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The electrochemistry of arylated anthraquinones in room temperature ionic liquids

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Arylated anthraquinone derivatives of different sizes and different π-basicities have been prepared, and the electrochemical behaviour of these substances has been studied on screen printed graphite electrodes in the three room temperature ionic liquids (RTILs), 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4MIM][PF_6]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6MIM][PF_6]) and 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]). Half redox potentials for the first and second one electron reduction waves were identified, and the diffusion coefficient values were estimated from cyclic voltammetry measurements. The influence of the nature of the RTIL and of the substitution pattern of the anthraquinone on the solvodynamic radii were studied. A correlation of the reductive potentials with the corresponding Hammett constants of the substituents was tested.

Supporting information may be found in the online version of this paper

Keywords: arylated anthraquinones; electron transfer; quinone; room temperature ionic liquid; screen printed graphite electrodes; solvodynamic radii

INTRODUCTION

Room temperature ionic liquids (RTILs) have become interesting media in electrochemistry.[1–7] The use of RTILs in batteries, electrochemical synthesis, electrocatalysis, electrochemical capacitors, electrochemical sensing and biosensing, and in modified electrode preparation, among others, has elicited attention. The advantages of RTILs as chemical media are deemed to be their relatively low toxicity, low vapor pressure and tunable solvent properties. Among the many available RTILs for electrochemical applications, they are chosen according to their viscosity, conductivity and accessible electrochemical potential windows; their increased use in electrochemical sensors and biosensors can be therefore be foreseen.[8]

The electrochemistry of quinones, especially of benzoquinone, in aqueous and organic medium is well-established.[9] Thus, the quinones constitute a class of molecules that can be used as model redox systems to study the behaviour of electrodes under diverse conditions. Additionally, quinone structures and their reduced forms can be found in biomolecules of importance.[10] In the 9,10-anthraquinone series, Osteryoung and co-workers were the first to study their electrochemical behaviour in room temperature chloroaluminate molten salts, namely in mixtures of $AlCl_3$ and 1-ethyl-3-methylimidazolium chloride (ImCl)[11] or *n*-butylpyridinium chloride (BuPyCl).[12] Subsequently, Nikitina's group have studied the electrochemical behaviour of 9,10-anthraquinone in 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4MIM][BF_4]) and in 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4MIM][PF_6]) at a platinum electrode,[13] and Compton's group have looked at the electrochemistry of glassy carbon microelectrodes modified with a multilayer film of 2-anthranyl groups in three different RTILs 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2MIM][NTf_2]), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ([C_4mpyrr][NTf_2]) and trihexyltetradecylphosphonium trifluorotris(pentafluoroethyl)phosphate ([$P_{6,6,6,14}$][FAP]).[14] While Nikitina and col. have reported on two well-resolved, one-electron reduction steps from the quinone to the radical anion and hence to the dianion,[13] as found for quinones under most conditions,[15] Compton and co-workers have found that the size and nature of the ionic liquid influenced the electrochemical behaviour of the bound anthraquinone, as in larger RTILs, steric hindrance inhibits charge compensation near the electrode, leading in certain cases to incomplete reduction to the dianion.[14] Also, Nikitina and co-workers showed an appreciable, specific solvation effect of

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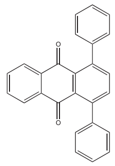
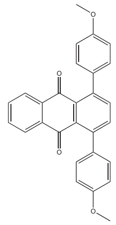
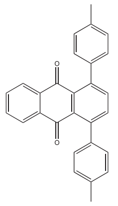
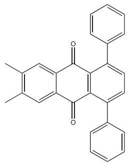
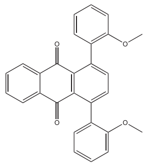
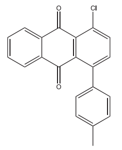
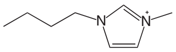
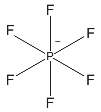
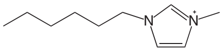
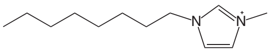
the different RTILs used on the anthraquinone-derived radical anion and the dihydroxyanthracene dianion.[13] This has established redox potential data of 9,10-anthraquinone in the RTILs ([C_4MIM][BF_4]) and ([C_4MIM][PF_6])[13] as an addition to the redox potential data of quinones previously known in a larger variety of organic solvents. Nikitina's group have added to their investigation with computational data that has led to the formulation of solvent-dependent redox-potential scales[16,17] for different quinones that also incorporate RTILs as solvents.[13]

Recently, the authors have developed a simple synthetic strategy to aryl-substituted 9,10-anthraquinones, based on an oxidative cycloaddition of halogenated thiophenes to benzoquinones with a subsequent Suzuki-type arylation of the haloanthraquinone intermediates.[18,19] As a continuation of the characterization of screen printed graphite electrodes (SPGEs) in ionic liquids,[7] this allowed us to investigate the electrochemical response at SPGEs of a number of arylated 9,10-anthraquinones of different sizes and different π-basicity (Fig. 1A) in the three RTILs, 1-butyl-3-methylimidazolium ([C_4MIM][PF_6]), 1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6MIM][PF_6]) and 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]) (Fig. 1B). The dependence of the half wave redox potential of the anthraquinone on the viscosity of the RTIL and therefore on the size of the cation have been tested. Diffusion coefficients are deduced for all tested arylated anthraquinones, together with their solvodynamic radii. Finally, the effect of different substituted groups on the aryl rings was considered in order to investigate how the polarity of the cation of RTIL influences the half wave redox potential.

	
5a: 1,4-diphenyl-9,10-anthraquinone	**5b**: 1, 4-bis-(*p*-methoxyphenyl)anthraquinone
	
5c: 1,4-di-(*p*-tolyl)anthraquinone	**5d**: 1,4-diphenyl-6,7-dimethylanthraquinone
	
5e: 1,4-bis-(*o*-methoxyphenyl)anthraquinone	**5f**: 1-chloro-4-(*p*-tolyl)anthraquinone

1A

RTIL	CATION	ANION
[C_4MIM][PF_6]		
[C_6MIM][PF_6]		
[C_8MIM][PF_6]		

1B

Figure 1. **1A**. The structures of the range of anthraquinones studied. **1B**. Structures of the ionic liquids (RTILs) utilized in this work

EXPERIMENTAL SECTION

All chemicals were of analytical grade and were used as received. RTILs [C_4MIM][PF_6], [C_6MIM][PF_6] and [C_8MIM][PF_6] were obtained from Merck (synthesis reagent). Anthraquinone derivatives were synthesized *via* halogenated thiophenes as precursors.[18] 1,4-diphenyl-9,10-anthraquinone (**5a**),[19] 1,4-bis-(*p*–methoxyphenyl) anthraquinone (**5b**),[19] 1,4-(bis-*p*-methylphenyl)anthraquinone (**5c**),[19] 6,7-dimethyl-1,4-diphenyl-anthraquinone (**5d**),[19] 1,4-bis-(*o*-methoxyphenyl)anthraquinone (**5e**)[19] and 1-chloro-4–(*p*-tolyl)anthraquinone (**5f**),[18] were prepared according to the literature.

Acetonitrile (HPLC grade, from Scharlau), chloroform (from AnalaR NORMAPUR) and tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (from Fluka) were used without further purification.

All anthraquinones examined in this work were weighted using microbalance and then dissolved in chloroform (25 μL), to which ionic liquid (100 μL) was added to obtain an established concentration. Thereafter, the solution was concentrated *in vacuo* overnight at 45 °C in order to remove the organic solvent. Water contents were determined, prior to electrochemical measurements, by coulometric Karl–Fischer titration, and were found to be 0.7 % for [C_4MIM][PF_6] and 0.6 % for both [C_6MIM][PF_6] and [C_8MIM][PF_6].

Cyclic voltammetric (CV) measurements were carried out using a μ-Autolab III (Eco Chemie, The Netherlands) potentiostat/galvanostat, controlled by Autolab, GPES software version 4.9 for Windows XP. All measurements were conducted using a three-electrode configuration, where the working and the counter electrode consisted of graphite ink with a pseudo silver/silver chloride reference electrode and were fabricated in-house.[20] The fabricated SPGEs have a 3.1 mm diameter with a carbon counter electrode and a silver/silver chloride pseudo-reference electrode on a flexible plastic base.[21] The type of carbon ink used in the SPGE preparation was described previously.[22] All electrochemical experiments were carried out under a high purity argon flow (from Air-liquide) in order to keep an inert atmosphere and avoid the electrochemical reduction of oxygen. A reference of ferrocinium/ferrocene (Fc^+/Fc) *versus* Ag/AgCl pseudo-reference electrode was used for all three RTILs. Connectors for the electrochemical connection of the SPGEs were purchased from Kanichi Research Services Ltd. (UK).[23] SPGEs were used as manufactured without further conditioning of the working electrode surface. CVs were carried out at 293 ± 2 K. Ultraviolet–Visible (UV–Vis) spectroscopy analysis was carried out using a UV–Vis spectrometer Shimadzu 2401 PC.

The cyclic voltammetry behaviour of distinct anthraquinones in conventional aprotic solvents such as acetonitrile was compared using a boron-doped diamond (BDD, Windsor Diamonds, U.K.) bare electrode with a 3.0 mm diameter. The counter electrode was a platinum wire, and the pseudo-reference electrode was a silver wire. The BDD electrode's surface was pre-treated before experiments by abrasive erosion using alumina (successively of 1.00, 0.30 and 0.05 μm in diameter) for 5 min for each alumina type used. Thereafter, the electrode was sonicated for 1 min in ultra pure water using an ultrasonic cleaning bath. Then, it was rinsed with acetonitrile and finally dried under an argon atmosphere. All measurements were carried out under an argon atmosphere. A reference Fc^+/Fc *versus* Ag electrode was used for all these measurements.

RESULTS AND DISCUSSION

Synthesis of arylated and halogenated anthraquinones

Shown in Figs. 2A and 2B are details of the synthesis of anthraquinone derivatives used in this study. The preparation of the arylated anthraquinones **5** was carried out following a sequence, developed earlier[18,19] using 2,5-dibromothiophene (**1a**) and 2,5-dichlorothiophene (**1b**) as starting materials. These are treated with *meta* chloroperoxybenzoic acid (*m*-CPBA) in the presence of benzoquinones. The peracid oxidizes the thiophenes **1** to the corresponding thiophene-*S*-oxides, which are very good dienes in Diels–Alder reactions, in contrast to their thiophene parents. *In situ* cycloaddition with the benzoquinones **2** as dienophiles gives the 15-thiatetracyclo[10.2.1.$0^{2,11}$.$0^{4,9}$]-pentadecatetraene-3,10-dione *S*-oxides **3** as intermediates. These can be isolated, but can be made to undergo an oxidative SO-extrusion reaction at slightly elevated temperatures in the presence of *m*-CPBA to give the halogenated 9,10-anthraquinones **4** directly (Fig. 2A). These lend themselves to Suzuki–Miyaura cross-coupling reactions with arylboronic acids, using Pd(0) catalysts, to give the arylated 9,10-anthraquinones **5** (Fig. 2B). It was found that also the chloro-9,10-anthraquinones such as **4c** undergo the cross-coupling reactions effectively, even with the commercial catalyst $Pd(PPh_3)_4$.[19]

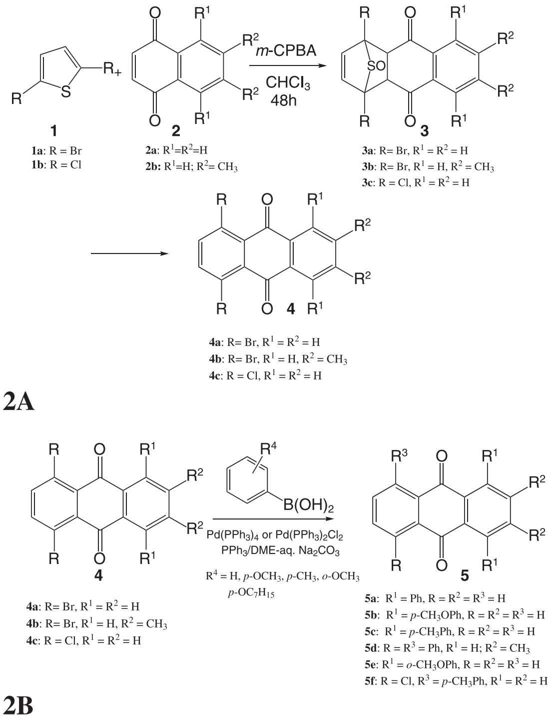


Figure 2. 2A. Reaction mechanism of the synthesis of halogenated anthraquinones. **2B**. Reaction mechanism of the synthesis of arylated anthraquinones **5a – 5 f**

UV–Vis spectroscopy analysis

The UV–Visible spectra of chloroform solutions of most of the arylated anthraquinones show at least three distinct bands, usually associated with π–π^* transitions.[24,25] For a particular study, Fig. SM-1 shows the comparison between UV–Vis spectrums of AQ **5a** and AQ with a C6/C7-methylated anthraquinone core (**5d)** leading to a shift of $\Delta\lambda = 10$ nm and $\lambda = 265$ – 270 nm, in the benzoid band and in 'quinoid band', respectively (Fig. SM-1).

Cyclic voltammetry of anthraquinones 5a and 5d

First, we investigated the cyclic voltammetric response of the redox couple Fc^+/Fc, used for the calibration of the pseudo-reference Ag/AgCl electrode for the three RTILs under study. CV revealed half wave potential ($E_{1/2}$) for the couple Fc^+/Fc of 0.278; 0.444 and 0.322 V *versus* Ag/AgCl for ferrocene in $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$, respectively (Fig. 3). These values are reliable with the number of experiments and the disposable SPGEs. $E_{1/2}$ data for the Fc^+/Fc redox couple do not obey any trend. We have found in the literature how the ionic liquid used might affect the value of formal potential against a pseudo-reference electrode. For example, Nikitina and col.[13] have observed that formal potentials of the Fc^+/Fc couple in $[C_4MIM][BF_4]$ and $[C_4MIM][PF_6]$ RTILs were equal to 0.19 and 0.15 V, respectively, *versus* a platinum pseudo-reference electrode. This difference was found to be 40 mV; here, $E_{1/2}$ difference was 44 mV between $[C_4MIM]$ and $[C_8MIM]$ cations. However, $E_{1/2}$ for the RTIL $[C_6MIM]$ is about 166 mV and 122 mV higher than those presented for $[C_4MIM]$ and $[C_8MIM]$ cations. A plausible explanation for this shifting in $E_{1/2}$ may be ascribed to the viscosity (371, 690 and 866 cP for the $[C_nMIM]$, $n = 4, 6, 8$) and the intrinsic amount of water present in the RTIL.

Ohmic resistances (R_{ohm}) have been calculated from CVs of Fig. 3. In order to compensate the ohmic drop, we have assumed Fe^+/Fe redox couple behaves reversibly in all RTILs tested in this study. For a theoretical CV trace with a value of 59 mV of ΔE between cathodic and anodic peak potentials. Table SM-1 summarizes the solution resistances for all three RTILs tested for experiments carried out upon the first and third scans. Moreover, $E_{1/2}$ data were also compared after ohmic drop correction. Thus, ohmic drop resulted to be almost constant for a wide range of scan rates (10–800 $mV\,s^{-1}$) denoting that deviation from reversibility is not associated to any kinetic component, but just related to the ohmic drop. Furthermore, Table SM-1 points out that $E_{1/2}$ values for the first scan for the three RTILs resulted to be similar, whereas after the reproducible CV traces on the second and third scans, $E_{1/2}$ values were found to be 0.250, 0.417 and 0.269 V for $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$, respectively. However, $E_{1/2}$ value for the $[C_6MIM][PF_6]$ still deviates from the other $E_{1/2}$ values obtained for $[C_4MIM][PF_6]$ and $[C_8MIM][PF_6]$ RTILs.

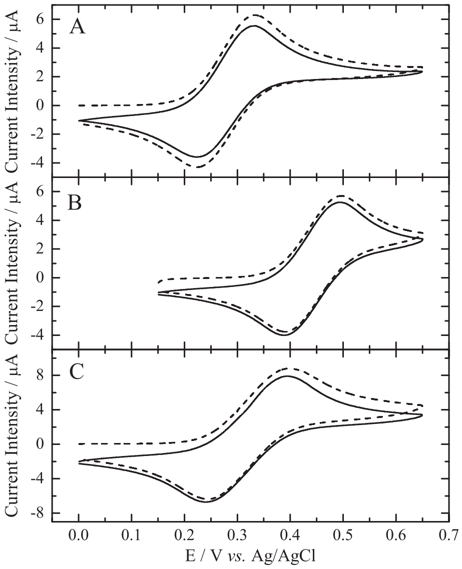


Figure 3. Cyclic voltammograms of ferrocene (A) 5.8 mM in $[C_4MIM][PF_6]$, (B) 6.7 mM in $[C_6MIM][PF_6]$ and (C) 7.6 mM in $[C_8MIM][PF_6]$ obtained at SPGE using 35 μL of sample solution. Scan rate $50\,mV\,s^{-1}$. First scan (dashed line) and third scan (solid line)

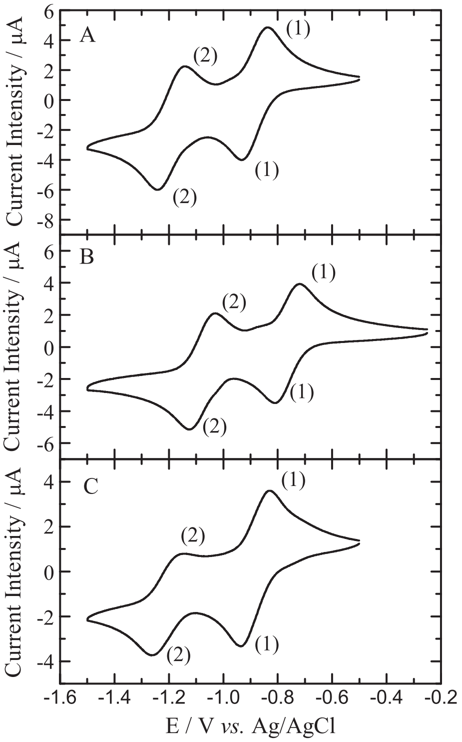


Figure 4. Cyclic voltammograms of (a) 7.81 mM AQ **5a** in $[C_4MIM][PF_6]$, (b) 5.36 mM AQ **5a** in $[C_6MIM][PF_6]$ and (c) 8.43 mM AQ **5a** in $[C_8MIM][PF_6]$ obtained at a SPGE. 35 μL of sample solution. Scan rate $50\,mV\,s^{-1}$. The third scan is shown

Figure 4 shows the CVs for the electrochemical behaviour of 7.81, 5.36 and 8.43 mM AQ **5a** in all three RTILs tested in this study, leading to two continuous one electron processes, leading to the quinone radical anion and subsequently to the dianion, as described previously for the electrochemistry of quinones in RTILs.[26,27] The peak-to-peak separation for the first redox couple (1) at slow scan rate ($20–50\,mV\,s^{-1}$) has an average value of 100 mV, typical of a quasi-reversible electrochemical process while the second redox couple (2) has a peak-to-peak separation close to 107 mV.

The same percentage of the radical anions of AQ **5a** was reduced in the three ionic liquids, as evidenced by the constant $I_p^{c(2)}/I_p^{c(1)}$ ratio, where $I_p^{c(2)}$ and $I_p^{c(1)}$ correspond to the peak currents of the $AQ^{\cdot-}/AQ^{2-}$ and $AQ/AQ^{\cdot-}$ reductions, respectively. In $[C_4MIM][PF_6]$, $I_p^{c(2)}/I_p^{c(1)}$ was found to be 0.69, in $[C_6MIM][PF_6]$ 0.78 and in $[C_8MIM][PF_6]$ 0.62, after base line corrections for a scan rate of $50\,mV\,s^{-1}$. For the second redox couple (2) of AQ **5a**, the ratio of cathodic to anodic currents was close to unity for all three RTILs used, whereas the I_p^c/I_p^a ratio deviated from unity for the first redox couple (1) with a value close to 1.92 for $[C_4MIM][PF_6]$ and 1.76 $[C_6MIM][PF_6]$ and 1.21 for $[C_8MIM][PF_6]$, possibly denoting a lower diffusion coefficient for the radical anion species in RTILs.

A comparison of the differences in the $E_{1/2}$ as a function of the RTIL is summarized in Table 1. $E_{1/2}$ for the first and second redox couples are very similar for the three RTILs under study. The difference in potential between the both half wave potentials $E_{1/2}$ for the processes (1) and (2) is *ca.* - 300 mV (Table 1). This $E_{1/2}$ separation indicates that the thermodynamic tendency of the equilibrium constant *K* for the reaction ($AQ^{2-} + AQ \leftrightarrow 2\,AQ^{\cdot-}$) is relatively small in these RTIL media. The equilibrium constant for the above reaction is given by eqn. (1):[28]

$$\Delta E = E_1^0 - E_2^0 = \frac{RT}{nF}\ln K \qquad (1)$$

where E_1^0 and E_2^0 are the formal potentials for the first and second reduction, respectively. R is the ideal gas constant, T the temperature and F is the Faraday´s constant. Equilibrium constant for the reaction $AQ^{2-} + AQ \leftrightarrow 2\,AQ^{\cdot-}$ was provided assuming that formal potentials for the processes (1) and (2) approximate $E_{1/2}$ data obtained in this study. For an average $E_{1/2}$ separation between processes (1) and (2) of 0.31 V, the equilibrium constant in all three RTILs tested was 8.4×10^{-5}, with a value of ΔG^0 of $-29.9\,kJ\,mol^{-1}$, which is significant. Previous reports by Compton's group studied the comproportionation of benzoquinone in $[C_4MIM][PF_6]$, providing an equilibrium constant with similar values.[28]

The plots of the first cathodic peak current for AQ **5a** in all three RTILs tested as a function of the square root of the scan rate are linear from 0.02 to $1\,V\,s^{-1}$ ($R^2 = 0.99$), which indicates that the process is purely diffusion controlled. These findings were confirmed by Cottrell plots, where the slopes are −0.483, −0.497 and −0.510 for $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$, respectively, values very close to the theoretical value of −0.5. The diffusion coefficient of neutral AQ **5a** species in the RTILs under study is presented in Table 2. Diffusion coefficient values are found to be in the range of 3.7 to $7.9 \times 10^{-13}\,m^2\,s^{-1}$. Interestingly, not much differences were found in the *D* values for $[C_4MIM][PF_6]$ and $[C_6MIM][PF_6]$. By contrast, the *D* value of AQ **5a** in an RTIL with a large ionic cation $[C_8MIM]$ decreases significantly, associated mainly to the higher viscosity of the $[C_8MIM][PF_6]$ RTIL. The authors have tested a range of concentration between 5 and 8 mM for the anthraquinone **5a**. For those concentrations, diffusion coefficients were of the same order for the $[C_6mim][PF_6]$. Any kind of association of the anthraquinone **5a** will lead to remarkable changes in diffusion coefficient values. However, the concentration of anthraquinone is limited to solubility. For example, Nikitina and col.[13] used 8 mM of

Table 1. Anthraquinones examined along with voltammetric potentials for the first (1) and second (2) reduction waves observed in $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$ obtained at a SPGE 35 μL of sample solution media. Scan rate 50 mV s^{-1}. Third scan recorded. All potentials are reported *versus* Fc^+/Fc

AQ/mM	Solvent	$E_c^{(1)}$/V	$E_c^{(2)}$/V	$\|\Delta E\|^{(1)}$/V	$\|\Delta E\|^{(2)}$/V	$E_c^{(2)}-E_c^{(1)}$/V	$E_{1/2}^{(1)}$/V	$E_{1/2}^{(2)}$/V
5a								
7.82	$[C_4MIM][PF_6]$	−1.21	−1.53	0.10	0.11	−0.31	−1.17	−1.47
5.36	$[C_6MIM][PF_6]$	−1.25	−1.57	0.09	0.10	−0.32	−1.21	−1.52
8.43	$[C_8MIM][PF_6]$	−1.26	−1.59	0.11	0.11	−0.32	−1.21	−1.53
5b								
6.32	$[C_4MIM][PF_6]$	−1.21	−1.53	0.09	0.10	−0.32	−1.17	−1.48
5.21	$[C_6MIM][PF_6]$	−1.24	−1.54	0.08	0.08	−0.30	−1.20	−1.50
5.51	$[C_8MIM][PF_6]$	−1.26	−1.60	0.09	0.10	−0.30	−1.22	−1.50
5c								
5.21	$[C_4MIM][PF_6]$	−1.22	−1.54	0.11	0.11	−0.32	−1.16	−1.48
6.20	$[C_6MIM][PF_6]$	−1.25	−1.57	0.09	0.11	−0.32	−1.20	−1.52
6.31	$[C_8MIM][PF_6]$	−1.25	−1.61	0.11	0.12	−0.35	−1.20	−1.54
5d								
5.34	$[C_4MIM][PF_6]$	−1.23	−1.56	0.09	0.10	−0.33	−1.19	−1.51
5.65	$[C_6MIM][PF_6]$	−1.29	−1.62	0.08	0.10	−0.33	−1.25	−1.57
4.75	$[C_8MIM][PF_6]$	−1.28	−1.58	0.08	0.09	−0.30	−1.25	−1.54
5e								
5.25	$[C_4MIM][PF_6]$	−1.29	−1.54	0.11	0.12	−0.26	−1.23	−1.48
5.02	$[C_6MIM][PF_6]$	−1.34	−1.54	0.12	0.13	−0.21	−1.28	−1.48
6.20	$[C_8MIM][PF_6]$	−1.34	−1.63	0.11	0.12	−0.29	−1.28	−1.56
5f								
4.65	$[C_4MIM][PF_6]$	−1.21	−1.47	0.17	0.18	−0.27	−1.12	−1.38
4.82	$[C_6MIM][PF_6]$	−1.23	−1.51	0.17	0.18	−0.28	−1.15	−1.42
5.81	$[C_8MIM][PF_6]$	−1.30	−1.54	0.20	0.20	−0.24	−1.19	−1.43

the 9,10-anthraquinone in $[C_4mim][BF_4]$. The same authors did not mention any possible π–π interaction and association, and therefore they did not study the effect of concentration on the electrochemical behaviour.

Furthermore, Gautrot and col.[29] studied the electrochemical behaviour of several anthraquinones such as 1,4-diphenyl-9,10-anthraquinone, 1,4-dithien-2′-yl-9,10-anthraquinone and 1,4-bis(9′,9′-dioctylfluoren-2′-yl)-9,10-anthraquinone in dichloromethane/0.1 M tetrabutylammonium hexafluorophosphate using a glassy carbon as working electrode. Though anthraquinones tested in the former study had a big aromaticity component, Gautrot's work did not study the effect of concentration on the CV response,

Table 2. Diffusion coefficients (D, $m^2\,s^{-1}$) determined for the studied anthraquinones together with the solvodynamic radius.

AQ	Solvent	$D/m^2\,s^{-1}$	Solvodynamic radius (r_s)/Å
5a	$[C_4MIM][PF_6]$	$(6.2 \pm 0.6) \times 10^{-13}$	11.7 ± 1.0
	$[C_6MIM][PF_6]$	$(7.9 \pm 0.8) \times 10^{-13}$	7.1 ± 0.8
	$[C_8MIM][PF_6]$	$(3.7 \pm 0.3) \times 10^{-13}$	13.0 ± 1.03
5b	$[C_4MIM][PF_6]$	$(8.4 \pm 0.7) \times 10^{-13}$	8.7 ± 0.8
	$[C_6MIM][PF_6]$	$(4.8 \pm 0.4) \times 10^{-13}$	11.7 ± 1.1
	$[C_8MIM][PF_6]$	$(2.9 \pm 0.2) \times 10^{-13}$	16.4 ± 1.3
5c	$[C_4MIM][PF_6]$	$(13.4 \pm 1.2) \times 10^{-13}$	5.4 ± 0.5
	$[C_6MIM][PF_6]$	$(1.5 \pm 0.13) \times 10^{-13}$	36.3 ± 3.4
	$[C_8MIM][PF_6]$	$(1.5 \pm 0.11) \times 10^{-13}$	31.4 ± 2.5
5d	$[C_4MIM][PF_6]$	$(6.6 \pm 0.6) \times 10^{-13}$	11.0 ± 1.1
	$[C_6MIM][PF_6]$	$(5.5 \pm 0.5) \times 10^{-13}$	10.2 ± 1.0
	$[C_8MIM][PF_6]$	$(1.8 \pm 0.13) \times 10^{-13}$	27.2 ± 2.2
5e	$[C_4MIM][PF_6]$	$(2.8 \pm 0.2) \times 10^{-13}$	26.1 ± 2.4
	$[C_6MIM][PF_6]$	$(0.9 \pm 0.10) \times 10^{-13}$	60.8 ± 6.0
	$[C_8MIM][PF_6]$	$(1.3 \pm 0.10) \times 10^{-13}$	37.2 ± 3.0
5f	$[C_4MIM][PF_6]$	$(7.5 \pm 0.5) \times 10^{-13}$	9.7 ± 0.8
	$[C_6MIM][PF_6]$	$(3.0 \pm 0.3) \times 10^{-13}$	18.8 ± 1.9
	$[C_8MIM][PF_6]$	$(1.3 \pm 0.10) \times 10^{-13}$	37.0 ± 2.9

and they do not state either any observation on the π–π interaction between aromatic rings nor association of anthraquinone molecules.

Substitution of positions 6 and 7 of the anthraquinone moiety with methyl groups, as in AQ **5d**, leads to a CV pattern similar to that shown by AQ **5a**. However, here, $E_{1/2}$ values for redox processes (1) and (2) show a very slight enhancement of *ca.* 20–40 mV as compared to the $E_{1/2}$ values of AQ **5a** in all RTIL tested, as depicted in Table 1. Moreover, the *D* values exhibited by **5d** are more similar in [C$_4$MIM][PF$_6$] and [C$_6$MIM][PF$_6$], with 6.6×10^{-13} and $5.5 \times 10^{-13}\,m^2\,s^{-1}$, respectively, and they were of similar magnitude with those presented by AQ **5a** for the same ionic liquids. Additionally, the *D* value of AQ **5d** in [C$_8$MIM][PF$_6$] was significantly lower, with a value of $1.8 \times 10^{-13}\,m^2\,s^{-1}$ (see Table 2). The incorporation of two methyl groups kept unchanged the difference $E_c^{(2)} - E_c^{(1)}$ of *ca.* −300 mV in all three RTILs tested, similar to that previous presented in the literature for anthraquinone in [C$_4$MIM][BF$_4$] RTIL with a value for $E_c^{(2)} - E_c^{(1)}$ of 0.34 V.[30] The same reference[30] gives a value for $E_c^{(2)} - E_c^{(1)}$ of 0.55 V for 9,10-anthraquinone in acetonitrile. Similarly, our value of $E_c^{(2)} - E_c^{(1)}$ obtained from the CV measurements of anthraquinone **5d** in acetonitrile, using a BDD electrode, was 0.53 V. This is shown in the cyclic voltammogram of AQ **5d** (0.62 mmol L^{-1} in acetonitrile, electrolyte: Bu$_4$NPF$_6$) in Fig. 5. A cyclic voltammogram of AQ **5a** under the same conditions provided a reduction peak-to-peak separation of 0.568 V *versus* Fc$^+$/Fc. The higher aprotic character of the solvent as well as the absence of a weak interaction due to ion-pair formation of the anion radical species with the solvent are predominantly the causes for this higher $E_c^{(2)} - E_c^{(1)}$ value, as shown in Table 3.

Cyclic voltammetry of substituted alkyl- and alkoxy-substituted 1,4 diphenylanthraquinone derivatives (5b, 5c, 5e and 5f)

The influence of the substitution pattern of the 1,4-diphenyl groups on the electrochemical behaviour in RTIL was investigated, also. Figure 6 compares the electrochemical behaviour of 1,4-di-*p*-methoxyphenylanthraquinone, AQ **5b** (Fig. 6i), and 1,4-di-*o*-methoxyphenylanthraquinone, AQ **5e** (Fig. 6ii), in which methoxy groups of aryl substituent are located in *para* and *ortho* positions, respectively. Voltammograms show a very well-defined two consecutive one electron processes, as shown previously in Fig. 4 for the anthraquinone **5a**. A comparison of $E_{1/2}$ to the first and second reductive couple of AQs **5a** and **5b** does not show significant differences. The methoxy group at the *para* position does not have a significant influence on the reduction potential. Similar values of $E_{1/2}$ are seen in all RTILs used. A comparison of both anthraquinones **5b** and **5e** reveals a quasi-reversible behaviour for both redox couples. Nevertheless, AQ **5b** showed a remarkable decrease in current intensity for the reoxidative process (2) from the butyl to the hexyl immidazolium cation. Moreover, the $E_c^{(2)} - E_c^{(1)}$ value for AQ **5b** remains similar to those values presented by AQ **5a** and AQ **5d**, whereas the methoxy groups in the *ortho* position led to a notable decrease in the $E_c^{(2)} - E_c^{(1)}$ value of about 100 mV for AQ **5e**, which is indicative of a higher comproportionation constant. The position of the methoxy group is also reflected in the *D* values. This can be seen in Table 2, which shows generally small *D* values for AQ **5e** (between 2.8×10^{-13} and $0.9 \times 10^{-13}\,m^2\,s^{-1}$), with the smallest value in [C$_6$MIM][PF$_6$], while *D* values for AQ **5b** were found to decrease with the size of the RTIL cation. The incorporation of methoxy groups, both in *ortho* and *para* positions, as in AQ **5b** and AQ **5e**, seems to have a significant influence on the *D* values, as can be seen when comparing them to those obtained from AQ **5a**.

Also, we investigated the influence of the methyl groups as substituents, namely 1,4-di-*p*-methylphenylanthraquinone (AQ **5c**). In this case, the substitution has little influence on the half wave potential shift, and hence there is no effect on the peak-to-peak separation (see Table 1). Finally, we studied the electrochemical behaviour of 1-chloro-4-tolylanthraquinone (AQ **5f**) in all three RTILs under study. A comparison between AQ **5c** and AQ **5f** revealed a slight decrease of $E_c^{(2)} - E_c^{(1)}$ values for AQ **5f**, denoted mainly by a reduction of about 100 mV for the second half wave potential of AQ **5 f**. Both anthraquinones **5c** and **5f** show higher values of *D* in the [C$_4$MIM][PF$_6$] RTIL. Strikingly, both AQs showed a notable diminution of *D* values for the hexyl and octyl RTILs, especially for the AQ **5c**. Methylation of the aryl groups resulted in lower *D* values for **5c** in the more highly viscous RTILs as compared to anthraquinone **5a** (see Table 2).

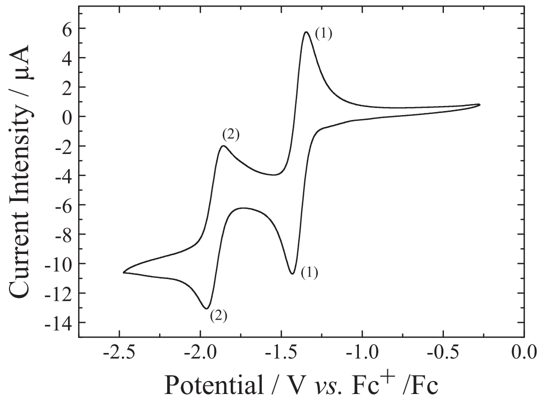


Figure 5. Example of a cyclic voltammogram for one of the anthraquinone tested, 1,4-diphenyl-6,7-dimethyl anthraquinone (**5d**) (0.62 mmol L^{-1}) in Bu$_4$NPF$_6$ (0.1 mol L^{-1}) solution in degassed acetonitrile (scan rate: 50 mV s^{-1}), *versus* Fc$^+$/Fc. The third scan is shown

Solvodynamic radius of anthraquinones

Data from the solvodynamic radii (r_s) provided in this work is useful for a comparison of the values of the molecular radii of isolated π-arylated anthaquinones. The stronger or weaker solvation of our model anthraquinones could be assumed to differences between the solvodynamic radii and the size of the isolated molecule. Additionally, some interpretation is obtained from the solvodynamic radii in terms of number of solvent molecules. Table 2 also shows solvodynamic radii (r_s) of AQs in all three RTILs. The values were obtained from the Stokes–Einstein equation (eqn. (2)):

$$r_s = \frac{K_B T}{4\pi\eta D} \qquad (2)$$

where K_B is the Boltzmann constant, *T* is the absolute temperature and η is the viscosity of the medium. The diffusion coefficients of the different anthraquinones were obtained from the Randles–Sevcik equation[31] in order to work out the solvodynamic radii of the diffusing species. For the calculations

Table 3. Potential data from CV measurements of AQ **5a** and AQ **5d** in degassed acetonitrile solutions (electrolyte: Bu_4NPF_6, 0.1 M; scan rate: 50 mV s^{-1}). All potentials are referred to Fc^+/Fc redox couple. Mostly, ΔE values exhibit quasi-reversible peaks (1) for the first reduction peak and (2) for the second reduction peak. Potential data are given ± 10 mV

AQ/mM	$E_c^{(1)}$/V	$E_c^{(2)}$/V	$\Delta E^{(1)}$/V	$\Delta E^{(2)}$/V	$E_c^{(2)} - E_c^{(1)}$/V	$E_{1/2}^{(1)}$/V	$E_{1/2}^{(2)}$/V
5a 0.58	−1.37	−1.94	0.07	0.14	−0.57	1.34	1.87
5d 0.62	−1.43	−1.96	0.09	0.10	−0.53	1.39	1.91

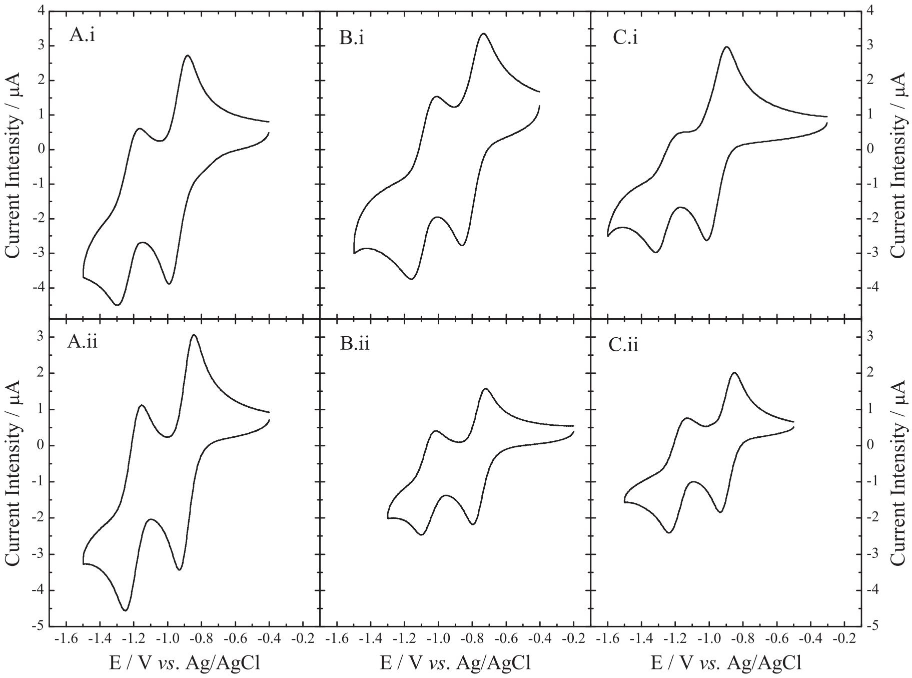


Figure 6. Cyclic voltammograms of 5.08, 7.50 and 6.33 mM 1,4-di-*o*-methoxyphenylanthraquinone (**5e**) (**i**) and 6.32, 5.21 and 5.51 mM 1,4-di-*p*-methoxyphenylanthraquinone (**5b**) (**ii**) in (A) $[C_4MIM][PF_6]$, (B) $[C_6MIM][PF_6]$ and (C) $[C_8MIM][PF_6]$ obtained at a SPGE, 35 μL of sample solution. Scan rate 50 mV s^{-1}. The third scan is shown

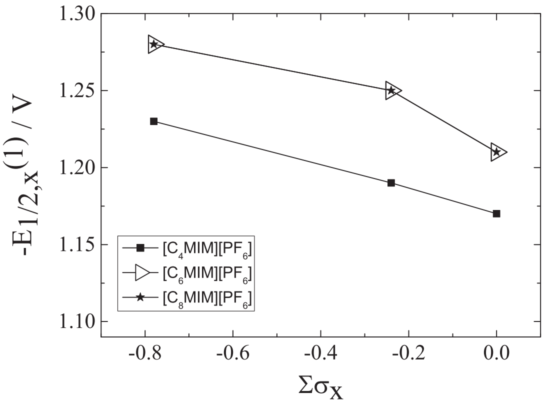


Figure 7. Hammett plots of -$E_{pc}^{(1)}$ *versus* ∑σ for the first reduction of anthraquinones **5a**, **5d** and **5e** in (—■—) $[C_4MIM][PF_6]$, (—△—) $[C_6MIM][PF_6]$ and (—★—) $[C_8MIM][PF_6]$ for the reduction

of r_s values, the viscosities of $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$ were obtained from the literature,[32] with values of 371, 690 and 866 cP, respectively.

In general, a dependence of the solvodynamic radii of all anthraquinones upon the cation size of the ionic liquid was observed. Thus, normally, the solvodynamic radii r_s increase with the length of the alkyl chain in the cation $[C_nMIM]$, with n = 4, 6 and 8. A close match in values was found for r_s of AQ **5a** when compared to that given in the literature for 9,10-anthraquinone, when using $[C_4MIM][BF_4]$ (9 ± 2 Å).[13] Furthermore, a comparison of the r_s values of substituted arylanthraquinone revealed that AQ **5e** provide the highest r_s values. Interestingly, a comparison between AQs **5b** and **5e** shows an effect of the substitution pattern on the phenyl groups (methoxy groups either in *ortho* or *para* position) on the solvodynamic radii. Similar values of the solvodynamic radii for AQ **5a** in all three RTILs tested indicate that there is not a clear-cut relation between the solvodynamic radius and the size of the cation of the RTILs for all AQs, although solvation is normally strongly influenced by the cation orientation and the structure of the neutral anthraquinone.

Polarity of the RTILs and its effect on the half wave potential of arylated anthraquinones

We tried to find out whether a correlation between the first redox potential of the anthraquinones to the anthraquinone radical anion for all distinct anthraquinones studied and the Hammett constants of the substituents exists[33,34] and whether it adheres to the following free-energy relationship (eqn. (3)):

$$E_{1/2,x} - E_{1/2,0} = \Delta E_{1/2} = \rho \sum \sigma_x \qquad (3)$$

where $E_{1/2,0}$ is the half wave potential for the first reduction of the unsubstituted anthraquinone, $E_{1/2,x}$ is the half wave potential for the first reduction of the substituted AQ x, $\sum\sigma_x$ is the relevant Hammett substituent constant and the slope, ρ, is the Hammett solvent-dependent reaction parameter. The ρ value varies according to the polarity of the solvent. Figure 7 shows Hammett plots of $-E_{1/2,x}{}^{(1)}$ *versus* $\sum\sigma_x$ for the first reduction of AQs **5a**, **5d** and **5e** in three RTILs under study. The half wave potential for the first reduction is perfectly linear with the value of $\sum\sigma$ involving anthraquinones **5a**, **5d** and **5e**, only, with a slope values (ρ) of −0.076 for [C$_4$MIM][PF$_6$] and −0.084 for [C$_6$MIM][PF$_6$] and [C$_8$MIM][PF$_6$]. Similar ρ values indicate that the nature of the cation of the RTILs has very little differential effect on the AQ interactions with the RTIL. Moreover, the relatively low values of ρ also reveal that substituents have little effect on the AQs ion pairing interaction with the RTIL. The similar values of ρ also indicate that the polarity of all ionic liquids under study is similar. Deviations from linearity observed in Fig. 7 may be due to a change in the position of the transition state. In such a situation, certain substituents may cause the transition state to appear at less negative potentials or at more negative potentials in the reaction mechanism.[35]

CONCLUSIONS

A detailed report of the redox potentials for 1,4-arylated anthraquinones in the RTILs [C$_4$MIM][PF$_6$], [C$_6$MIM][PF$_6$] and [C$_8$MIM][PF$_6$] on screen printed graphite surfaces has been provided. Redox processes of anthraquinones **5a–d** exhibit reversibility for the first reduction wave, corresponding to the neutral quinones and the quinone radical anions, whereas anthraquinones **5e** and **5f** show a quasi-reversible process. Moreover, the second redox wave for the arylated anthraquinones is quasi-reversible, as gleaned from cyclic voltammetric measurements. The diffusion values of the arylated anthraquinones in the RTILs tested were obtained; it is shown that in general, the diffusion coefficient values were dominated by the cation size of the respective RTIL, and hence its viscosity. However, the nature and position of substituents on the aryl ring of the arylated anthraquinones also played a role, especially in the case of methoxy substituents. Solvodynamic radii were calculated *via* use of the Stokes–Einstein equation, and diffusion coefficients were also estimated by using Randles–Sevcik equation. In general, the solvodynamic radii were found to be dependent on the nature of the RTIL cation and, in some cases, on the position of the substituent on the aryl ring of the arylated anthraquinones. Only the first redox half potentials of anthraquinones **5a**, **5d** and **5e** were found to be a direct function of the corresponding Hammett's substituent constants, irrespective of the RTIL used. Low values of ρ indicate that [C$_4$MIM][PF$_6$], [C$_6$MIM][PF$_6$] and [C$_8$MIM][PF$_6$] exhibited similar polarity.

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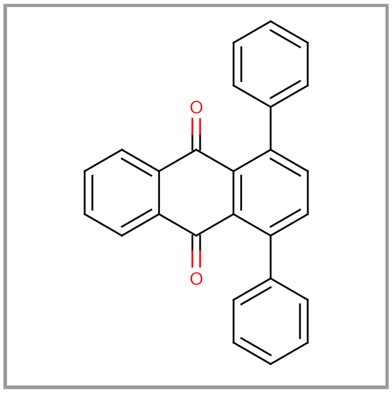
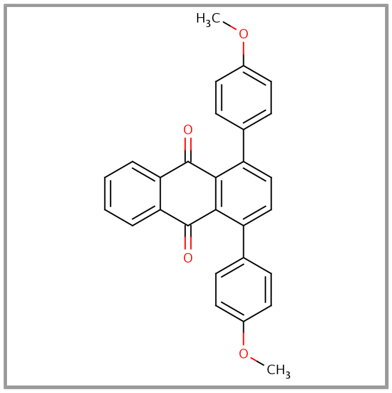
5a



Compound Details Structure Search

5b



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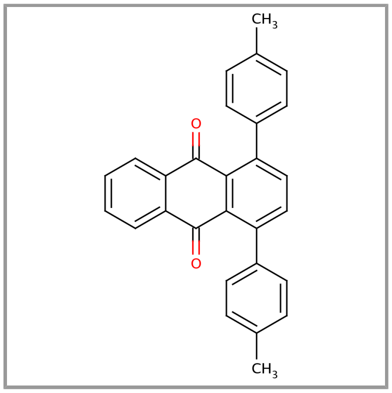

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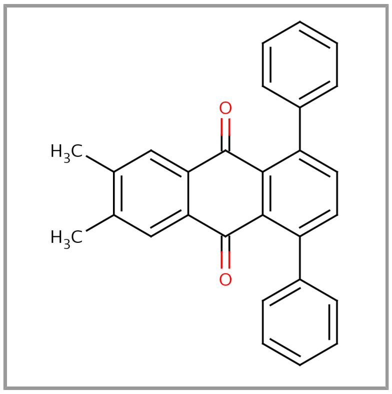

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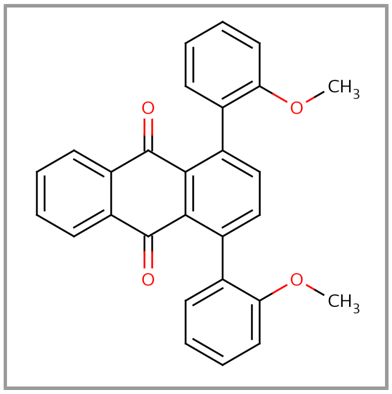

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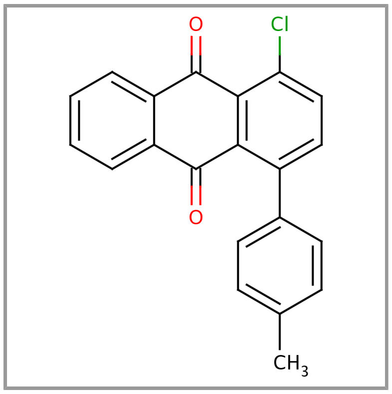

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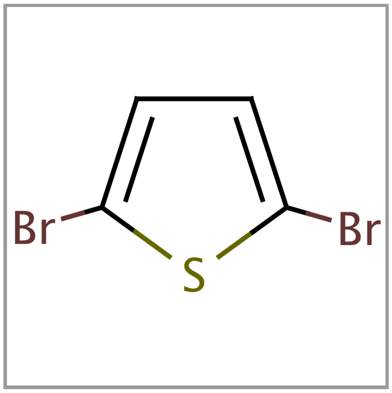

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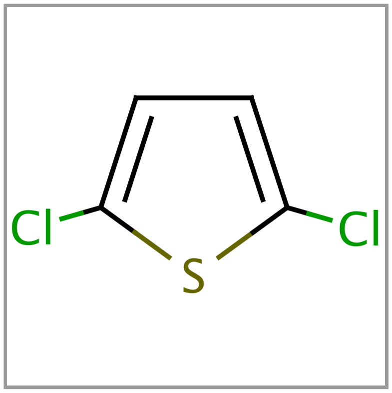

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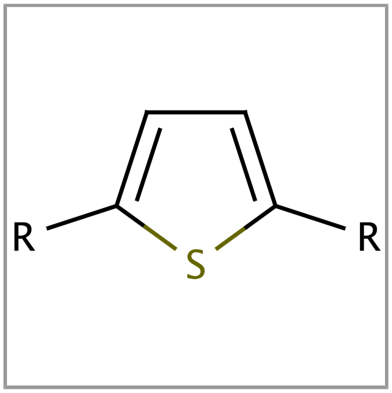

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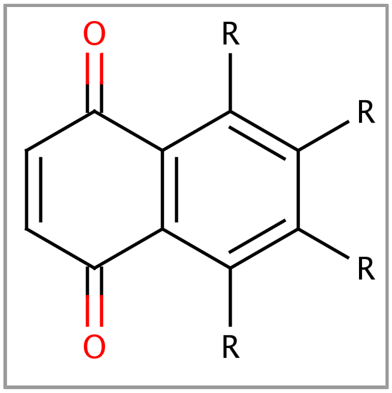
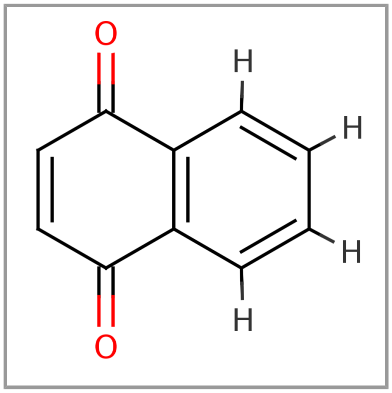


Compound Details Structure Search

2a



Compound Details Structure Search

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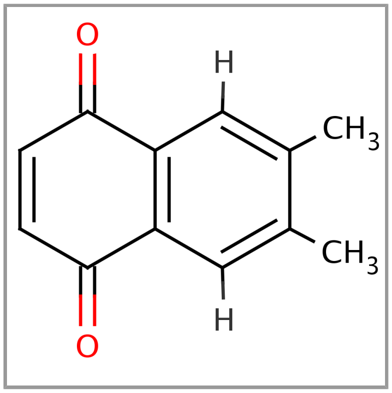

Compound Details Structure Search

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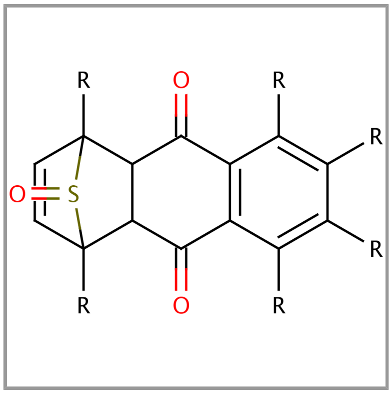
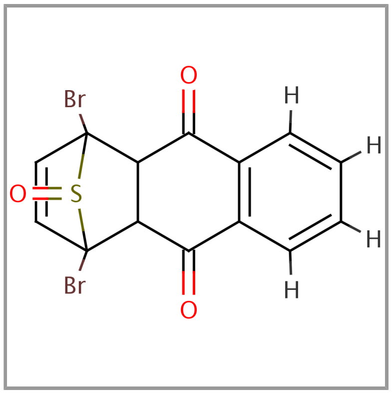


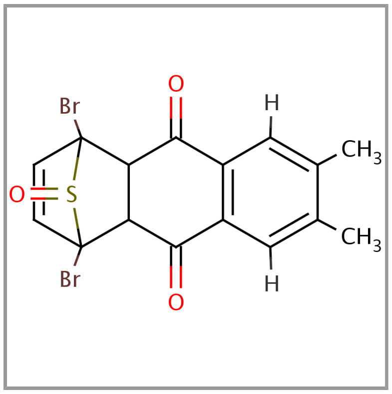
Compound Details Structure Search

3a



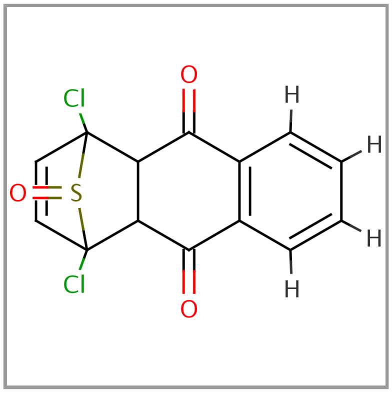
Compound Details Structure Search

3b



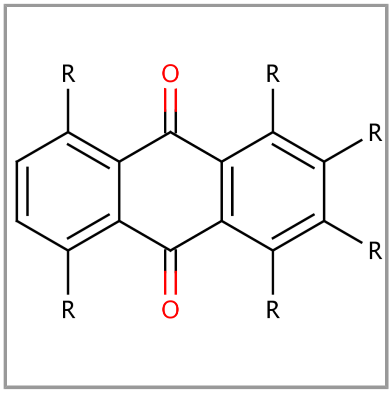
Compound Details Structure Search

3c



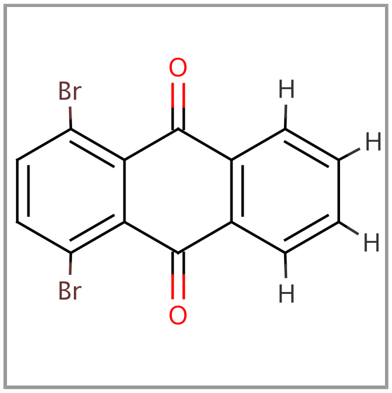
Compound Details Structure Search

4



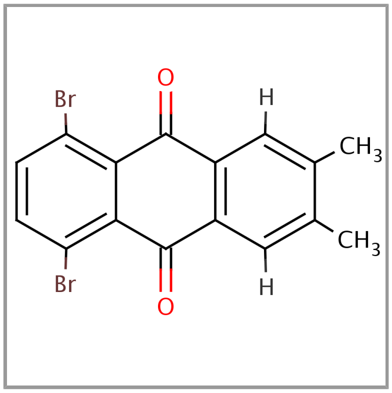
Compound Details Structure Search

4a



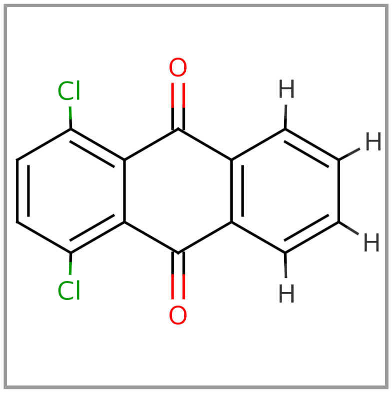
Compound Details Structure Search

4b



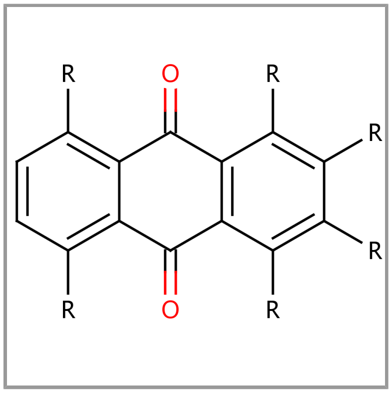
Compound Details Structure Search

4c



Compound Details Structure Search

5



Compound Details Structure Search