ACCESSIBILITY OF ZWITTERIONIC COMPOUNDS FROM PRIMARY AMINES AND 2,5-DIHYDROXY-1,4-BENZOQUINONE

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Following the discovery of an unprecedented transamination reaction between primary alkylamines and a quinonoid molecule of the type $C_6H_2(NHCH_2R)_2(=O)2$ (I), obtained from commercially available diaminoresorcinol.2HCl, we have extended this method to the use of primary arylamines and found that, in contrast, secondary amines led to a different outcome. Whereas functionalized molecules of type **I**, which are best described as 6π +6π zwitterions, were obtained with aniline or 4-methoxyaniline, no transamination was observed with $tBuNH_2$ in ethanol. However, a reaction which afforded salt 2-methylpropan-2-aminium 4-(methylamino)-3,6-dioxocyclohexa-1,4-dien-1-olate (**2b)** took place in water and resulted from hydrolysis of the imine group and deprotonation of 5-hydroxy-2-(methylamino)-4-(methylimino)-cyclohexa-2,5-dienone (**1a)**. Under similar conditions, secondary amines led to comparable results. The cations associated with the anionic quinonoid are readily exchanged in the presence of a primary amine. Whereas for the transamination reaction, basic amines react under mild conditions, slightly harsher conditions are needed for less basic amines such as piperidine, diisopropylamine, or diethylamine. Transamination reactions were also performed with 5-hydroxy-2-(methylamino)-4-(methylimino)-cyclohexa-2,5-dienone (**1a)**, which is more soluble in organic solvents than 2-amino-5-hydroxy-4-iminocyclohexa-2,5-dienone (compound **I**) This led to the first examples of quinonoidal zwitterions functionalized with different alkyl groups on the nitrogen atoms. A number of compounds were characterized by X-ray diffraction, which allowed a better understanding of their electronic situation, and in many cases, the presence of multiple hydrogen-bond donors and acceptors results in crystal packings dominated by these interactions.

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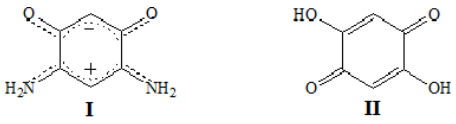
Introduction

Organic compounds containing a quinonoid fragment are of great interest because of their intrinsic properties and their numerous applications in chemistry, physical chemistry and biology.[1-26] In particular, benzoquinonemonoimines have been found to display unique properties in various areas such as coloring,[27] organic,[28,29] supramolecular,[30] coordination, organometallic chemistry[30,31,38,39] and homogeneous catalysis.[32-37] Previous studies have shown that the reactions between alkylamines or arylamines and benzoquinone gave a trans-dialkylaminobenzoquinone or trans-diarylamino-benzoquinone and monoarylamino products.[40-41] Similar reactions with 2,5-dihydroxybenzoquinone have been achieved yielding trans-dialkylaminobenzoquinone and diarylaminobenzoquinone products whose nickel complexes are very active in catalysis.[42] Benzoquinonemonoimines were obtained by transamination reaction of alkyl and arylamines with specific reactants like diaminoresorcinol dihydrochloride or by esterification reaction followed by reduction.[38] The aim of this paper is to show that trans-dialkylaminobenzoquinone and diarylaminobenzoquinones can be obtained with 2,5-dihydroxybenzoquinone at high temperature. Benzoquinonemonoimines products can be obtained by classical condensation reaction followed by nucleophilic substitution of alkylamines with 2,5-dihydroxybenzoquinone.



I II

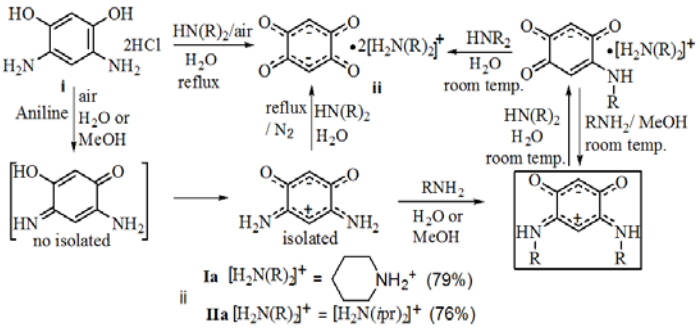
Scheme 1. A zwitterion 6π + 6 π electrons (**I**) and a precursor of zwitterion 12π electrons (2,5-dihydroxy benzoquinone) (**II**).

The first member of this family of 12π-electron quinine was the dianion ligand resulting from deprotonation of compound **II**. The compound **I** is a zwitterion type involving 6π + 6 π electrons chemically not but electronically connected (Scheme 1).

From these reactions, it's possible to convert **I** to **II** by hydrolysis reactions with bulky primary amines or secondary amines in water. The zwitterionic products obtained by reaction of **I** with primary alkylamines were isolated from the reactions of **II** and primary alkylamines at room temperature. The para aminoalkyl-1,4-benzoquinone were obtained after reflux or a long time reaction from **II**.

Result and discussion

The dianionic salts were obtained by hydrolysis reactions of benzoquinonemonoimine in an aqueous solution containing the primary or secondary alkylamine (Scheme 2).



Scheme 2. Amination and hydrolyzed reactions on the parent quinonmonimine zwitterion

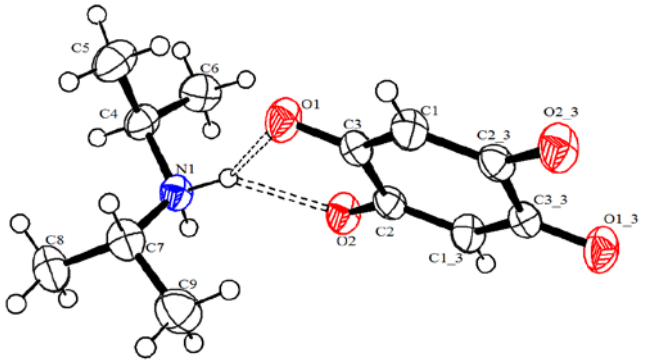
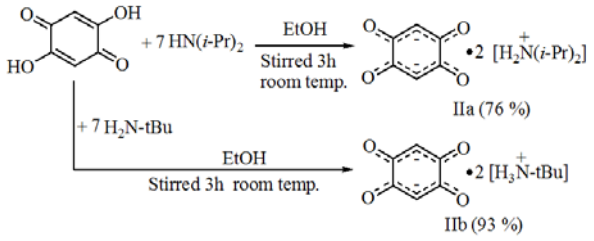


Figure 1. Partially labeled plot of compound **IIa**. Dashed lines indicate H-bonding interactions. The thermal ellipsoids are shown at 50% probability.

The first alkylamine selected for the synthesis of functionalized 2,5-dihydroxy-1,4-benzoquinone was *t*-butylamine. Using a large excess of *t*-butylamine, a dianionic salt was obtained with a yield of 93 % (Scheme 3). The reaction of 2,5-dihydroxy-1,4-benzoquinone **II** with the bulky primary and secondary amine, respectively (NH_2-*t*Bu) and NH(*i*-Pr)$_2$ resulted in the deprotonation of the dihydroxybenzoquinone (Scheme 3).

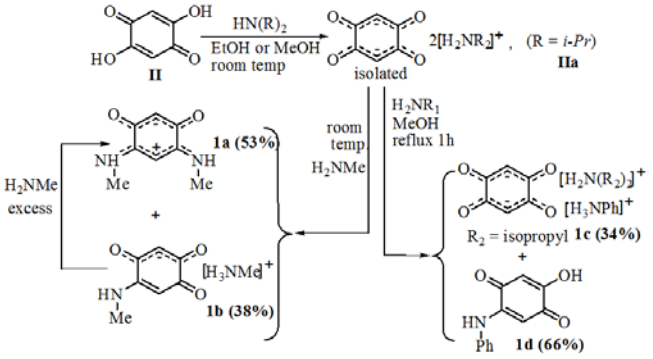


Scheme 3. Encumbered primary amine and secondary amines effect on the 2,5-dihydroxy-1,4-benzoquinone

On the course, except the *t*-butylamine, all primary alkylamines react by transamination on the parent zwitterion **I**. Probably the steric effect of these amines is low. In the alcohol solution, ^{t}BuNH$_2$ react with 2,5-dihydroxy-1,4-benzoquinone to afford an organic salt **IIb**. The NMR data show one singlet for *O···C···CH* group at 5.74 ppm for **IIb**, 5.15 ppm for the first dialkylamine **IIa** (76% yield). The ^{13}C{^{1}H} NMR spectra reveal signals at 115.29 ppm for **IIb** and 101.46 ppm for **IIa** for CH group (*O···C···CH*). The chemical shift of *O···C* group was shown at 181.88 ppm for **IIb** and 181.75 ppm for **IIa**, which was confirmed by single-crystal X-ray diffraction (**Figure 1**). All crystal structures determined in the course of this work are discussed in a separate paragraph (see below).

Surprisingly, when organic salt **IIa** was treated with MeNH$_2$, a complete transamination product **1a** and uncomplete transamination product **1b** was observed. In alcohol or water, **1b** can react with the excess of MeNH$_2$ to afford the product **1a** (see Scheme 2). The NMR spectra of these two products were described in analog reaction in our previous work.[44] In this optic, the organic salt **IIa** was treated by an excess of aniline under reflux in methanol.

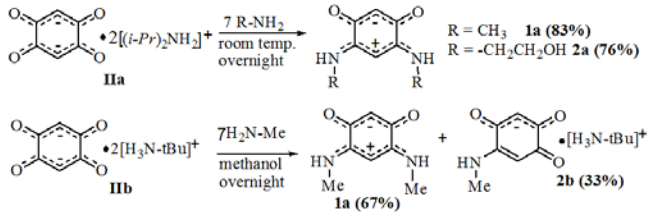
Two products were isolated. The organic diammonium salt [NH$_2$(*i-Pr*)$_2$(PhNH$_3$)(C$_6$H$_2$O$_4$)] (**1c**) was observed as a solid compound while the filtrate solution afforded the monoamino derivative (2-hydroxy-5-(phenylamino)-cyclohexa-2,5-diene-1,4-dione [(PhNHC$_6$H$_3$O$_3$)] (**1d**) (Scheme 4). The ^{1}H NMR spectra contain two signals at 5.74 and 5.84 ppm, which are characteristic of the CH groups of the substituted benzoquinone fragment (N-C=CH and O=CH-C, respectively). ^{13}C{^{1}H} NMR spectroscopic data show two signals for the CH groups, and the one corresponding to N-C=CH shift to 95.80 ppm, downfield with respect to that of the zwitterion. The O=C-**CH**=C-OH resonance was found at 103.97 ppm. The quaternary carbon atoms give rise to five singlets, two of them corresponding to the two O=C carbon atoms with very close chemical shifts to 180.38 and 182.68 ppm. One of the single bond HO-C is shifted to 161.03 ppm. In the aromatic ring, the quaternary carbon atoms give two singlets corresponding to N-C= and =C-N bonds shifted to 146.11 and 137.71 ppm respectively.



Scheme 4. Mono and di-condensation reactions between organic salt and methyl and arylamine

The **IIa** was reacted at room temperature during 3 h with methylamine to form **1a** and with the (2-hydroxyethyl)amine to give **2a**. Both zwitterions **1a** and **2a** have been characterized in the course of previous work.[33] The salt **IIb** reacts with methylamine in methanol solution at room temperature to afford a mixture of **1a** and the organic

salt [(NH_3-tBu)($C_7H_6O_3$)] (**2b**). The **2b** compound can be obtained by hydrolysis reaction of **1a** with tert-butylamine in water from a mixture of **2b** and [(NH_3-Me)($C_7H_6O_3$)] (**1b**) (Scheme 5). In dichloromethane solution, it's possible that the **1b** exchange the methylammonium cation by tert-butylammonium cation yielding **2b**. Surprisingly, **1b** reacts by condensation and transamination reaction with methylamine to afford **1a**. The same compound was obtained by condensation reaction between the organic salt **IIa** or **IIb** and alkyl amines. From the compound **IIa**, it's possible to access the zwitterionic compounds by condensation reactions between **IIa** and primary alkyl amines (methylamine) (**1a**) or (2-aminoethanol) (**2a**). It's an interesting route to access from the quinonemonoimines to products obtained exclusively by transamination reactions or by a more efficient synthesis subsequently developed, which involved the diaminoresorcinol acylation followed by reduction by $LiAlH_4$.[26]



Scheme 5. Reactivity of monoalkylamines on the organic salts by direct condensation reaction

Herein, we report that the scope of this reaction can be extended to primary arylamine. In contrast, secondary amines afforded only organics salts. Gratifyingly, $^tBuNH_2$ reacted at room temperature in methanol, within 1 h, to yield the corresponding salt of type **IIb**, in 93 % yield. Its ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data are consistent with the expected structure, which was confirmed by single-crystal X-ray diffraction (**Figure 2**).

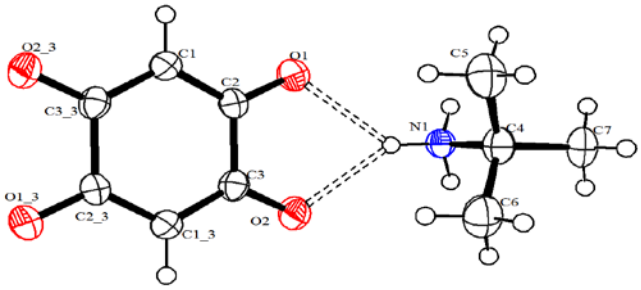
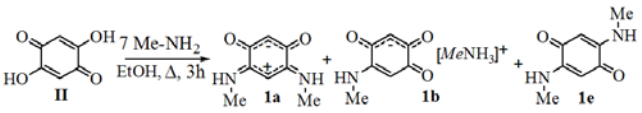


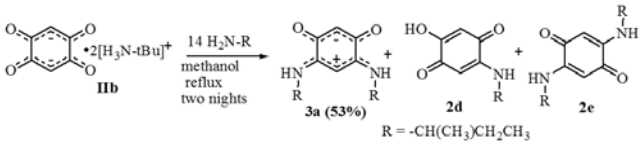
Figure 2. Partially labeled plot of compound **IIb**. Dashed lines indicate H-bonding interactions. The thermal ellipsoids are shown at 50 % probability.

The reaction of **II** with methylamine was performed under reflux within 3 h, whereas the reaction with diisopropylamine afforded **IIa** at room temperature**.** The monoanionic salt **1b** which was previously isolated acts as a reaction intermediate in the conversion of **1a** into **1e** (Scheme 6).



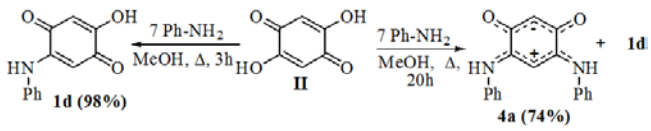
Scheme 6. Reactivity of methylamine on the 2,5-dihydroxy-1,4-benzoquinone giving free different products

Knowing that **1a** reacts with primary amines by transamination reaction, we verified that aniline is not basic enough to perform this transformation. Upon crystallization of the reaction mixture, **1a** was indeed recovered, but the composition of the crystals was found to be [(**1a**)$_2$PhNH$_2$].[44] Another zwitterionic benzoquinonemonoimine was obtained by a condensation reaction between the corresponding alkylamine and the organic salt **IIb** (Scheme 7). The sec-butylamine and organic salt **IIb** react under reflux for overnight to yield three products **3a**, **2d** and **2e**. The main product **3a** was obtained after dissolved the crude product in chloroform solution. The ^1H NMR of **3a** reveal signals of the quinonoid fragment at 5.14 (s, 1H, N···C···C**H**), 5.48 (s, 1H, O···C···C**H**), 8.10 (br s, 2H, 2N**H**). $^{13}C\{^1H\}$ NMR 80.52 (s, N···C···**C**), 98.85 (s, O···C···**C**), 155.73 (s, N···**C**), 172.23 (s, O···**C**). For **2d**, two singlets at 5.42 (s, 1H, N-C=CH) and 5.90 (s, 1H, O=C-CH) were revealed, while one singlet is obtained for the **2e** product at 5.97 (s, 2H, O=C-CH).



Scheme 7. Obtaining symmetrical zwitterionic and two neutrals organics products

The reaction of **II** with excess of aniline yield the monoarylamino derivative **1d** after 3 hours under reflux. Progressively **1d** was converted into the zwitterionic 3-hydroxy-4-(phenylamino)-6-(phenylimino)cyclohexa-2,4-di-enone derivative **4a** (Scheme 8).

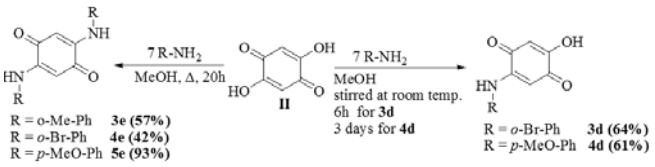


Scheme 8. Effect of reflux time on condensation between aniline and 2,5-dihydroxy-1,4-benzoquinone

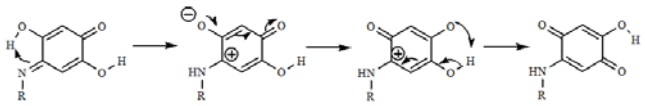
This species **4a** was only observed from **II** and aniline reaction. Other similar reactions give p-diamino-1,4-benzoquinone products. It's observed that the substituted arylamines have high reactivity with the reagent **II**. The product **4a** was obtained[56] from the other transamination reaction between the parent zwitterion **I** and an excess of aniline in the ethanol solution under reflux. The products **1d** (98 %), **3d** (64 %) and **4d** (61 %) were isolated with high purity. The {^1H} NMR spectra of these products contain singlets at 5.13 (s, 1H, N-C=C**H**); 5.87 (s, 1H, O=C-C**H**) for

3d and at 5.57 (s, 1H, N-C=C**H**); 5.81 (s, 1H, O=C-C**H**) for **4d** (Scheme 9).

These monoaminohydroxybenzoquinones products were considered like intermediaries of reactions synthesis between reagent **II** and alkylamines. For a long time or under reflux, these reactions lead only the trans-diarylamino-1,4-benzoquinones. When **II** was reacted with substituted anilines, such as *o*-$MeC_6H_4NH_2$, *o*-$BrC_6H_4NH_2$, *o*-$ClC_6H_4NH_2$, and (*p*-MeO)$C_6H_4NH_2$ the corresponding disubstituted diamino benzoquinones respectively **3e, 4e** and **5e** were isolated. The yield was respectively, 57; 42 and 93 %. We noted from the NMR spectra that the monoamino derivatives **3d** and **4d** were found to be intermediates in the synthesis of **4e** and **5e** respectively. A mechanism of the monocondensation is achieved in Scheme 10.



Scheme 9. Obtaining different products under reflux and at room temperature



Scheme 10. Mechanism of monocondensation with the formation of 2-hydroxy-5-(arylamino)-1,4-benzoquinone

X-ray crystal structure determination for IIa and IIb

The title compounds **IIa** and **IIb** crystallize in the monoclinic space group $P2_1/c$, with one complete zwitterion comprising the asymmetric unit. The two ammonium groups are orientated *trans* with respect to the plane of the central 3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate) ring. Intramolecular interactions within the solid-state structure of the zwitterion are between the two oxygen atoms of each side of the central ring and one H atoms of the nitrogen atom of the ammonium groups. The distances C—O, which are in the range 1.256(2)–1.2667(19) Å are indicative of a bond character slightly different from a double bond (Table 1). In both rings, two moieties of O···C···C···C···O which contain a fully delocalized 6π electrons system are connected by two single bonds with distances of 1.531(3) Å and 1.526(3) Å respectively in **IIa** and **IIb**. These facts show that the non-conjugation of the two 6π electrons systems in the central rings of the zwitterions. As shown by the torsion angles (Table 1) whole atoms of the rings are quasi- coplanar. The torsions angles are slightly different from the ideal angle of 180° and 0° in the planar ring.

Experimental

Chemical reagents in high purity were purchased from Merck and Aldrich and were used without further purification.

Table 1. Selected bond lengths (Å) and torsions angles (°) for the central ring **IIa** and **IIb**

IIa		**IIb**	
O1—C3	1.256(2)	C3—O2	1.259(2)
O2—C2	1.2677(19)	C2—O1	1.261(2)
C1—C2i	1.385(3)	C3—C1i	1.395(2)
C1—C3	1.402(2)	C1—C2	1.394(2)
C2—C3	1.531(3)	C2—C3	1.526(3)
C2i—C1—C3—O1	−178.8 2)	C2i—C1—C3—O2	-179.1(2)
C2i—C1—C3—C2	0.7(3)	C2i—C1—C3—C2	1.0(3)
O2—C2—C3—O1	−1.0(3)	O1—C2—C3—O2	-1.1(3)

The ^1H NMR spectra were recorded at 300 MHz and $^{13}C\{^1H\}$ NMR spectra at 75 MHz on a Bruker AC-300 instrument. Mass spectra were recorded with a Bruker Daltonics microTOF (ESI; positive and/or negative mode; capillary voltage: 4.8 kV; nebulizer pressure: 0.2 bar; desolvation temperature: 180°C; desolvation gas flow rate: 4.5 L/min). Elemental analysis was performed by the Service de Microanalyse, Université de Strasbourg (Strasbourg, France) and the Service Central d'Analyse (Lyon, France).

X-ray data collection, structure determination and refinement

Single crystals of **IIa** and **IIb** were grown by slow evaporation of MeOH solution. A suitable crystal was selected and mounted on a Bruker APEX-II CCD diffractometer with graphite monochromatized MoKα radiation (λ = 0.71073 Å). The crystal was kept at 173(2) K during data collection. Details of the X-ray crystal structure solution and refinement are given in Table 1. The structure was solved with the *SHELXT*[45] structure solution program using direct methods and refined with the *SHELXTL*[46] Software Package. Molecular graphics were generated using *ORTEP-3*.[47]

Synthesis of the compounds

Compound Ia: dipiperidinium 3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate)

Piperidine (0.43 g, 5.07 mmol) was added to a water (30 mL) solution of 2-amino-5-hydroxy-4-iminocyclohexa-2,5-dièнone (0.1 g, 0.724 mmol). The mixture was heated to reflux for five hours. After cooling the solution was washed with dichloromethane solution (3 x 10 mL) then the excess of piperidine was eliminated. The aqueous phase was evaporated and a red solid was obtained (0.178 g, 79 %)

^1H (300 MHz, dmso-d_6) δ(ppm): 8.363 (m, 4H, $2NH_2^+$); 4.969 (s, 2H, N-C=CH-C=O); 2.943 (t, 8H, -CH_2-N-CH_2-); 1.60 (tt, 8H, -CH_2-CH_2-CH_2-); 1.55 (tt, 4H, -CH_2-CH_2-CH_2-)

Table 2. Data collection and refinement parameters for **IIa** and **IIb**

	IIa	**IIb**
Formula	$C_{18}H_{34}N_2O_4$	$C_{14}H_{26}N_2O_4$
M_r	342.47	286.37
Cell setting, Space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a, b, c (Å)	8.7510(6), 9.8940(6), 13.6680	8.4560(10), 7.3850(9), 15.0882(12)
β (°)	122.505(3)	116.893(6)
V (Å^3)	998.02(11)	840.32(6)
Z	2	2
D_x (Mg m^{-3})	1.140	1.132
μ (mm^{-1})	0.08	0.08
Crystal size (mm)	0.18x0.14x0.12	0.22×0.20×0.10
meas.,indep., obs. refl.	3761, 2277, 1073	2517, 1590, 968
R_{int}	0.0579	0.092
θ_{max} (°)	27.485	26.32
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0571, 0.1416, 0.94	0.0534, 0.1517, 0.99
Parameters	117	106
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.18, –0.212	0.21, –0.23

^{13}C (75 MHz, dmso-d_6), δ(ppm): 179.275 (O-C-CH-C-O); 99.86 (O-C-CH); 43.84(s, CH_2-N-CH_2-); 22.09 (s, CH_2-CH_2-CH_2-); 22.54 (s, CH_2-CH_2-CH_2-). RMN ^{13}C-DEPT 135 (75 MHz, dmso-d_6), δ(ppm): 99.86 (O-C-CH-C-O); 43.84 (s, CH_2-N-CH_2-); 22.09 (s, CH_2-CH_2-CH_2-); 22.54 (s, CH2-CH_2-CH_2-). Anal. Found C, 50.82; H, 6.91; N, 7.26. Calc. for $C_{17}H_{26}N_2O_4 \cdot CH_2Cl_2$ C, 51.65; H, 7.14; N, 7.09.

Compound IIa: diisopropylammonium 3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate)

Diisopropylamine (1.53 g, 15.16 mmol) was added to an ethanol (10 mL) solution of 2,5-dihydroxy-1,4-benzoquinone 1 (0.304 g, 2.17 mmol). Immediately a precipitate appeared in the mixture which is stirred for 3h. The pink solid product was filtered, washed with diethyl ether (2 x 40 mL) and then dried. The product was obtained as a pink solid (0.57 g, 1.66 mmol, 76 %). Suitable crystals for X-ray diffraction were obtained by slow evaporation of an ethanol solution of the product. From the zwitterionic reactant, this product was obtained after reflux in water.

^{1}H NMR (300 MHz, dmso-d_6), δ(ppm): 5.15 (s, 2H, O-C-CH); 3.24-3.25 (m, 4H, -CH-NH_2^+); 1.14 (d, 24H, CH_{3iPr}). ^{13}C{^{1}H} NMR (75 MHz, D_2O), δ(ppm): 18.28 (s, CH_3ipr); 47.22(s, CHipr); 101.46 (s, O-C-CH); 181.75 (s, O-C). These ammonium salts react with primary amines to lead symmetric zwitterionic compounds.

Compounds IIb: 2-methylpropan-2-aminium 3,6-dioxocyclo-hexa-1,4-diene-1,4-bis(olate)

Tert-butylamine (1.096 g, 14.98 mmol) was added to an ethanol (20 mL) solution of 2,5-dihydroxy-1,4-benzoquinone 1 (0.3 g, 2.14 mmol). Red precipitate was immediately formed. The reaction mixture was stirred at room temperature for 3h and then filtered. The red solid was washed with diethyl ether (4 x 20 mL) and air dried (0.57 g, 1.99 mmol, 93 %). Suitable crystals for X-ray diffraction were obtained by slow evaporation of an ethanol solution of the product.

^{1}H NMR (300 MHz, dmso-d_6), δ(ppm): 5.74 (s, 2H, O-C-CH); 1.20 (s, 18H, -CH_3). ^{13}C{^{1}H} NMR (75 MHz, dmso-d_6), δ(ppm: 26.57 (s, CH_3); 51.86 (s, C_{tBu}) 115.29 (s, O-C-CH); 181.88 (s, O-C).

Compound 1a: 5-hydroxy-2-(methylamino)-4-(methylimino)-cyclohexa-2,5-dienone and compound 2b: 2-methylpropan-2-aminium 4-(methylamino)-3,6-dioxocyclohexa-1,4-dien-1-olate from the tert-butylammonium salt (IIb):

Methylamine (0.152 g, 4.89 mmol) was added to an ethanol (20 mL) solution of the salt 2 (0.2 g, 0.698 mmol). The mixture was stirred for 24 hours at room temperature. The mixture was checked by NMR ^{1}H analysis after the solution was evaporated under reduced pressure. A brown solid was analyzed by NMR ^{1}H, which shows the formation of two products 1a (67%) and 1b (33 %). After stirring for three nights, 1a was afforded.

Compound 1a: ^{1}H NMR (300 MHz, dmso-d_6), δ(ppm): 2.99 (s, br, 6H, CH_3); 4.93 (s, 1H, N-C-C-H); 5.32 (s, 1H, O-C-C-H); The broad signal of NH is not observed near to 9.13 ppm. ^{13}C NMR (75 MHz, dmso-d_6), δ(ppm) = 29.57(s, CH_3); 81.26 (s, N-C-C-H); 97.42(s, O-C-C-H); 156,80(s, C-N); 172,12(s, C-O). Compound 2b: δ(ppm): 1.22 (s, 9H, CH_{3tBu}); 2.70-2.68 (d, 3H, ^3J = 4.98 Hz, CH_3); 4.88 (s, 1H, N-C=C-H); 4.90 (s, 1H, O-C-C-H); 7.24 (br s, 1H, NH) ; 7.86 (br s, 3H, NH_3).

Compound 1a: 4-(methylamino)-6-(methylimino)-3-oxocyclohexa-1,4-dien-1-olate and 1b: methylammonium 6-(methylamino)-3,4-dioxocyclohexa-1,5-dien-1-olate from the 2,5-dihydroxy-1,4-benzoquinone (II):

Methylamine (0.31 g, 10 mmol) was added to an ethanol (20 mL) solution of 2,5-dihydroxy-1,4-benzoquinone 1 (0.2 g, 1.43 mmol). Immediately a precipitate was formed (acid-basic reaction). The reaction mixture was stirred under reflux during 3h and a clear red solution is obtained. After cooling, the red solution was reduced by slow evaporation. The product was precipitated in diethyl ether (2x30 mL). The crude brown solid was obtained by filtration then dried under reduced pressure. The crude mixture was composed of two products **1a** and **1b**. The ^{1}HNMR analysis shows results in accordance with those reported above for **1a**.

Compound 1b: ^{1}H NMR (300 MHz, dmso-d_6), δ(ppm): 2.37 (s, 3H, CH_3); 2.69-2.70 (d, 3H, ^{3}J = 4.83 Hz, CH_3); 4.94 (s, 1H, N-C=C-H); 4.99 (s, 1H, O-C=C-H); 7.28 (s, 1H, NH); 7.67 (br s, 3H, NH_3).

The diethyl ether solution was evaporated and a small quantity of product was obtained. The ^{1}H NMR analysis of this product revealed to be a mixture of **1a** and **1e**. The crude product was suspended in dichloromethane (20 mL) and stirred at room temperature during 1 h. The solid obtained after filtration is essentially constituted by **1a** (0.14 g, 0.76 mmol, 53 %). The product **1b** (0.09 g, 0.54 mmol, 38 %) was obtained by evaporation of dichloromethane solution.

Compound 1a: 4-(methylamino)-6-(methyliminio)-3-oxocyclohexa-1,4-dien-1-olate

Methylamine (0.125 g, 4.08 mmol) was added to an ethanol (20 mL) solution of the diisopropylammonium salt of 3,6-dihydroxy-1,4-benzoquinone (**IIa)** (0.2 g, 0.58 mmol). The reaction mixture was stirred at room temperature for two days. The solvent was evaporated and the remaining solid was washed with diethyl ether (2x10 mL). The product was obtained as a brown solid (0.08 g, 0.48 mmol, 83 %). The ^{1}H NMR spectrum analysis revealed that this product contained essentially the compound 1a.

Direct synthesis of compound 1d: 2-hydroxy-5-(phenyl amino) cyclohexa-2, 5-diène-1, 4-dione

Aniline (0.46 g, 4.97 mmol) was added to a methanol (20 mL) solution of 2,5-dihydroxy-1, 4-benzoquinone **II** (0.1 g, 0.71 mmol). The reaction mixture was heated to reflux during 3h. The solvent was removed in vacuum, and the crude solid was washed with pentane (4 x 20 mL). The product was obtained as a purple solid 1d (0.15 g, 0.697 mmol, 98 %).

^{1}H NMR (300 MHz, dmso-d_6), δ(ppm): 5.74 (s, 1H, N-C=C-H); 5.84 (s, 1H, O=C-C-H); 7.20-7.22 (t, 1H,CH) ; 7.36-7.42 (m, 4H, CH_{Ar}) ; 9.24 (s, 1H, NH); 11.21 (s, br 1H, OH). ^{13}C{^{1}H} NMR (75 MHz, dmso-d_6), δ(ppm): 95.80(s, C-C=N) ; 103.97 (s, O=C-C-H) ; 123.49 (s, CH) ; 125.36 (s, CH); 129.14(s, CH); 137.71(s, Cq); 146.11 (s, C-N) ; 161.03 (s, C-O) ; 180.38(s, C=O); 182.68 (s, C=O). The mass spectrum indicates different fragments corresponding to cationic molecules MS (ESI$^+$): m/z = 222.074(15) {[M+Li]$^+$, 15 %, [$C_{12}H_9LiNO_3$]$^+$}; m/z = 228.082 ([{(M-H)+Li}+Li]$^+$, 11 %, {$C_{12}H_9Li_2NO_3$}$^+$); m/z = 238.048 ([M+Na]$^+$, 9 %, {$C_{12}H_9NaNO_3$}$^+$); m/z =244.056 ([{(M-H) + Li} + Na]$^+$, 2 %, {$C_{12}H_9LiNaNO_3$}$^+$). Anal. Calcd. for $C_{12}H_9NO_3.4/3H_2O$: C, 60.25; H, 4.92; N, 5.86; found C, 60.92; H, 4.95; N, 5.65.

Compounds 3a: 4-(butan-2-ylamino)-6-(butan-2-yliminio)-3-oxocyclohexa-1,4-dien-1-olate , 2d: 2-(sec-butylamino)-5-hydroxycyclohexa-2,5-diene-1,4-dione and 2e: 2,5-bis(sec-butylamino)cyclohexa-2,5-diene-1,4-dione

Sec-Butylamine (0.620 g, 8.43 mmol) was added to a methanol (20 mL) suspension of the organic salt **IIb** (0.172 g, 0.602 mmol). The reaction mixture was heated to reflux for two days, allowed to cool to room temperature and after removal of the solvent; the crude red product was obtained and suspended in chloroform (20 mL). The suspension was stirred a room temperature for two hours. The solid was separated by filtration and the red filtrate was evaporated. The product was obtained as a red solid (0.080 g, 0.32 mmol, 53 %). For the NMR analysis, two minor products were detected. ^{1}H NMR (300 MHz, chloroform-d_1), δ(ppm): 5.42 (s, 1H, N-C=CH), 5.90 (s, 1H, O=C-CH) monoalkylamino-hydroxybenzoquinone 2d. ^{1}H NMR (300 MHz, chloroform-d_1), δ(ppm): 5.97 (s, 2H, O=C-CH) trans-dialkylamino-1, 4-benzoquinone 2e.

Compound 3a: ^{1}H NMR (300 MHz, chloroform-d_1), δ(ppm): 0.98 (t, ^{3}J= 7.5 Hz, 6H, CH_2CH_3), 1.31 (d, ^{3}J=6.5Hz, 6H, $CHCH_3$), 1.69 (pent, ^{3}J=7.2 Hz, 4H, CH_2), 3.62 (m, 2H, NCH), 5.14 (s, 1H, N-C-CH), 5.48 (s, 1H, O-C-CH), 8.10 (br s, 2H, NH); ^{13}C NMR (75 MHz, chloroform-d_1), δ(ppm): 10.40 (s, CH_2CH_3), 19.55 (s, $CHCH_3$), 29.16 (s, CH_2), 50.87 (s, NCH), 80.52 (s, N-C-C), 98.85 (s, O-C-C), 155.73 (s, N-C), 172.23 (s, O-C).

Compound 4a: 3-oxo-4-(phenylamino)-6-(phenylimino)cyclohexa-1,4-dienolate

Aniline (4.65 g, 49.96 mmol) was added to a methanol (100 mL) solution of the 2,5-dihydroxy-1,4-benzoquinone **II** (1 g, 7.14 mmol). The reaction mixture was heated to reflux for 19 h. The solvent was partially removed, then the solid product was isolated by precipitation with the addition of pentane (200 mL). The crude solid was obtained as a brown mixture containing two products **4a** and **1d**.

The ^{1}H NMR spectrum indicates that the brown solid was a mixture of two products: the monoaniline **1d** and the bis-aniline **4a** in the respective proportions 26 % and 74 %.

Compound **4a**: ^{1}H NMR (300 MHz, dmso-d_6), δ(ppm: 5.20 (s, 1H, N-C=C-H); 5.81(s, 1H, O-C=C-H); 7.29-7.46 (m, 10H, CH_{Ar}); 10.96 (s, 2H, NH). To complete the assignment of the carbons, those carrying protons H were identified by the sequence ^{13}C{^{1}H} DEPT 135. ^{13}C{^{1}H} NMR (75 MHz, dmso-d_6), δ(ppm: 85.13 (s, N-C-CH) ; 98.07 (s, O-C-CH) ; 124.74 (s, CH) ; 127.39 (s, CH); 129.12 (s, CH); 136.37 (s, Cq); 155.42 (s, C-N) ; 177.76 (s, C-O). MS (ESI$^+$) m/z = 291.11([M+H]$^+$; 70 %). Anal. Cald.

for $C_{18}H_{14}N_2O_2 \cdot 1/6H_2O$: C, 73.71; H, 4.93; N, 9.55; Found: C, 73.72; H, 5.23; N, 9.77.

After several washing with acetonitrile solvent, the compound 4a was obtained with a majority proportion (the estimated percentage of monoamine (**1d**) by ^{1}H NMR was <15 %).

Compound 1d: 2-hydroxy-5-(phenylamino)cyclohexane-1,4-dione and 1c: benzenaminium diisopropylammonium 3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate)

Aniline (0.29 g, 3.08 mmol) was added to a methanol (20 mL) solution of diisopropylammonium salt of 3,6-dihydroxy-1,4-benzoquinone **IIa** (0.077 g, 0.22 mmol). The reaction mixture was heated to reflux during 1 h. The solvent was removed in vacuum and the crude solid was washed with pentane (2x10 mL). The product was obtained as a red solid. The ^{1}H NMR analysis reveals that the crude solid was a mixture of two products. A sample was suspended in the dichloromethane (20 mL) and stirred at room temperature during 1 h, and filtered. The orange solid precipitate is identified as **1d** (0.031 g, 0.14 mmol, 66 %). The remaining solution was evaporated to afford compound **1c** (0.025 g, 0.074 mmol, 34 %).

Compound 1c: ^{1}H NMR (300 MHz, dmso-d_6) δ(ppm): 1.10-1.13 (d, 12H, CH_3isop) ; 3.14-3.23 (m, 2H, CHipr) ; 5,15(s, 2H, O-C-C-H); 6.44-7.0142 (m, 5H, CH_{Ar}); 8.65 (br, 3H, NH); 9.31 (br, 2H, NH) .

Compound 2a: 4-[(2-hydroxyethyl)amino]-6-[(2-hydroxyethyl)iminio]-3-oxocyclohexa-1,4-dien-1-olate

Ethanolamine (0.125 g, 2.04 mmol) was added to an ethanol (10 mL) solution of the diisopropylammonium salt of 2,5-dihydroxy-1,4-benzoquinone 3 (0.1 g, 0.29 mmol). The reaction mixture was stirred during 20 h at room temperature under nitrogen atmosphere. The solvent was removed under vacuum and then the solid product was washed with pentane (2x10 ml) and diethyl ether (10 mL). The product was obtained as a brown solid (0.05 g, 0.22 mmol, 76 %).

^{1}H NMR (300 MHz, dmso-d_6), δ(ppm): 7.70 (s, 2H, 2HN-); 5.59 (s, 1H, CH-C-O); 4.97 (m, 3H, CH-C-N, 2OH); 3.62 (t, 4H CH_2O); 3.46 (t, 4H, CH_2N). ^{1}H NMR (300 MHz, water-d_2): δ(ppm): 5.55 (s, 1H, CH-C-O); 5.28 (s, 1H, CH-C-N); 3.77 (t, 4H, ^3J = 5.2 Hz, CH_2O); 3.56 (t, ^3J = 5.2 Hz, 4H, CH_2N).

Compound 3d: 2-(2-bromophenylamino)-5-hydroxycyclohexa-2,5-diene-1,4-dione

2-Bromoaniline (1.28 g, 7.44 mmol) was added to a methanol (50 mL) solution of 2,5-dihydroxy-1,4-benzoquinone **II** (0.15 g, 1.07 mmol). The reaction mixture was firstly stirred for 6 h but the conversion was very small. Then the reaction mixture was heated to reflux during 1 h and cooled to room temperature. After reduction of the solvent by evaporation, the product was precipitated with addition of diethyl ether (20 mL). The compound 3d was obtained as pink solid (0.2 g, 0.68 mmol, 64%). ^{1}H NMR (300 MHz, dmso-d_6), δ(ppm) : 5.13 (s, 1H, N-C=CH); 5.87 (s, 1H, O=C-CH) ; 7.24-7.30 (m, 1H, CH) ; 7.41-7.51 (m, 2H, CH) ; 7.75-7.78 (m, 1H, CH); 9.05 (s, 1H, NH); 11.56 (br,1H, OH). ^{13}C NMR (75 MHz, dmso-d_6), δ(ppm) = 99.53(s, CH); 104.04 (s, CH); 120.03 (s, Cq_{Ar}); 127.67 (s, CH_{Ar}); 128.63 (s, CH_{Ar}), 128.86 (s, CH_{Ar}); 133.32 (s, CH_{Ar}); 135.97 (s, Cq_{Ar}); 146.61 (s, Cq_{Ar}); 160.78 (s, =C-OH); 180.12 (s, C=O); 182.54 (s, C=O).

Compound 4d: 2-hydroxy-5-(4-methoxyphenylamino)cyclohexa-2,5-diene-1,4-dione

4-Methoxyaniline (0.92 g, 7.49 mmol) was added to a methanol (50 mL) solution of 2,5-dihydroxy-1,4-benzoquinone **II** (0.15 g, 1.07 mmol). The reaction mixture was stirred a room temperature for 3 days. After reduction of the solvent by slow evaporation, the suspension was precipitated by addition of diethyl ether (20 mL), then filtered. The product was obtained is dried into the air, resulting in brown solid (0.16 g, 0.65 mmol, 61 %). The remaining solution obtained after filtration contained essentially 4-methoxyaniline.

^{1}H NMR (300 MHz, dmso-d_6), δ(ppm): 5.57 (s, 1H, N-C=CH); 5.81 (s, 1H, O=C-CH); 6.97 - 6.99 (d, 2H, =CH); 7.25-7.28 (d, 2H, =CH) ; 9.20 (s, 1H, NH); 11.12 (br, 1H, OH). The ^{1}H NMR spectrum further shows a singlet proton signal is observed at 5.61 ppm, this signal is attributed to the protons of the para-substituted product. ^{13}C NMR (75 MHz, dmso-d_6), δ(ppm): 55.23 (s, CH_3); 94.85 (s, CH); 103.79 (s, CH); 114.37 (s, CH); 125.28 (s, CHAr); 130.28 (s, CHAr); 146.83 (s, CHAr); 156.95 (s, CHAr); 179.83 (s, C=O).

Compound 3e: 2,5-bis(methylamino)cyclohexa-2,5-diene-1,4-dione

2-Methylaniline (4.12 g, 38.49 mmol) was added to a methanol (20 mL) solution of 2,5-dihydroxy-1,4-benzoquinone **II** (0.77 g, 5.49 mmol). The reaction mixture was stirred to reflux 20 h, allowed cool to room temperature. The precipitate was recovered by filtration and washed with diethyl ether (2x15 mL) to obtain a brown solid (1g, 3.14 mmol, 57 %). The melting point of the compound 3e is in the range 252-254 °C. ^{1}H NMR (300 MHz, dmso-d_6), δ(ppm): 2.20 (s, 6H, $2CH_3$); 5.01 (s, 2H, N-C=CH); 7.22-7.36 (m, 8H, CH) ; 8.85 (s, 2H, NH). ^{13}C{^{1}H} DEPT (75 MHz, dmso-d_6), δ(ppm): 16.71 (s, CH_3); 94.14(s, O=C-CH C-) ; 125.60 (s, CH_{Ar}) ; 126.32(s, CH_{Ar}); 126.65 (s, CH_{Ar}); 130.51 (s, CH_{Ar}); 133.51 (s, Cq, C_{Ar}); 135.60 (s, Cq, C_{Ar}); 148.95 (s, C-N); 178.48 (s, C=O). MS (ESI$^+$): m/z = 341.13 ([(M+Na)]$^+$, 51%, {$C_{20}H_{18}N_2O_2Na$}$^+$); m/z = 318.14 ([(M)], 28 %, {$C_{20}H_{18}N_2O_2$}$^+$). Anal. Calcd. for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80: found C, 75.36, H, 5.80; N, 8.78.

Compound 4e: 2,5-bis(2-bromophenylamino)cyclohexa-2,5-diene-1,4-dione

2-Bromoaniline (1.28 g, 7.44 mmol) was added to a methanol (50 mL) solution of 2,5-dihydroxy-1,4-benzoquinone **II** (0.15 g, 1.07 mmol). The reaction mixture was heated to reflux 20 h and allowed to cool to room temperature. The precipitate was recovered by filtration and washed with diethyl ether (2x10 mL). The product was

obtained as pink solid (0.2 g, 0.45 mmol, 42 %). ^{1}H NMR (300 MHz, dmso-d_6), δ(ppm): 5.31 (s, 2H, N-C=CH); 7.32-7.29 (m, 2H, CH) ; 7.50-7.46(m, 4H, CH); 7.80-7.77 (m, 2H, CH); 8.94 (s, 2H, NH). ^{13}C{^{1}H} DEPT (75 MHz, dmso-d), δ(ppm): 95.45 (s, -C=CH-C-) ; 126.80 (s, CH_{Ar}) ; 128.11(s, CH_{Ar}); 128.52 (s, CH_{Ar}); 133.0 (s, CH_{Ar}). ^{13}C{^{1}H} NMR (75 MHz, dmso- d_6), δ(ppm): 95.70 (s, -C=CH-C-); 119.30 (s, Cq , C_{Ar}); 126.80 (s, CH_{Ar}); 128.12 (s, CH_{Ar}); 128.52 (s, CH_{Ar}); 133.0 (s, CH_{Ar}); 135.66 (s, Cq, C_{Ar}); 147.31 (s, Cq, Ar); 178.92 (s, Cq, C=O). MS (ESI$^+$): m/z = 454.94 ([(M+2H) +Li]$^+$, 87 %, [$C_{18}H_{14}Br_2N_2O_2Li$]$^+$). Anal. Calcd. for $C_{18}H_{12}Br_2N_2O_2$: C, 48.25; H, 2.70; N, 6.25: found C, 48.31, H, 2.44; N, 6.18.

Compound 5e: 2,5-bis(4-methoxyphenylamino)cyclohexa-2,5-diene-1,4-dione

4-Methoxyaniline (0.92 g, 7.49 mmol) was added to a methanol (50 mL) solution of 2, 5-dihydroxy-1, 4-benzoquinone **II** (0.15 g, 1.07 mmol). The reaction mixture was heated to reflux 20h. After cooling, the product precipitated and the solvent was slowly evaporated. The precipitate was washed with acetone then dried in air. The product was obtained as a brown solid (0.35 g, 0.99 mmol, 93 %). ^{1}H (300 MHz, dmso-d_6) at room temperature, δ(ppm): 3.67 (s, 6H, OCH_3); 5.61 (s, 2H, N-C=C-H); 6.98-7.01 (d, 4H, $^3J_{HH}$ =9.95 Hz, CH); 7.27-7.29 (d, 4H, $^3J_{HH}$ =9.95 Hz, CH); 9.25 (s, 2H, NH). ^{1}H and ^{13}C NMR was achieved at temperature near (~80 °C). ^{1}H NMR (300 MHz, dmso-d d_6), δ(ppm): 3.80 (s, 6H, -OCH_3); 5.63 (s, 2H, N-C=C-H); 6.99-7.01 (d, 4H, $^3J_{HH}$ =9.95 Hz, CH); 7.27-7.29 (d, 4H, $^3J_{HH}$ =9.95 Hz, CH); 8.89 (s, 2H, NH). ^{13}C{^{1}H} DEPT (75 MHz, dmso-d d_6), δ(ppm) = 54.98 (s, OCH_3); 94.11 (s, -C=CH-C-); 114.23 (s, CH_{Ar}); 124.73 (s, CH_{Ar}). ^{13}C{^{1}H} NMR (75 MHz, dmso-d d_6), δ(ppm) = 54.98 (s, OCH_3); 94.11 (s, -C=CH-C-) ; 114.23 (s, CH_{Ar}) ; 124.73 (s, CH_{Ar}); 130.08 (s, Cq_{Ar}); 147.71 (s, Cq_{Ar}); 156.84 (s, N-C=C) ; 178.72 (s, C=O). The infrared analysis revealed absorption bands around: 1635(s, C=O), 1610(s, C=N) , 1557(s, C=C), 1515(s, C=C), 1481 (s), 1460 (s), 1413 (s) , 1358 (s), 1288 (s), 1257 (s), 1188 (s), 1172 (s), 1110 (m), 1030 (s), 822 (s), 776 (s), 718 (s). MS(ESI$^+$) m/z = 351.13([M+H]$^+$, 62 %). Anal. Calcd. for $C_{20}H_{18}N_2O_4.CH_2Cl_2$: C, 57.94; H, 4.63; N, 6.44; found C, 58.21; H, 4.36; N, 6.67. MS(ESI$^+$) m/z(%) = 351.13(62) ([M+H]$^+$

Conclusions

We have shown that the scope of the reaction leading to the functionalization of the 2,5-dihydroxy-1,4-benzoquinone can be extended from the alkyl to aryl groups. Furthermore, by performing a condensation reaction on the 2,5-dihydroxy-1,4-benzoquinone bearing substituent on the hydroxyl group, the organics salts were obtained. Further extension of the scope of these reactions to secondary amines has proved impossible because 2,5-dihydroxy-1,4-benzoquinone undergoes total acid-base reactions, leading to a series of ionic salts. Finally, we showed that these salts react with primary alkyl amines or aryl amines to generate à zwitterionic structure which can be hydrolyzed, leading to a new series of ionic salts or to give dianionic salts. Two crystals structures have been determined which provide a firm basis for the description of electronic situation in these molecules.

Supplementary material

CCDC 1914357 and 769670 contain the supplementary crystallographic data for the reported complex. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk. or www: http:// www.ccdc.cam.ac.uk).

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