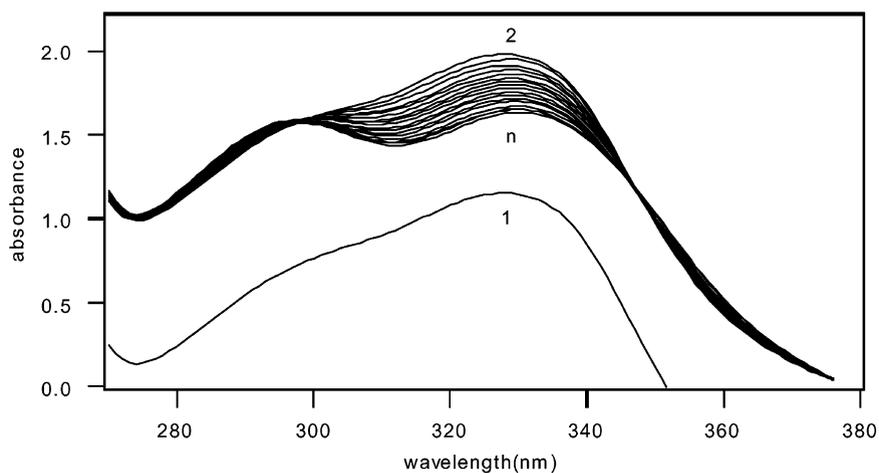


Fig. 2. UV-VIS spectra of an equimolar mixture of 1,4-naphthalenediol (0.002 mmol) and 1,4-benzoquinone (0.002 mmol) in acetonitrile (3 ml): (1) after 1 min of mixing; (2–n) after every minute from the initial plot (1).

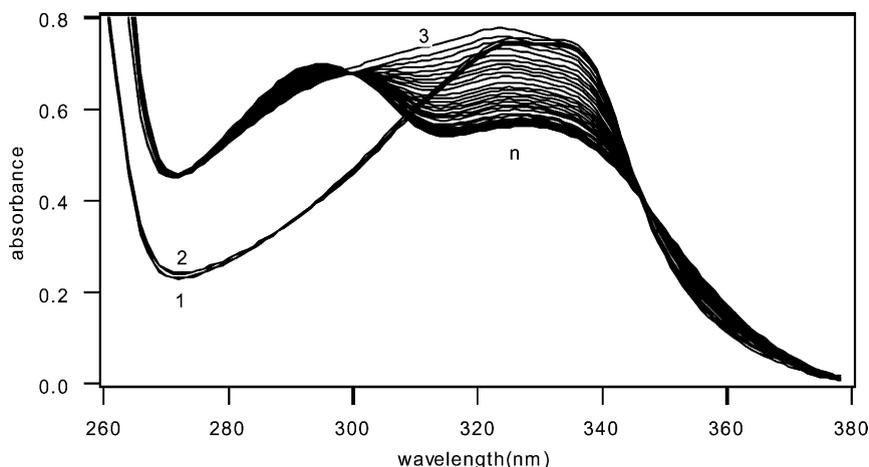
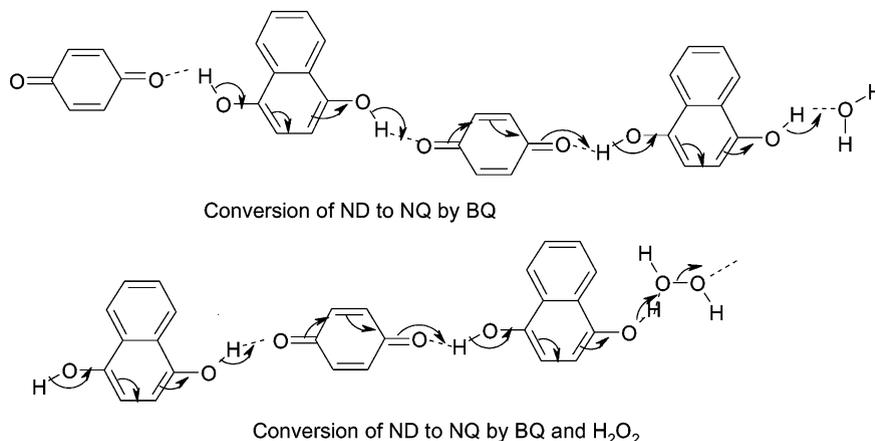


Fig. 3. UV–VIS spectra of: (1) 1,4-naphthalenediol (0.00055 mmol in 3 ml acetonitrile); (2) 1,4-naphthalenediol with hydrogen peroxide (5  $\mu$ l, 6%); (3–n) scans with intervals of 1 min after addition of 1,4-benzoquinone (trace amount) to (2).

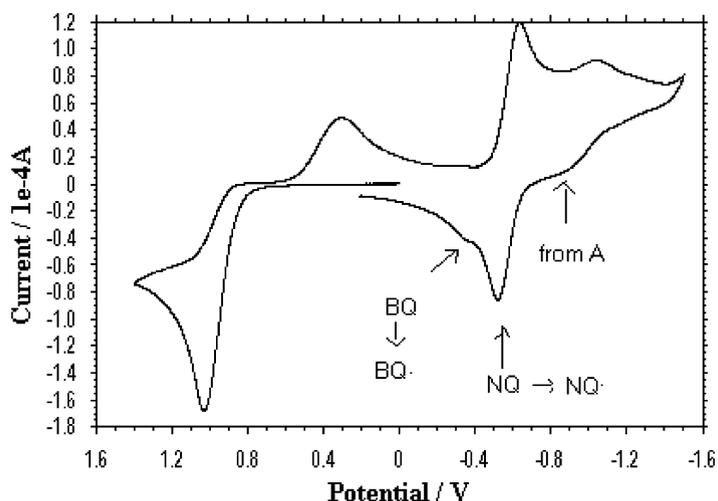
charge transfer adduct (Scheme 2). The conversion of ND by hydrogen peroxide was not possible at ambient condition without addition of a trace amount of BQ. This suggests that hydroperoxide can participate in the proton transfer process through hydrogen bonded structure as shown in Scheme 2. The water molecule, shown in the scheme to terminate such process comes from the solvent. Control experiments were carried out to confirm the interconversion of ND to NQ by recording UV–VIS spectra of the mixtures of ND and BQ with different concentration ratios. It was observed that the conversion of ND to NQ was independent of the concentration of BQ. This observation also

favoured the mechanism shown in Scheme 2 rather than a possible alternative path involving radical.

The electrochemistry of quinonic compounds is of great value in understanding the role of quinone in photosynthetic energy conversion [22]. The redox properties of free quinones and the quinones bound to a host varies and a large reduction in the reduction potential is observed [23]. Thus, redox properties of the donor and acceptor counterparts vary from the original counterpart [24]. The electrochemical study in the range of 0–1.2 V showed similar cyclic voltamogram for the adducts of NQ and BD as well as ND and BQ (**A** and **B**). The adduct of NQ with BD has oxidation



Scheme 2.

Fig. 4. Cyclic voltammogram of **A**.

wave at 1030 mV and reduction wave at 337 mV. When slow scan rate was used it showed only the oxidation peak at 1030 mV in the range of 0–1.2 V. Since the adduct of NQ and BD could be obtained as stable in solution, we have checked its cyclic voltammogram in the negative side and observed two couples arising from the reduction of NQ to NQ monoanion radical and dianion [21]. However, adduct prepared from equimolar amount of ND with BQ showed two pairs of redox potentials arising from the two quinonic

units. Although identical number of peaks for reduction and oxidation of NQ and BQ are observed, the redox pairs are shifted in each case from a free state showing them to be bound state. For example, free state of NQ has oxidations at –539 and –937 mV and reduction peaks at –621 and –1100 mV, respectively. BQ has oxidation at –307 mV and reduction at –472 mV. The cyclic voltammograms of **A** and **B** in the region of 0 to –1.5 V are shown in Figs. 4 and 5. The electrochemical processes of the adduct obtained

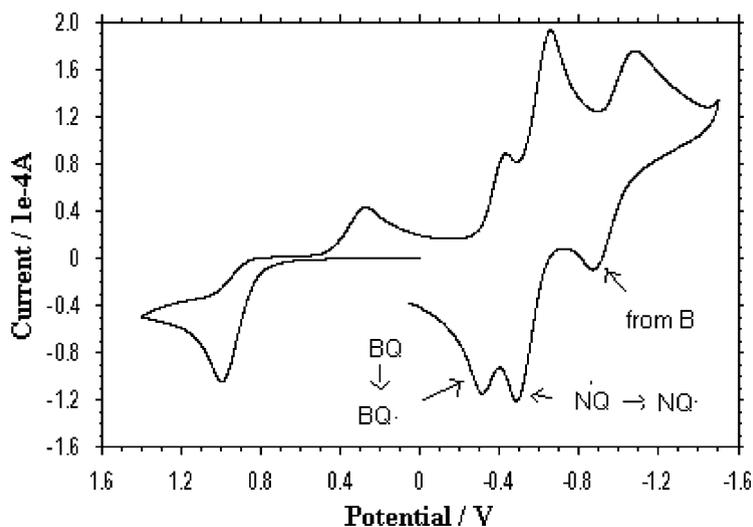
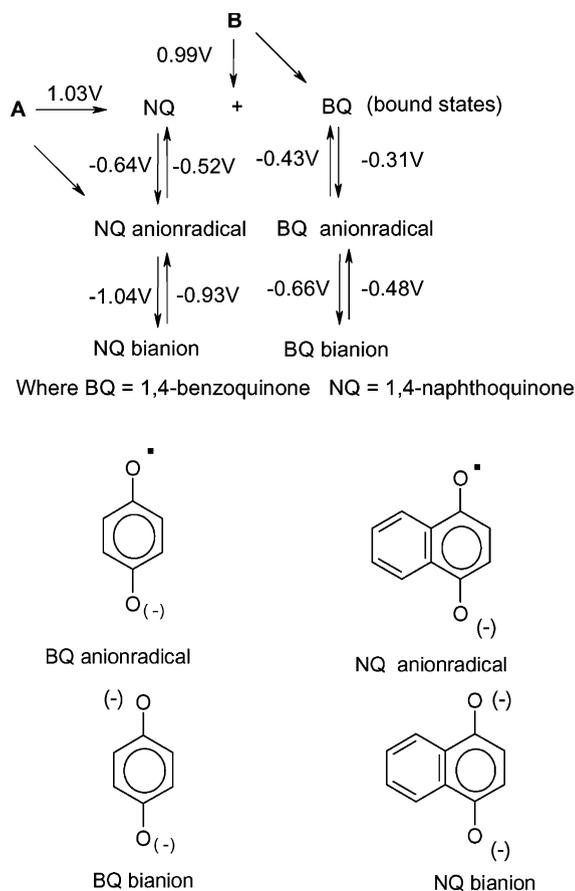


Fig. 5. Cyclic voltammogram of the crude products of the reaction of ND and BQ.

from NQ and BD (**A**); and ND and BQ (**B**) that arise from dissociation of the charge transfer adducts can be represented by Scheme 3.

At slow scan rate ( $1 \text{ mV s}^{-1}$ ) the reduction peaks that were present in the positive side (310 mV) disappeared. In the case of **B**, a negative scan led to an additional redox couple having oxidation at  $-928 \text{ mV}$  and reduction at  $-1040 \text{ mV}$ . This couple is assigned to a redox couple of NQ dianion and NQ monoanionic radical that is generated from a series of charge transfer adducts aggregated together and are formed through electrochemical reduction [25]. Such observations are made on the basis of the existing data on quinonic compounds that are held together in space with intervening atoms [4]. Polyquinonic systems, with methylene units separating quinonic units, are known to show multiple number of cycles generated from anionic species with different charges [15–17]. In the cyclic voltamogram of **A**, the first cycle does not lead to the reduction peak at  $-430 \text{ mV}$  and oxidation peak at  $-316 \text{ mV}$  but after multiple cycles and sufficient lapse of time, degradation of the charge transfer complex gives detectable amount of BQ. This process led to the growth of this redox couple for BQ and its anionic radical. The AM1 calculation of heat of formation shows that the isomer **A** has about 12 kcal energy difference from **B**, and it is more stable. Thus, all the results described above supports that **A** and **B** can co-exist, however, low energy difference makes



Scheme 3.

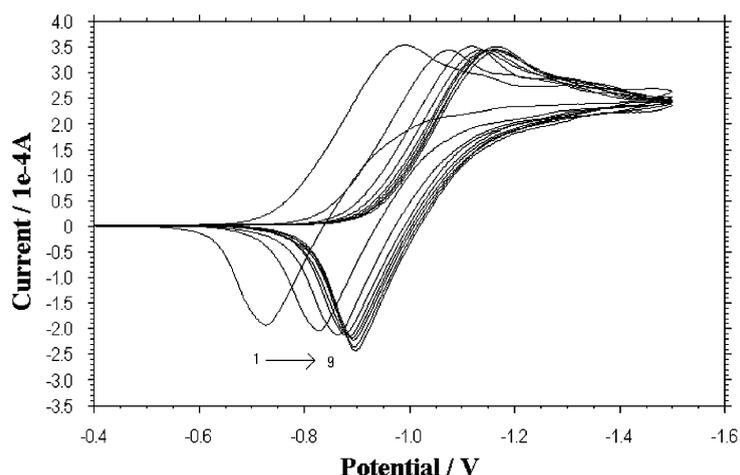


Fig. 6. Formation of charge transfer adduct monitored by cyclic voltamograms of equimolar amount of 1,4-naphthoquinone (0.001 mmol) with 1,4-benzenediol (0.001 mmol) in acetonitrile (3 ml) with tetrabutylammoniumperchlorate (0.1 M) as supporting electrolyte. Scan rate =  $100 \text{ mV s}^{-1}$ .

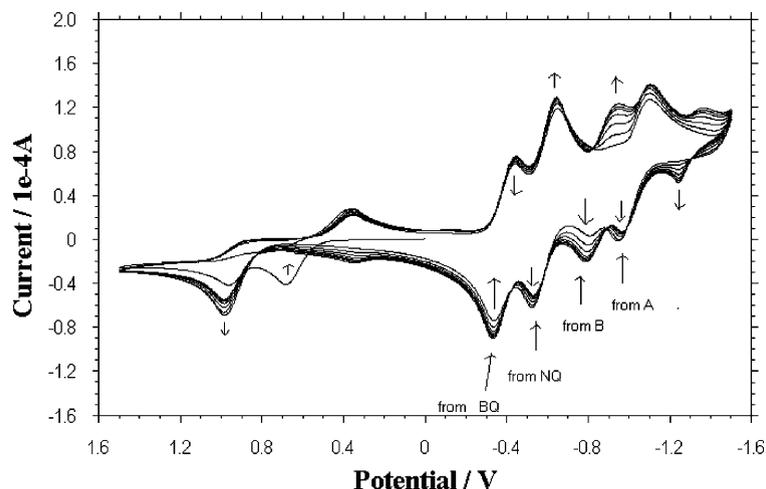


Fig. 7. Formation of charge transfer adduct monitored by cyclic voltammograms of equimolar amount of 1,4-naphthalenediol (0.001 mmol) with 1,4-benzoquinone (0.001 mmol) in acetonitrile (3 ml) with tetrabutylammoniumperchlorate (0.1 M) as supporting electrolyte. Scan rate =  $100 \text{ mV s}^{-1}$  (nine scans are shown: 1–9).

**B** to get converted to **A** in solution. To understand the actual picture about the interconversion of **A** and **B** in solution, several scans of freshly prepared equimolar solutions of NQ and BD (Fig. 6) and that of ND and BQ (Fig. 7) were recorded. In the latter case, we have observed as soon as NQ and BD are mixed the two redox couples in the negative side appear as only one. This couple further shifts towards negative side and attains a stable state after about 20 min, showing the stability of **A**. However, a similar study with an equimolar mixture of ND and BQ has led to the decrease in the oxidation potential of BQ and increase in the oxidation potential of NQ. It had shown growth of the redox potential of **A** (as observed in the earlier case with the other pair) as well as an additional redox couple is assigned to the isomer **B** (Fig. 7). All these studies support that the isomers **A** and **B** are formed in solution, however, the isomer **B** interchanges to **A**.

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