Toward a 6π+6π Zwitterion or a Bioinhibitors-Related OH-Substituted Aminoquinone: Identification of a Key Intermediate in Their pH Controlled Synthesis

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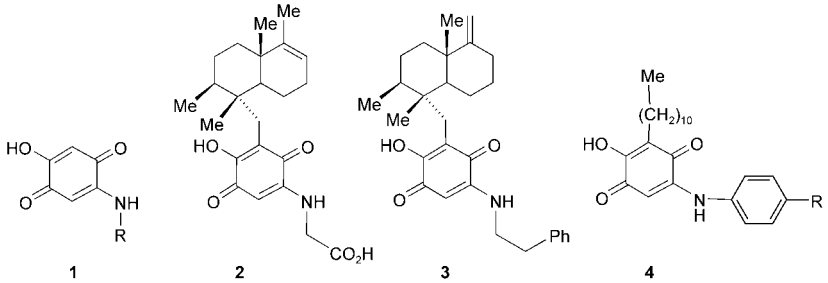
Dedicated to Professor Pierre Potier on the occasion of his 70th birthday

Abstract: Their pH-controlled reactivity places the *N,N′*-dialkyl-2-amino-5-lithium alcoholate-1,4-benzoquinonemonoimines $[C_6H_2(NHCH_2R')(=NCH_2R')(=O)(OLi)]$ **7** ($R'=tBu$) and **8** ($R'=p\text{-}C_6H_4\text{-}tBu$) at the crossroads of a new versatile strategy for the preparation of two very different classes of substituted quinones. We describe new 2-(*N*-alkyl)amino-5-hydroxy-1,4-benzoquinones, which are parent molecules to biologically active substituted aminobenzoquinones, for which changes of the N-substituent will become readily possible. The results of the first X-ray structural determination of such compounds ($[C_6H_2(NHCH_2tBu)(OH)(=O)_2]$ **13**) are also reported and we compare the influence of the number of N-substituents of the C_6 ring on the supramolecular networks resulting from self-assembling of **13**, zwitterionic *N,N′*-dineopentyl-2-amino-5-alcoholate-1,4-benzoquinonemonoiminium $[C_6H_2(=NHCH_2tBu)_2(=O)_2]$ **9** and *N,N′,N″,N‴*-tetraneopentyl-2,5-diamino-1,4-benzoquinone diimine $[C_6H_2(NHCH_2tBu)_2(=NCH_2tBu)_2]$ **15**.

Keywords: π interactions · aminoquinones · supramolecular chemistry · synthetic methods · zwitterions

Introduction

The synthesis of quinonoid molecules has attracted the attention of a large scientific community for decades owing to their importance in many areas of chemistry and biology.[1] In particular, benzoquinones containing an hydroxy group of type **1** are of considerable interest in biochemistry since closely related C-substituted benzoquinones such as the marine quinone sesquiterpenes nakijiquinone A (**2**) and smenospongidine (**3**) or embelin derivatives **4** possess very diverse and remarkable biological activities.[2–10]



1 2 3 4

Quinones with an OH substituent play an important role as inhibitors of hydroxyphenylpyruvate dioxygenase,[4] of tumors[2] or of the receptor tyrosine kinase involved in angiogenesis by interaction with the ATP binding site through hydrogen bonding.[2] The development of low molecular weight analogues of these inhibitors is considered to represent a most promising approach towards the development of new alternative antitumor drugs.[2]

Despite very intensive research efforts directed towards the synthesis of OH-substituted benzoquinones, their access has remained rather limited.[5,9–11] A simple and more versatile route that would not require their extraction from natural products,[4,5,10] multisteps procedures,[2,3] or oxidation processes before nucleophilic attack of amines[11] or water[12] on the quinonoid skeleton would obviously be of considerable interest.

To the best of our knowledge, only four molecules of type **1** (i.e., without substitution at the olefinic carbon) have been described in the literature: one compound for which R is a phenyl group[11] and three compounds for which R is a carbonyl substituent.[12,13] Although theoretical calculations

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have been performed on molecules such as **1** for which R is a phenyl group and on hypothetical analogues with aryl substituents, no X-ray structural analysis is available.[5]

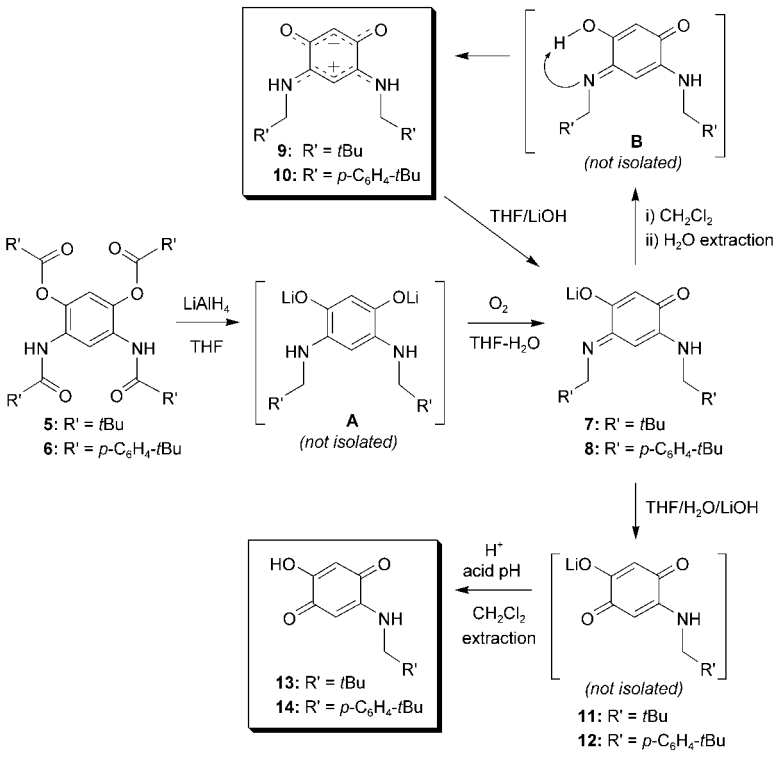
Herein, we report the high yield synthesis of new OH-substituted aminoquinones $[C_6H_2(NHCH_2R')(OH)(=O)_2]$ related to **1**, for which the N-susbtituent is an alkyl group. These compounds, **13** ($R'=t$Bu) and **14** ($R'=p$-C_6H_4-tBu), which may be considered as parent compounds to **2** and **3**, were obtained from versatile alcoholate precursors $[C_6H_2(NHCH_2R')(=NCH_2R')(=O)(OLi)]$ **7** ($R'=t$Bu) and **8** ($R'=p$-C_6H_4-tBu), that are also able to lead under different pH conditions to zwitterionic *p*-benzoquinonemonoimines, known $[C_6H_2(=NHCH_2tBu)_2(=O)_2]$ **9**[15] and new $[C_6H_2(=NHCH_2p\text{-}C_6H_4\text{-}tBu)_2(=O)_2]$ **10**, respectively. Noncovalent interactions such as hydrogen bonding are suggested to participate in the interactions between nakijiquinones and the ATP binding sites of kinases,[2] and we will examine if our systems have interesting potential as tunable building blocks in hydrogen-bonded molecular networks.

Results and Discussion

A straightforward synthesis of the *p*-benzoquinonemonoimine (**9**), which is a rare example of zwitterion being more stable than its canonical forms, was recently described from **5**.[14] To explain the formation of this unique 12 π electron system, which is actually best described as constituted of two chemically connected but electronically not conjugated 6 π electron subunits (Scheme 1),[14] we suggested that intermediate **B** (not isolated in CH_2Cl_2) would rearrange to **9** by proton migration from oxygen onto the more basic nitrogen atom.[15] By studying this reaction in more detail, we have now isolated and characterized a new intermediate **7**, obtained during the air oxidation workup of intermediate **A**. Its ^{13}C NMR spectrum contains two signals at $\delta=162.53$ and 180.07 ppm which are consistent with a localized π-system (δ(C–O) and δ(C=O), respectively), in contrast to **9** for which the negative charge is delocalized between the two oxygen atoms ($\delta(C{=}O)=172.13$ ppm).[15] The diester diamido derivative **6**, obtained by reaction between 4,6-diaminoresorcinol dihydrochloride and (4-*tert*-butyl)-benzoyl chloride, was reduced with $LiAlH_4$ and the subsequent aerobic workup similarly led to **8** (Scheme 1). In the presence of water, **7** and **8** afforded by rapid protonation intermediate **B** which rearranges to the zwitterions **9** and **10** in high yield (assignment of the ^1H NMR resonance for the NCH_2 protons is facilitated by the occurrence of a $^3J_{HH}$ coupling in $[D_6]$DMSO, see Experimental Section). We have now found that prior dissolution of **7** and **8** in a mixture of THF/H_2O containing LiOH (basic pH) prevents protonation and instead leads by slow hydrolysis to the alcoholates intermediates **11** and **12**, which can be subsequently protonated to the OH-substituted amino-*p*-benzoquinones $[C_6H_2(NHCH_2tBu)(OH)(=O)_2]$ **13** and $[C_6H_2(NHCH_2\text{-}p\text{-}C_6H_4\text{-}tBu)(OH)(=O)_2]$ **14**, respectively, in good yields (Scheme 1).

The highest yields of **13** and **14** were obtained by direct synthesis without isolation of the intermediates **7** and **8** since their competitive protonation which leads to the zwitterions **9** and **10** cannot be completely avoided (see Experimental Section). However, we have found that selective mono-deprotonation of **9** or **10** with LiOH in THF affords in high yields **7** and **8**, respectively.

The ^1H NMR spectrum of **13** contains two signals at 6.62 and 8.24 ppm for the N-H and O-H protons, respectively, whereas its ^{13}C NMR spectrum confirmed the presence of two carbonyl groups ($\delta(C{=}O)=178.27$ and 182.52 ppm). Contrary to the UV/Vis spectra of the zwitterions which revealed two strong absorptions at 350 nm ($\log\varepsilon=4.49$) and 343 nm ($\log\varepsilon=4.45$) for **9**,[15] 352 nm ($\log\varepsilon=4.25$) and 340 nm ($\log\varepsilon=4.23$) for **10**, that of **13** is characterized by only one strong absorption at 303 nm ($\log\varepsilon=4.11$) which corresponds to the intraquinone charge transfer, and by the presence of one more band at 486 nm ($\log\varepsilon=3.26$). Similarly, **14** revealed in CH_2Cl_2 two absorption bands at 301 nm ($\log\varepsilon=3.97$) and 478 nm ($\log\varepsilon=3.16$). The main absorptions can be attributed to the π–π* transition of the benzo-



Scheme 1.

quinone derivatives, whereas the weak absorption band corresponds to a n–π* transition originating at the nitrogen lone pair.[16] Recent publications[17,18] have described theoretical analyses of **9**. Sawicka, Skurski and Simons[17] assigned the band at 350 nm to the first π–π* absorption and that at 343 nm to a vibrational excitation on top of the electronic transition, whereas if Delaere, Nam and Nguyen[18a] confirmed that both UV absorption peaks at 350 and 343 nm belong to the same electronic transition but with different vibrational states, they assigned them to a transition from the ground electronic state to the second 2^1B_2 state rather than to the first 1^1B_2 state.

An X-ray diffraction study on single crystals of **13**,[19] obtained by slow evaporation of a dichloromethane solution, established the *p*-benzoquinone structure of the molecule and showed that the C(1)–C(2) and C(4)–C(5) distances of 1.504(2) and 1.521(2) Å, respectively, correspond to two single bonds (Figure 1).

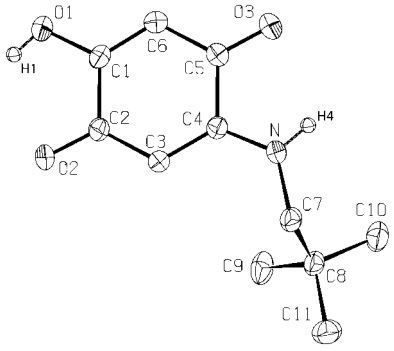


Figure 1. View of the structure of **13** in the crystal. Selected bond lengths [Å] and angles [°]: O(1)–C(5) 1.330(2), C(5)–C(8) 1.344(2), C(8)–C(6) 1.440(2), C(6)–O(2) 1.231(2), C(5)–C(2) 1.504(2), C(6)–C(4) 1.521(2), O(3)–C(2) 1.242(2), C(2)–C(3) 1.418(2), C(3)–C(4) 1.374(2), C(4)–N(1) 1.332(2); O(1)-C(5)-C(8) 121.8(1), C(5)-C(8)-C(6) 120.2(1), C(8)-C(6)-O(2) 122.7(1), O(1)-C(5)-C(2) 116.4(1), O(2)-C(6)-C(4) 118.7(1), C(5)-C(2)-O(3) 117.0(1), C(6)-C(4)-N(1) 113.6(1), O(3)-C(2)-C(3) 124.4(1), C(2)-C(3)-C(4) 121.0(1), C(3)-C(4)-N(1) 126.7(1).

Examination of the bond lengths within the O(1)-C(1)-C(6)-C(5)-O(3) and O(2)-C(2)-C(3)-C(4)-N moieties reveal an alternating succession of single and double bonds which is consistent with two independent conjugated but not delocalized π systems. Furthermore, the O(1)-H(1) and N-H(4) protons of **13** establish intramolecular hydrogen bonding with the H-bond acceptor quinone oxygen atoms O(2) and O(3), respectively. Compound **13** forms intermolecular interactions in the solid state which lead to a π-stacking arrangement of head-to-tail H-bonded coplanar six-membered rings

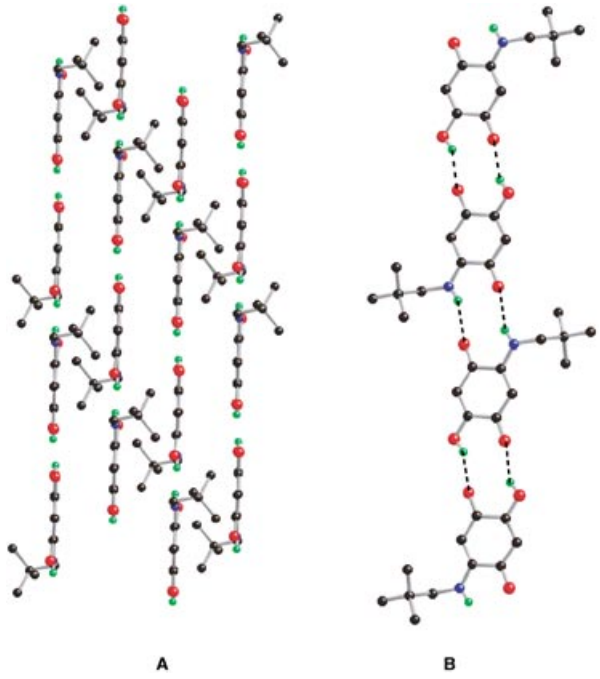


Figure 2. a) View of the stacking arrangement generated by **13** in the solid state. b) View of the supramolecular array generated by **13** in the solid state. Colour coding: nitrogen, blue; oxygen, red; hydrogen, green.

(Figure 2). It is interesting to recall that similar H-bond donors in nakijiquinones are suggested to participate in hydrogen bonding to the ATP binding sites of kinases.[2]

For comparison, it is relevant to recall that two related molecules, which also possess two H-donor sites and two H-acceptor sites, form different supramolecular architectures in the solid state. Although **9** led also to the formation of a head-to-tail hydrogen-bonded network, it revealed an unexpected wave-like arrangement owing to the presence of two N-neopentyl substituents (Figure 3a).[15]

With four N-neopentyl substituents, the 2,5-diamino-1,4-benzoquinonediimine $[C_6H_2(NHCH_2tBu)_2(=NCH_2tBu)_2]$

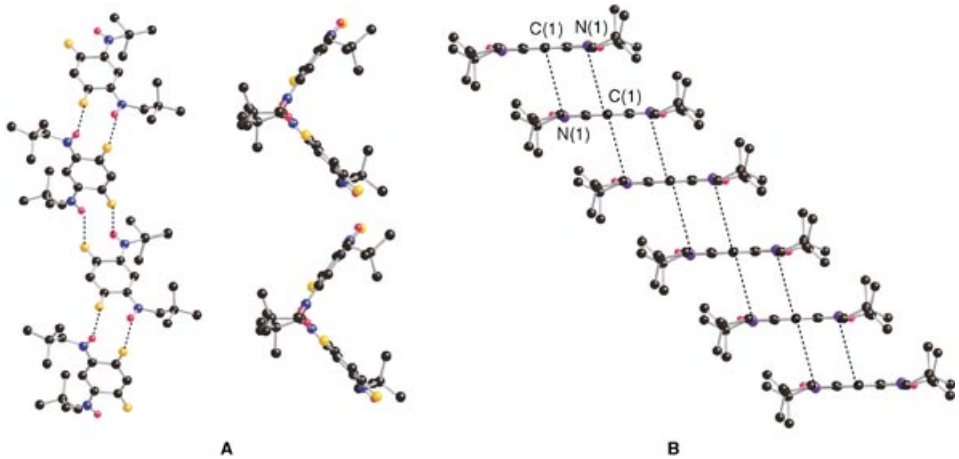
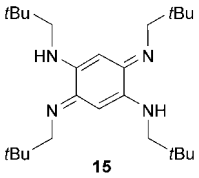


Figure 3. a) View of the head-to-tail array generated by **9** in the solid state. b) View of the stacking arrangement generated by **15** in the solid state. Colour coding: nitrogen, blue; oxygen, yellow; hydrogen, red.



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15[20] led instead to a different packing arrangement owing to the steric hindrance induced by the presence of these four substituents (Figure 3b).[21] In this case, the stacking results from intermolecular π–π interactions.

The present study has demonstrated the chemical versatility of the intermediates **7** and **8** and confirmed that although molecules **9**, **13** and **15** possess two H-donor sites and two H-acceptor sites, the number of N-substituents as well as the nature of the atoms involved in the hydrogen-bonding interactions (i.e., oxygen or nitrogen) play a key role in the construction of supramolecular architectures.

Conclusion

Because of their versatile pH-controlled reactivity, compounds **7** and **8** are at the crossroads of a new strategy for the preparation of two very different classes of substituted aminobenzoquinones: 6π+6π zwitterions such as **9** and **10** or OH-substituted aminobenzoquinones of type **1**, such as **13** and **14**, for which changes of the N-substituent become readily possible. The first structural determination of a compound of the latter type is now available with molecule **13** which can be used for future correlations with theoretical calculations performed on analogues.[5] In addition to their relevance to bioinhibitor molecules, these OH-substituted aminobenzoquinones have furthermore a considerable potential in inorganic chemistry since they present two different bidentate donor sets suitable for the preparation of heterobinuclear complexes.

Experimental Section

General: Analytical-grade reagents were obtained from commercial suppliers and were used directly without further purification. Solvents were distilled under argon prior to use and dried by standard methods. All reduction reactions were performed under N_2. ^{1}H NMR spectra were recorded in $CDCl_3$ and [D$_6$]DMSO with a AC300 Bruker spectrometer, operating at 300 MHz for ^{1}H spectra. Chemical shifts are reported in parts per million (ppm) relative to the singlet at $\delta = 7.26$ for $CDCl_3$. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; br, broad. Elemental analyses were performed by the "service de microanalyse de l'université Louis Pasteur," Strasbourg. FAB mass spectral analyses were recorded on an autospec HF mass spectrometer and EI high resolution mass spectral analyses were recorded on a Finnigan TSQ 700.

Synthesis of the diester diamidobenzene 6: Similarly to the procedure described for the synthesis of analogues,[15] compound **6** was obtained as a white solid (2.38 g, 65%). HRMS (EI$^+$, 70 eV): *m*/*z*: calcd for: 781.4216; found: 781.4042 $[M+H]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.30$ (s, 18H, CH_3), 1.36 (s, 18H, CH_3), 7.34 (s, 1H, aromatic), 7.39 (d, A part of an AB system, $^3J_{HH} = 8.7$ Hz, 4H, C–H aryl), 7.52 (d, A part of an AB system, $^3J_{HH} = 8.7$ Hz, 4H, C–H aryl), 7.72 (d, B part of an AB system, $^3J_{HH} = 8.7$ Hz, 4H, C–H aryl), 8.12 (d, B part of an AB system, $^3J_{HH} = 8.7$ Hz, 4H, C–H aryl), 8.16 (s, 2H, N-H), 9.05 (s, 1H, aromatic); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 31.09 (C*Me$_3$*), 31.12 (C*Me$_3$*), 34.96 (*C*Me$_3$), 35.30 (*C*Me$_3$), 116.68, 118.93, 126.65, 125.84, 127.08, 130.33 (H-C aryl), 125.72, 128.19, 131.50, 138.56, 155.43, 158.14 (C aryl), 164.39 (C=O), 165.27 (C=O); elemental analysis calcd (%) for $C_{50}H_{56}N_2O_6$: C 76.89, H 7.23, N 3.59; found: C 76.78, H 7.29, N 3.56.

***N*,*N*′-Dineopentyl-2-amino-5-lithiumalcoholate-1,4-benzoquinonemonoimine (7) and *N*,*N*′-di-(4-*tert*-butylbenzyl)-2-amino-5-lithium alcoholate-1,4-benzoquinonemonoimine (8)**

General procedure A: Diamido diester **5** or **6** was dissolved in dry THF and an excess of $LiAlH_4$ (10 equiv) was added to the solution. The mixture was then refluxed for 4 h and excess of $LiAlH_4$ was quenched by addition of water (2 mL). After filtration of aluminium salts and evaporation of the solution to dryness, the orange product was suspended in dichloromethane to remove soluble zwitterion and residual impurities, and the solid was collected by filtration.

General procedure B: Zwitterion **9** or **10** was dissolved in anhydrous THF (50 mL) and 1 equiv solid LiOH was added to the solution. The mixture was then stirred overnight at room temperature. After evaporation of the solvent, **7** and **8**, respectively, were obtained quantitatively as orange powders and used without further purification.

Compound ***7***: MS (FAB$^+$, 70 eV): *m*/*z*: 285.2 $[M+H]^+$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.93 (brs, 18H, CH_3), 2.86 (d, $^3J_{HH} = 5.7$ Hz, 2H, HNC*H$_2$*), 3.05 (s, 2H, CH_2), 4.98 (s, 1H, N-C=C-H), 5.20 (s, 1H, O-C=C-H), 6.28 (brt, 1H, N-H); ^{13}C{^{1}H} NMR (125.8 MHz, [D$_6$]DMSO): δ = 27.34 (C*Me$_3$*), 28.10 (C*Me$_3$*), 32.05 (*C*Me$_3$), 32.16 (*C*Me$_3$), 52.73 (CH_2N), 62.17 (CH_2N), 83.47 (H-*C*=C), 99.78 (H-*C*=C), 147.16 (C-N), 162.53 (C-O), 176.68 (C=N), 180.07 (C=O); ^{7}Li NMR (155.5 MHz, [D$_6$]DMSO) δ = 0.35 (brs).

Compound ***8***: MS (FAB$^+$, 70 eV): *m*/*z*: 437.5 $[M+H]^+$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.27 (brs, 18H, CH_3), 4.35 (brs, 4H, CH_2), 4.90 (brs, 1H, N-C=C-H), 5.30 (brs, 1H, O–C=C–H), 7.20 (brd, A part of an AB system, $^3J_{HH} = 7.5$ Hz, 4H, C-H aryl), 7.30 (brd, B part of an AB system, $^3J_{HH} = 7.5$ Hz, 4H, C–H aryl. Owing to the poor solubility of **8**, it was impossible to obtain a ^{13}C NMR spectrum.

***N*,*N*′-Dineopentyl-2-amino-5-alcoholate-1,4-benzoquinonemonoiminium (9) and *N*,*N*′-di-(4-*tert*-butylbenzyl)-2-amino-5-alcoholate-1,4-benzoquinonemonoiminium (10)**

General procedure A (one-pot procedure from 5 and 6 without isolation of 7 and 8): Similarly to the procedure previously described for the synthesis of **9**,[15] compound **10** was obtained as a purple solid.

General procedure B (procedure from 7 and 8): Compound **7** or **8** was dissolved in a water/dichloromethane mixture. The zwitterions **9**[15] and **10** were extracted in the dichloromethane phase and after drying on magnesium sulfate, evaporation of the solvent and recrystallisation from a dichloromethane/hexane, isolated in quantitative yields as purple solids. In order to see all ^{13}C NMR signals, it was essential to increase the pulse delay from 0.8 to 2 s.

Compound ***10***: (1.05 g, 80% based on **6**). HRMS (EI$^+$, 70 eV): *m*/*z*: calcd for: 431.2698; found: 431.2657 $[M+H]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 18H, CH_3), 4.50 (s, 4H, CH_2), 5.34 (s, 1H, N=C=C-H), 5.44 (s, 1H, O=C=C–H), 7.20 (d, A part of an AB system, $^3J_{HH} = 8.35$ Hz, 4H, C-H aryl), 7.42 (d, B part of an AB system, $^3J_{HH} = 8.35$ Hz, 4H, C-H aryl), 8.52 (brs, 2H, N-H); ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.27 (s, 18H, CH_3), 4.58 (d, $^3J_{HH} = 6.3$ Hz, 4H, CH_2), 4.97 (s, 1H, N=C=C-H), 5.76 (s, 1H, O=C=C-H), 7.28 (d, A part of an AB system, $^3J_{HH} = 8.35$ Hz, 4H, C-H aryl), 7.35 (d, B part of an AB system, $^3J_{HH} = 8.35$ Hz, 4H, C-H aryl), 9.66 (t, 2H, N-H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 31.29 (C*Me$_3$*), 34.70 (*C*Me$_3$), 47.24 (CH_2N), 81.61 (H-*C*=C), 98.91 (H-*C*=C), 126.23, 127.71 (H-C aryl), 131.00, 151.98 (C aryl), 156.95 (C=N), 172.13 (C=O); elemental analysis calcd (%) for $C_{28}H_{34}N_2O_2 \cdot H_2O$: C 74.97, H 8.09, N 6.24; found: C 74.87, H 7.48, N 6.28.

2-(Neopentyl)amino-5-hydroxy-1,4-benzoquinone (13) and 2-(4-*tert*-butylbenzyl)amino-5-hydroxy-1,4-benzoquinone (14)

General procedures

Procedure A (one-pot procedure from 5 and 6 without isolation of 7 and 8): Diamido diester **5** (1.00 g, 2.10 mmol) or **6** (1.00 g, 1.28 mmol) was dissolved in dry THF and an excess of $LiAlH_4$ (10 equiv) was added to the solution. The mixture was then refluxed for 4 h, excess $LiAlH_4$ was quenched by addition of water (100 mL) and this suspension was stirred overnight at room temperature. The aluminium salts were filtered and dichloromethane added to the THF/H_2O. Protonation of the water-soluble alcoholate **11** followed by dichloromethane extraction, drying on magnesium sulfate and evaporation of the solvent afforded **13** as a red-orange solid. For **14**, addition of dichloromethane to the THF/H_2O solution ex-

tracts traces of zwitterion **10** and leads to the formation of a pink precipitate collected by filtration. The THF/H_2O phase is then discarded and the precipitate suspended in a water/dichloromethane mixture. Addition of HCl, dichloromethane extraction, drying of the solution on magnesium sulfate and evaporation of the solvent leads to **14** as a red-orange solid.

Procedure B (procedure from 7 and 8): Compound **7** or **8**, best obtained from **9** and **10**, were dissolved in THF/H_2O 1:1 (100 mL) and a concentrated solution of LiOH in water (pH > 10) was added to the solution which was then stirred overnight at room temperature. Protonation of the water-soluble alcoholates **11** and **12**, respectively, followed by dichloromethane extraction, drying on magnesium sulfate and evaporation of the solvent afforded quantitatively **13** and **14** as red-orange solids. Red crystals of **13** suitable for X-ray analysis were isolated by slow evaporation of a dichloromethane solution.

*Compound **13***: (80% based on **5**). MS (FAB$^+$, 70 eV): *m*/*z*: 210 $[M+H]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01 (s, 9H, CH_3), 2.95 (d, $^3J_{HH}$ = 6.4 Hz, 2H, CH_2), 5.46 (s, 1H, N-C=C-H), 5.91 (s, 1H, O−C=C−H), 6.62 (brs, 1H, N-H), 8.24 (brs, 1H, OH); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 27.44 (s, C*Me*$_3$), 32.42 (s, *C*Me$_3$), 54.26 (s, CH_2N), 92.22 (s, H-*C*=C), 102.25 (s, H-*C*=C), 150.44 (s, C−N), 159.49 (s, C−O), 178.27 (s, C=O), 182.52 (s, C=O); elemental analysis calcd (%) for $C_{11}H_{15}NO_3$: C 63.14, H 7.23, N 6.69; found: C 62.77, H 7.52, N 6.67.

*Compound **14***: (46% based on **6**). HRMS (EI$^-$, 70 eV): *m*/*z*: calcd for: 284.1286; found: 284.1326 $[M-H]^+$; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 9H, CH_3), 4.31 (d, $^3J_{HH}$ = 5.7 Hz, 2H, CH_2), 5.51 (s, 1H, N-C=C-H), 5.92 (s, 1H, O-C=C-H), 6.63 (brs, 1H, N-H), 7.20 (d, A part of an AB system, $^3J_{HH}$ = 8.1 Hz, 2H, C-H aryl), 7.40 (d, B part of an AB system, $^3J_{HH}$ = 8.1 Hz, 2H, C-H aryl), 8.14 (brs, 1H, OH); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 31.33 (s, C*Me*$_3$), 34.69 (s, *C*Me$_3$), 46.83 (s, CH_2N), 93.09 (s, H-*C*=C), 102.51 (s, H-*C*=C), 126.13, 127.63 (s, H-C aryl), 131.97, 149.70 (C aryl), 151.66 (s, C−N), 159.11 (s, C−O), 178.59 (s, C=O), 182.57 (s, C=O);); elemental analysis calcd (%) for $C_{17}H_{19}NO_3$: C 71.56, H 6.71, N 4.91; found: C 71.42, H 6.86, N 4.74.

Acknowledgments

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[19] Crystal data for **13**: $C_{11}H_{15}NO_3$, M = 209.24, triclinic, space group $P\bar{1}$; a = 5.732(5), b = 9.787(5), c = 10.020(5) Å, α = 105.188(5), β = 100.990(5), γ = 90.945(5)°, V = 531.2(6) Å^3, Z = 2, $\mu(Mo_{K\alpha})$ = 0.71069 mm^{-1}, T = 173(2) K, 2309 data with $I > 2\sigma(I)$, final R = 0.0696, Rw = 0.1217, GOF = 0.923. Selected crystal was mounted on a Nonius Kappa-CCD area detector diffractometer ($Mo_{K\alpha}$, λ = 0.71073 Å). The cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in phi angle), each at 20 s exposure. The structure was solved using direct methods (SIR97) and refined against F^2 using the SHELXL97 software. The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97. CCDC-236259 contains the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+)(1223)336–033; or deposit@ccdc.cam.ac.uk).
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