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Spectroscopic and electrochemical properties of 4-[(4′-hydroxy-3′,5′-dimethylphenyl)(aryl)-methylene]-2,6-dimethylcyclohexa-2,5-dienones

Rupam J. Sarma [a], Ritu Kataky [b], Jubaraj B. Baruah [a,*]

[a] Department of Chemistry, Indian Institute of Technology, Guwahati 781 039 Assam, India
[b] Department of Chemistry, University of Durham, Durham DH1 3LE, United Kingdom

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Abstract

Diaryl quinone methides, 4-[(4′-hydroxy-3′,5′-dimethylphenyl)(aryl)-methylene]-2,6-dimethylcyclohexa-2,5-dienone (where aryl = 4-hydroxyphenyl, **1a**; 4-methoxyphenyl, **1b**; 3,4,5-trimethoxyphenyl, **1c**) are synthesised by oxidation of the corresponding bis-phenols. These molecules are solvatochromic and have interesting acid–base properties. The neutral cationic and anionic states of **1** have characteristic visible absorptions, thus they can be used as indicators. Isomeric cations generated from **1b** can be clearly distinguished by visible spectroscopy. The electrochemical properties of these diaryl quinone methides, **1a**–**1c** are studied by cyclic voltammetry and coupled ESR. In the case of **1a**, a quasi-reversible redox process is observed. In the case of either **1b** or **1c** two quasi-reversible redox couples are observed. The electrochemical processes are explained in terms of radical intermediates which are resonance stabilised. Stabilisation of this radical intermediate by methoxy group is inferred.

Keywords: Quinone methides; Tautomerism; Solvaochromicity; Electrochemistry; Electron spin resonance

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1. Introduction

Triphenylmethyl systems are suitable substrates for generation of stable anions [1], cations [2–5] and radicals [6,7]. Analogous triphenyl reactive intermediates can also be prepared from quinone methides having a triphenylmethyl framework [8–14]. Among the different radical intermediates that can be obtained from quinone methides, the biradical generated from tris-(oxo-phenylene) methane, known as Yang's biradical [15,16] has been well-studied. Dougherty et al. [17] reported the presence of ferromagnetic coupling between the radicals generated in conjugated quinone methide systems. Extensive studies [11–14,18] on perchlorotriphenylmethyl units show that steric crowding of chlorine substituents make the radical so stable that some of such systems have half-life of the order of 100 years. If the delocalisation in these types of molecules is extended over substituents attached to a ring then there is possibility to either stabilise or destabilise a radical intermediate. Thus, formation and stability of radicals in simple molecules such as **1a**–**1c** (Fig. 1) will clarify the role of phenolic hydroxyl groups in stablising a radical species. The phenyl rings in **1a**–**1c** are twisted about the central carbon atom due to steric factors [10,21,24] so that the cationic or radical intermediates generated from these molecules are not able to adopt planar conformations. In this study we discuss the spectroscopic properties of different intermediates generated from diaryl quinone methides (**1a**–**1c**).

2. Experimental section

The UV–visible spectra were recorded on a Hitachi U1600 spectrophotometer. The UV–visible spectra were recorded in appropriate solvent HPLC grade without further purification. For

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* Corresponding author. Tel.: +91 3612582301; fax: +91 3612690762.
E-mail address: juba@iitg.ernet.in (J.B. Baruah).

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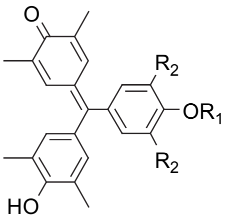


when R_1=H, R_2=H (1a); R_1=Me; R_2=H (1b); R_1=Me R_2=OMe (1c)

Fig. 1.

acid–base titration the samples are taken in quartz cuvette of 3 ml capacity (1 cm path length) and titrations were carried out by externally adding the acid or amine by a microsyringe in aliquots. The solvatochromic properties were studied using solutions in identical concentration of the substrates in the mixed solvent and recording the visible spectra of each of the solution. Volume corrections are made to make consistent study in each case. The NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer with TMS as internal standard. The cyclic voltammograms were recorded using PG263 potentiostat from Princeton Applied Research (USA). They were measured for 0.1 mM solutions of **1a**–**1c** in dry and degassed acetonitrile at 298 K. Tetrabutylammonium perchlorate was used as supporting electrolyte and the experimental solutions were purged with dry argon before each scan. The glassy-carbon working electrode was cleaned with electrode polishing materials available from BAS, washed with deionised water and acetone. The non-aqueous Ag/AgCl electrode was used as reference in all the measurements while a Pt-foil (1 cm^2) was used as counter electrode. The coupled ESR experiments were performed using a specially designed ESR cell in a Bruker X-band spectrometer calibrated with internal teslameter. Simulations of the ESR data were done using standard WinEPR software available from Bruker. Simultaneous ESR and electrochemistry were carried out under conditions identical to those maintained during cyclic voltammetry experiments. The solutions of the compounds **1a**–**1c** were made in dry acetonitrile and degassed before each experiment. In this case the working electrode was a Pt-mesh while a Pt-wire (diameter 0.5 mm) was used as the counter electrode. Potentials were measured against a non-aqueous Ag/AgCl electrode.

The compounds **1a**–**1c** were prepared by oxidation of the parent bis-phenols bis-(4-hydroxy-3,5-dimethylphenyl)(aryl)-methane. For this purpose the parent bis-phenols were synthesised from condensation of 2,6-dimethylphenol with corresponding aldehydes [10]. The structures of **1a**–**1c** are also reported [25] (CCDC nos. 253495, 253496 and 253497).

*2.1. Synthesis of 4-[(4′-hydroxy-3′,5′-dimethylphenyl)(aryl)-methylene]-2,6-dimethylcyclohexa-2,5-dienone (**1a**–**1c**)*

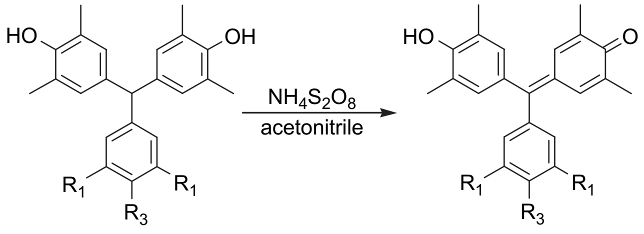
In a typical procedure 4-[(4′-hydroxy-3′,5′-dimethylphenyl)(4-methoxyphenyl)-methylene]-2,6-dimethylcyclohexa-2,5-dienone (**1b**) was prepared as follows: the bis-(4-hydroxy-3,5-dimethylphenyl)(4-hydroxyphenyl)methane (0.362 g, 1 mmol) was dissolved in acetonitrile (5 ml) and added to a stirred solution of ammonium persulfate (0.50 g, 2.2 mmol) in water (3 ml). The resulting mixture was put on a water bath (60 °C) for 6 h. As the compound gets oxidized the solution becomes slightly red and the quinone methide **1b** separates out as purple crystals. After 6 h the reaction mixture was cooled and filtered. The crystals were washed with acetonitrile (5 ml) and dried in air (yield 0.24 g, 63%). IR (KBr, cm^{-1}): 3300, 2914, 1600, 1592, 1460, 1265, 1182, 1140; ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) 7.07 (4H, dd, $J = 8.8$ Hz), 6.91(2H, dd, $J = 8.8$ Hz), 6.60(2H, s), 3.85(3H, s), 2.08 (12H, br d). ^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) 160.7, 158.7, 133.9, 132.6, 128.6, 113.8, 55.3, 16.6, 16.5; Elemental analysis calcd. for $C_{24}H_{24}O_3$: C, 80.0; H, 6.67; found: C, 79.97; H, 6.62.

4-[(4′-Hydroxy-3′,5′-dimethylphenyl)(4-hydroxyphenyl)-methylene]-2,6-dimethylcyclohexa-2,5-dienone, **1a**: Purple crystals (yield 0. 14 g, 40%; mp 202 °C decomp.), IR (KBr, cm^{-1}): 3450, 2922, 1624, 1595, 1542, 1478, 1328, 1170, 1141, 1045, 845; ^1H NMR (DMSO-d_6, 400 MHz): δ (ppm) 10.02 (1H, br s), 7.01 (2H, d, $J = 8.8$ Hz), 6.92 (4H, s), 6.83 (2H, d, $J = 8.8$ Hz), 2.03 (12H, br s). ^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) 159.6, 134.3, 131.7, 129.5, 128.4, 123.1, 115.1, 114.4, 16.5.

4-[(4′-Hydroxy-3′,5′-dimethylphenyl)(3,4,5-trimethoxyphenyl)-methylene]-2,6-dimethylcyclohexa-2,5-dienone, **1c**: Red needles (0.328 g, 78%; mp > 250 °C.); MW 420; IR (KBr, cm^{-1}): 3428, 2944, 1618, 1562, 1468, 1330, 1127, 1028; ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.94 (4H, s), 6.35(2H, s), 3.89 (3H,s), 3.73 (6H,s), 2.09 (12H, br s). ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 152.6, 13.3, 134.6, 110.1, 61.0, 56.3, 16.3.

3. Results and discussion

Diaryl quinone methides, 4-[(4′-hydroxy-3′,5′-dimethylphenyl)(aryl)-methylene]-2,6-dimethylcyclohexa-2,5-dienones, **1a**–**1c**, are obtained by oxidation of the corresponding bis-phenols with ammonium persulfate (Eq. (1)). The ^1H NMR spectra of these compounds are solvent dependent.



1a-1c

R_1 = H; R_2 = OH
R_1 = H; R_2 = OMe
R_1 = OMe, R_2 = OMe (1)

As an illustrative example, the effect of solvent on the proton NMR spectra of **1a** is shown in Fig. 2. For example, if the two

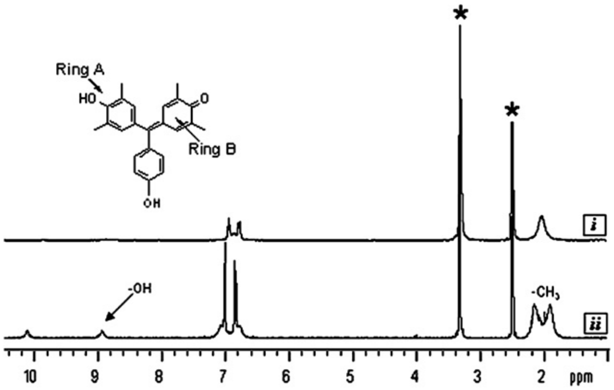


Fig. 2. ^{1}H NMR spectra of **1a** (i) in dimethylsulfoxide-d_6 and; (ii) in mixed solvent of dimethylsulfoxide-d_6 and acetone-d_6 (9:1) (* indicates solvent signals).

rings are highly delocalised it would result in a symmetric spectra and would make the four methyl groups attached to the *ortho*-positions of the −OH groups of either ring A or ring B chemically equivalent (Fig. 2). When the quinone and the phenol units are distinguishable, they will show two sets of methyl signals. Thus, the spectra (Fig. 2) can be interpreted in terms of a resonance effect that occurs due to delocalisation between the two different types of rings. This effect in related systems was reported earlier [19] and as expected the polarity and hydrogen-bonding ability of the solvent are key factors in this process. We have observed that in dimethylsulfoxide-d_6 (Fig. 2(i)), **1a** shows a single signal for methyl protons. Similarly the aromatic protons on the phenol and the quinonic groups coalesce into a broad signal at ca. 6.9 ppm. This indicates that in dimethylsulfoxide-d_6 extensive delocalisation takes place and the aromatic rings are free to rotate.

However, the ^{1}H NMR spectra of **1a** in a 9:1 mixture of dimethylsulfoxide-d_6 and acetone-d_6 the methyl protons appear as two broad singlets. The two −OH signals appear as two singlets at 8.96 and 10.09 ppm. In neat acetone-d_6, the signals due to the protons of the two kinds of methyl groups appear at 1.96 (two singlets) and 2.19 ppm (singlet), whereas the −OH protons of **1a** appear at 7.91 and 8.92 ppm, respectively. This indicates that the two −OH groups are in different environments and there is less delocalisation between the rings in acetone-d_6. The identity of the OH protons is further confirmed by exchanging these two protons with deuterium oxide. Similar phenomena are evident from the ^{1}H NMR of **1c**. The ^{1}H NMR spectrum of **1c** was studied in $CDCl_3$ at room temperature and the molecule was found to be delocalised. Accordingly only one singlet for the four methyl groups at *ortho*-position of the quinone and the phenol units was observed. The proton signals due to the methyl groups of the same compound remain unchanged when the ^{1}H NMR spectra were recorded at −30 °C, however, there was a broadening of the methyl groups signal on lowering of temperature as well as broadening of OH signals. This suggests that the solvent polarity is an important factor that decides the extent of delocalisation. Further support to the delocalisation effect comes from the fact that the ^{1}H NMR of **1c** in acetone-d_6 shows two well-resolved signals from the methyl protons of quinone and phenolic groups at 1.95 and 2.27 ppm, respectively. However, in dimethylsulfoxide-d_6 the methyl signals merged into a broad signal at 2.06 ppm, suggesting extensive delocalisation. The effect is translated to the NMR signals of the ring protons, namely the protons on the quinone and phenyl rings could not be distinguished and they appeared as a broad signal.

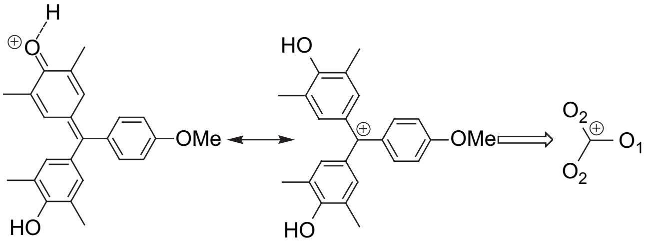
We have observed that molecules **1a**−**1c** were highly solvatochromic. The absorption spectra of **1a**−**1c** in the visible region are sensitive to the polarity of solvents (Table 1). The solvatochromic behaviour of the compounds shows that the extent of delocalisation is sensitive to the microenvironment caused by the solvents.

The compounds **1a**−**1c** at $pH < 3$ show characteristic absorptions due to the corresponding cation formation (Scheme 1). For examples in acetonitrile compound **1b** absorbs at 496 nm ($\epsilon = 68{,}200\ M^{-1}\ cm^{-1}$); **1c** at 515 nm ($\epsilon = 63{,}400\ M^{-1}\ cm^{-1}$). Due to high extinction coefficient of the absorption peak arising from the carbocations they can be detected at very low concentrations (Fig. 3). The absorption maximum of the cation is also influenced by solvent (refer to entry nos 4, 10, 12 of Table 1). Typically, the absorption maximum for the cation of **1b** in methanol occurs at 504 nm with a shoulder at 466 nm. Whereas the same cation in acetonitrile has absorbance at 496 nm.

In the case of **1b** we have observed two peaks for the cation in methanol. This is attributed to the two non-equivalent structures obtained from the two unsymmetrical resonance structures involving the participation of −OMe and −OH groups (cf. O1−O2 in the motif of Scheme 1). This asymmetric effect arises due to such delocalisation extending over only two rings at a time due to propeller like shape of the molecule [19]. However, such features are not observed in the case of the cationic species of **1b** in acetonitrile (Fig. 4(b)). Acetonitrile being an aprotic solvent does not interfere in the delocalisation of the −OMe group thereby making a highly delocalised system, whereas in the case of the methanol as the solvent, the delocalisation of lone pair competes with the hydrogen-bonding interaction with the protic solvent. This leads to two forms of the cation and is revealed in the visible spectra. Such isomeric forms of triphenylmethane derivatives were first

Table 1
Solvatochromic properties of **1a**−**1c**

Entry no	Solvents	λ_{max} (nm)		
		1a	**1b**	**1c**
1	Dichloromethane	–	418	416
2	Chloroform	–	418	417
3	Acetonitrile	417	416	411
4	Acetonitrile + HCl	492	496	515
5	Dimethylformamide	434	428	422
6	Dimethylsulfoxide	438	432	429
7	Tetrahydrofuran	417	416	416
8	Dioxane	412	410	411
9	Methanol	456	445	438
10	Methanol + HCl	496	504	524
11	Ethanol	453	447	440
12	Ethanol + HCl	498	508	525



Scheme 1. Resonance form of protonated **1b**.

demonstrated by Strohbusch [20]; however, he studied it purely from the unsymmetric ring systems but we demonstrate the effect of generation isomeric cations via substituent effect. Studies involving the generation of triphenylmethyl cation [21–24,26–29] often involve the use of superacids [30,31]. But, the quinone methide system is advantageous simple as mineral acids can lead to the generation of the cations.

Compounds **1a**–**1c** form anions upon reacting with amines such as triethylamine leading to its corresponding anion in polar solvents. The anion of compound **1b** generated in ethanol has λ_{max} at 584 nm (Fig. 5). This absorption of the anion is also solvent dependent. The results on absorption maximum of the anions of **1** are shown in Table 2.

The effect of solvent on the formation of anion of **1b** has been studied in mixed solvent systems containing ethanol and dichloromethane (v/v). It is found that the absorbance decreases linearly with increase in the volume of dichloromethane (Fig. 6). This is expected because dichloromethane is a less polar solvent compared to ethanol.

Cyclic voltammograms of **1a** in acetonitrile show a quasi-reversible couple with E_{pa} −750 mV and E_{pc} −955 mV at 100 mV/s scan rate (Fig. 7). The i_{pa}/i_{pc} of this redox couple is close to unity. These peaks are due to the formation of the radical anion, and their position and intensities are dependent on scan rate. As the scan rate increases, the cathodic peak shifts to more negative potentials while the anodic peak current decreases. This is shown in Fig. 7 (left) for the **1a**/**1a**$^{\bullet-}$ redox couple at scans rates of 100 mV/s and 300 mV/s. This characteristic quasi-reversible redox couple resulting from the formation of the radical anion is observed in both **1b** and **1c**. However, compounds **1b** and **1c** exhibit another quasi-reversible redox process, occurring at potentials of −1400 mV, for **1b** and −1380 mV for **1c** when the scan rate was 100 mV/s. There is a marked decrease in i_{pc} with respect to the corresponding i_{pa} on increasing scan rates; as shown in Fig. 7, at a higher scan rate for example with 300 mV/s, the second quasi-reversible redox couple becomes irreversible and shifts to −1500 mV (**1b**) and −1400 mV (**1c**), respectively.

On increasing the scan rate, the i_{pa}/i_{pc} value also differs much from unity in the case of the other couple. Typical cyclic voltammograms at two different scan rates of the three compounds **1a**–**1c** are shown in Fig. 3. These results can be explained with the help of a sequence of interconvertible species that are illustrated in Scheme 2. As shown in Scheme 2, the radical anion is obtained by one electron reduction of neutral **1a** by supply of electron from external source. The key step in detecting a radical is the rate at which it degrades (step 2). The intermediates of the type **A** are well known in literature and can be generated by electrochemical means [7,19]. The step 1 is crucial in deciding whether there will be generation of a radical or not.

In the case of **1a** the radical **A** would have only option to revert back to the parent compound. If this decay process is fast the system should not show any property of radical but should form the parent compound and still be electroactive with a reversible one electron redox process, which is in fact seen in the cyclic voltammogram of **1a**. But in the case of **1b** and **1c** the presence of −OMe group at the *para* position allows an additional delocalisation step that is represented in Scheme 3. The radical species **A** and **B** (Scheme 3) are energetically different thus if they are to be generated independently they would require different oxidation potentials. Accordingly one can observe two sets of couples corresponding to generation of each of them. In the case of **1b** at scan rate of 300 mV/s, **A** is generated at −965 mV whereas **B** is generated at −1500 mV. As expected in the case of **1c** we get two sets of redox potentials.

Support to the electrochemical process is obtained by performing controlled electrolysis along with in situ detection of the radical species by ESR. In order to establish Scheme 2, we have carried out controlled electrolysis coupled with electron spin resonance spectroscopy. It is found that during

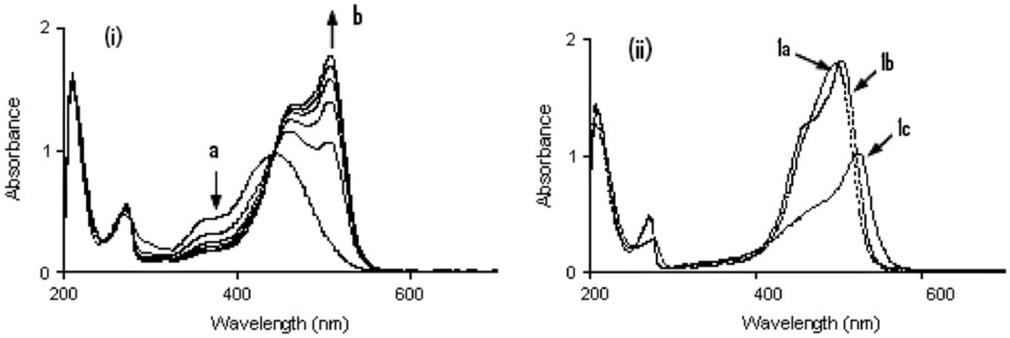
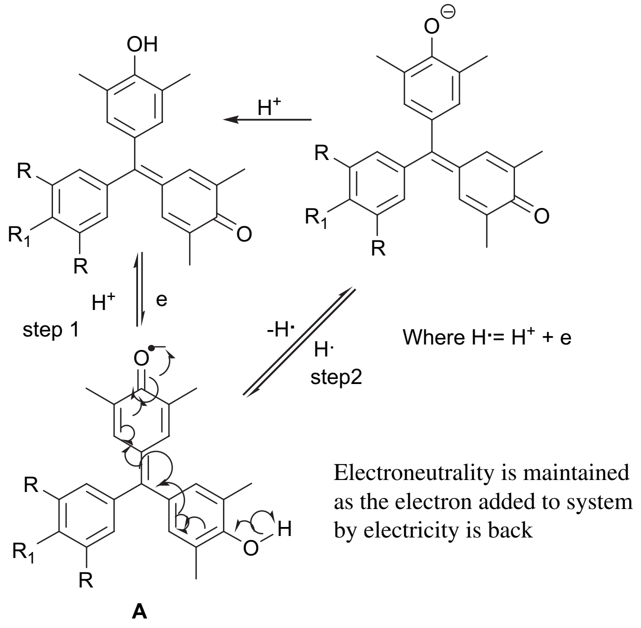


Fig. 3. (i) Changes in the absorption spectra of **1b** (10^{-5} mM) in MeOH (a) parent compound, (b) upon adding HCl (0.01 M, 2 μl aliquots); (ii) Visible spectra of cations of **1a**–**1c**.



Scheme 2. Different forms of intermediates formed during spectroelectrochemistry of **1a**–**c**.

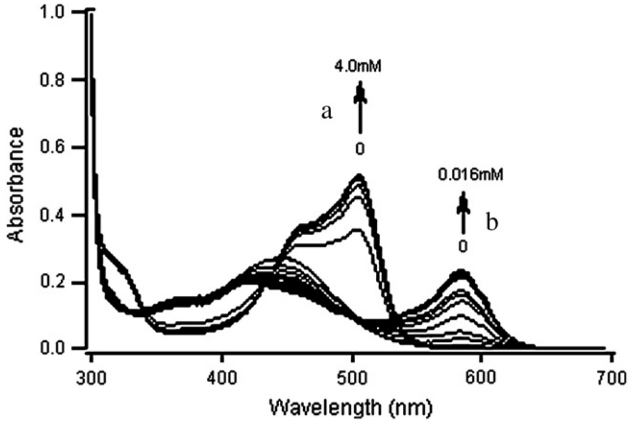


Fig. 5. (a) Cation formation of **1b** in ethanol (10^{-5} mM) upon addition of 0.1 M hydrochloric acid (2 μl aliquots). (b) Anion formation of **1b** by addition of triethylamine (aliquots of 2 μl of 0.1 M) to **1b** in ethanol (10^{-5} mM).

controlled electrolysis with −1200 mV the acetonitrile solution **1a** does not show ESR signal. This can only happen due to a fast conversion of the radical anion to the parent compound, i.e. to say step 1 is the rate-determining step of electrochemical process. Complete conclusion on Scheme 2 cannot be made on the basis of the results from cyclic voltammetry alone. The ESR spectra coupled with electrolysis of the **1b** and **1c** provide further support for this scheme. The ESR spectrum of **1b** (Fig. 8) recorded at an applied potential of $E = -1000$ mV is very interesting; it shows nine distinct signals corresponding to coupling of the electron to eight hydrogen atoms. This is expected, as there are eight hydrogen atoms attached to the three aromatic rings of radical **A** generated from **1b**. Spectral analysis shows that the signals are uniformly spaced with the hyperfine coupling constants (a^H) being 1.864 G for six hydrogens and 0.195 G for two hydrogens. This was simulated using these parameters and overlaid with the experimental spectra. The exact matching of the spectra with simulated spectra with the given parameters suggests that the radical formed is delocalised over the entire molecular framework. This clearly indicates that the lifetime of **A** in the case of **1b** is sufficient to get the signals in ESR spectra. This is obvious for the possible stabilisation of the radical as presented in Scheme 3. However, the ESR spectra of **1b** changes with time as electrolysis of the solution progresses. This may be due to the decay of this radical to form the parent compound as suggested in step 2 of Scheme 2. But this is not necessarily being the only reason, as one can see the line shape changes and the hyperfine coupling are lost on prolonged electrolysis. After 20 min, the hyperfine are lost but it leads to a broad signal centering at 3447 G. This observation is not unusual as similar observation on decay of signal leading to merger of peaks in the case of coupled systems in which coupling between anionic and radical species are observed earlier [32]. In their study they have studied the effect of 1:1 mixture of anion and anion radical. It had also been observed that triplet radical in an analogous quinone methide system couples ferromagnetically [15]. Since these systems comprise donor quinone and acceptor phenol units their assembling is quite likely and this could result in the broadening of the ESR signal on prolonged electrolysis. The results obtained from the electrochemical reduction **1c** under similar conditions are as

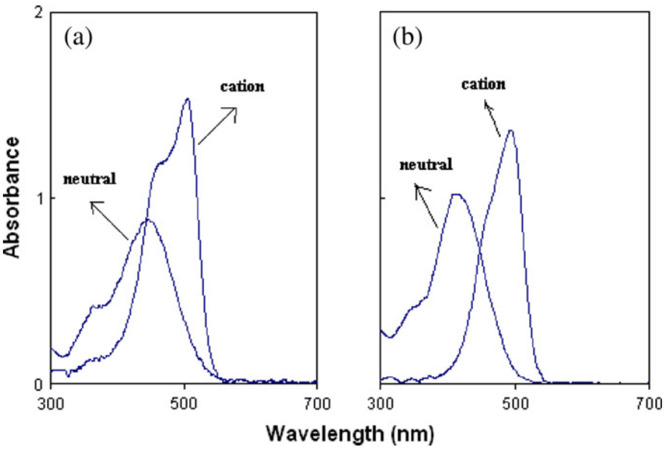


Fig. 4. Visible spectra of **1b** and corresponding cation in (a) methanol and (b) acetonitrile.

Table 2
Absorption maxima of the anions of **1a**–**1c**

Entry no	Solvents	λ_{max} (nm)		
		1a	**1b**	**1c**
1	Methanol	566	584	591
2	Ethanol	576	592	600
3	Acetonitrile	596	600	603
4	Dimethylformamide	600	608	610
5	Dimethylsulfoxide	606	610	613
6	Ethanol + water (1:4,*v*/*v*)	572	578	581

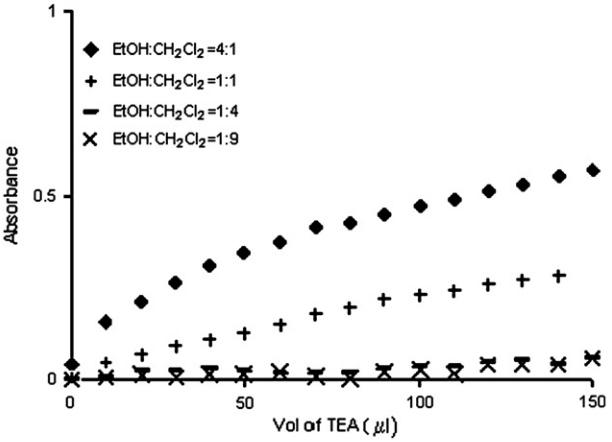


Fig. 6. Titration of **1b** with triethylamine (0.1 M solution in ethanol) at different compositions of ethanol–dichloromethane. Change in absorbance at 593 nm, which decreases from 4:1, 1:1, 1:4 to 1:9 (v/v) ethanol–dichloromethane.

expected, and can be explained on the basis of Schemes 2 and 3. The compound **1c** when electrolysed at potential $E = -1050$ mV in acetonitrile produces the anion radical (**1c**$^\bullet$) which is ESR active (Fig. 9). The ESR spectrum of **1c**$^\bullet$ thus obtained, consists of 49 lines as shown in Fig. 9. This spectrum indicates that the electron in **1c**$^\bullet$ is extensively delocalised. When simulated using the coupling constants of 2.035 G and 0.204 G, it becomes evident that this spectrum of **1c**$^\bullet$ consists of seven signals corresponding to the coupling of the electron with six-*meta* protons.

Each of the seven signals in the ESR spectrum are thus split into sets of seven signals (septet) corresponding to a second coupling of the electron with the two –Me groups adjacent to the quinonoid C=O group, with the hyperfine coupling constant for these protons being a^H 0.204 G. In a recent paper it is demonstrated that the second-order coupling constant of methyl group varies with the orientation of the methyl groups [33]. The six protons *ortho*- to the central carbon atom are equivalent indicating that the spin density is delocalised over the entire triphenylmethyl ring system. The symmetry of the ESR spectra of **1c** also indicates that the phenyl groups of the quinone and the phenol rings are equivalent on the given timescale. Thus, this radical, **1c**$^\bullet$, is most stable compared to either **1a** or **1b**, and there is no noticeable change in the ESR spectrum after 2 h of standing. This is also in the expected direction, as the multiple units of methoxy groups would provide steric congestion so that the coupling with another unit would not be possible.

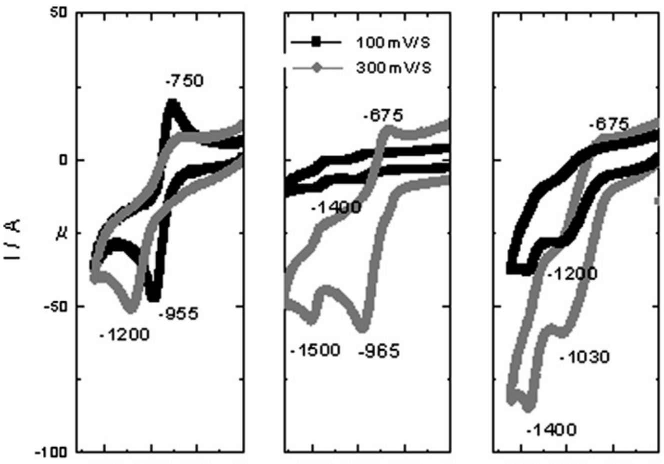
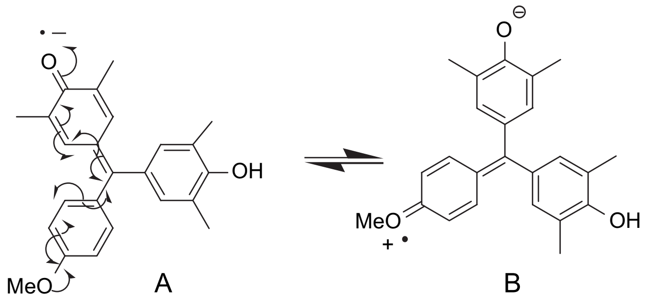


Fig. 7. Cyclic voltammogram of (left to right) **1a**, **1b** and **1c** in acetonitrile at different scan rates.



Scheme 3. Resonance stablisation of electrochemically produced radicals by a methoxy group.

In conclusion, we have shown the visible spectroscopic properties and electrochemical properties of a new class of

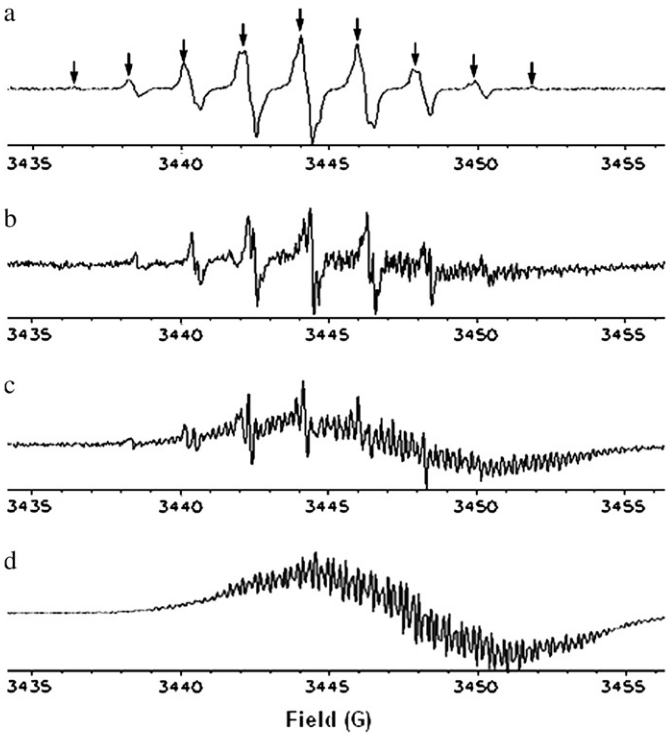


Fig. 8. Evolution of the ESR spectra of **1b** with time (**a**–**d** each recorded after time = 5min) in dry acetonitrile ($E = -1000$ mV vs Ag/AgCl; TBAP as supporting electrolyte; 294.5 K); X-band frequency 9.66590 GHz and center field 3445 G; g 2.0041; experimental hyperfine splitting constants are a^H 1.864 G (6H) and 0.195 G (2H); line broadening 0.05 G.

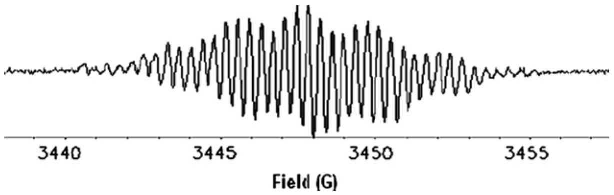


Fig. 9. ESR spectra of anion radical of **1c** in acetonitrile ($E = -1050$ mV vs Ag/AgCl; 0.1 M TBAP; 294.5 K); X-band frequency 9.66595 GHz and center field 3448 G; g 2.0043; a^H 2.035 G (6H) and 0.204 G (6H). Line broadening 0.05 G.

compounds that result in facile formation of anion, cation and radical under different conditions.

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