DOI: 10.1002/ejoc.200800087

Selective Reduction of Carbonyl Amides: Toward the First Unsymmetrical Bischelating *N*-Substituted 1,2-Diamino-4,5-diamidobenzene

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Keywords: Reduction / N ligands / Amides

Selective reduction of carbonyl amides from key tetraamido intermediate **12** afforded an unprecedented *N*-substituted 1,2-diamino-4,5-diamidobenzene (**13**) and/or the first member (**14**) of a new family of unsymmetrical 12π-electron quinonediimines.

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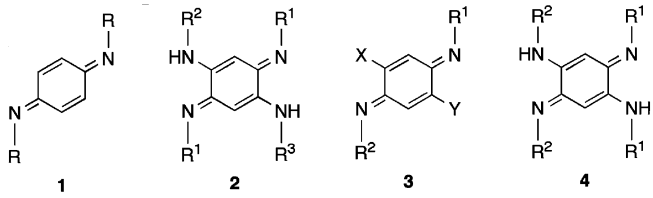
Introduction

p-Benzoquinonediimines constitute a large and important class of organic compounds that display interesting colors and are endowed with very rich chemical and physical properties.[1,2] They can be classified under three major categories, namely, I, II, and III.[1] Class I molecules (**1**) contain no substituent attached to the benzoquinoid ring and have been described mainly with electron-withdrawing R groups that stabilize the systems.[2] Class II (**2**) contains amino substituents at the 2- and 5-positions of the benzoquinoid ring (R^1 = or ≠ R^2 = or ≠ R^3).[1,3–11] Class III derivatives (**3**) contains all other 1,4-benzoquinonediimines (X = or ≠ Y, but both are different from N).[1]

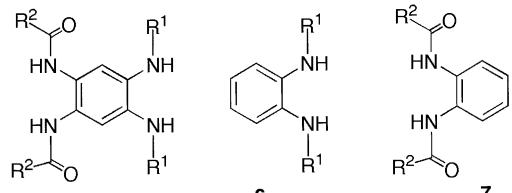


1 **2** **3** **4**

The second class of quinonediimines is the largest owing to easy access to symmetrical systems (R^1 = R^2 = R^3) and a high stability, which have allowed their use in different fields ranging from hair coloring[12] and biosensors[13] to supramolecular[14] and coordination chemistry.[15] This high stability is explained by the *coupling principle*[16,17] of the 12π-electron system of the quinoid skeleton, which is best described as being constituted of two 6π-electron subunits chemically connected by two single C–C bonds but each unit is electronically independent (no conjugation).[5]

As an extension of these studies, it appeared very attractive to develop the synthesis of new *N*-substituted *p*-benzoquinonediimines such as **4**, for which a fine tuning of the substituents in the two different, potentially bischelating sites would allow new developments in quinoid and coordination chemistry.

During the course of this work, we developed access to *N*-substituted 1,2-diamino-4,5-diamidobenzenes such as **5**, which were hitherto unknown. Note that only the unsubstituted amino analog was recently described [molecule **5** with R^1 = H and R^2 = C(O)OEt] as an intermediate in the preparation of ligands containing salophen and bis(oxamato) cavities.[18,19]



5 **6** **7**

Systems of type **5** combine the structural elements of **6** and **7**, which have generated much interest in organic,[20–22] organometallic,[23–28] and/or supramolecular chemistry[29,30] owing to the ability of the amino and/or amido groups to act as nucleophiles, coordinating moieties, or H-donor sites. The preparation of *N*-substituted aromatic amide amines has mainly involved a strategy based on the selective monoacylation of one of the amino groups.[31–36] The development of new procedures is thus still of great interest.

Herein, we report a rare example of selective reduction of carbonyl amides from key tetraamido intermediate **12**, which allows access to unprecedented *N*-substituted 1,2-diamino-4,5-diamidobenzene **13** and the first member (**14**) of a new family of unsymmetrical 12π-electron quinonediimines.

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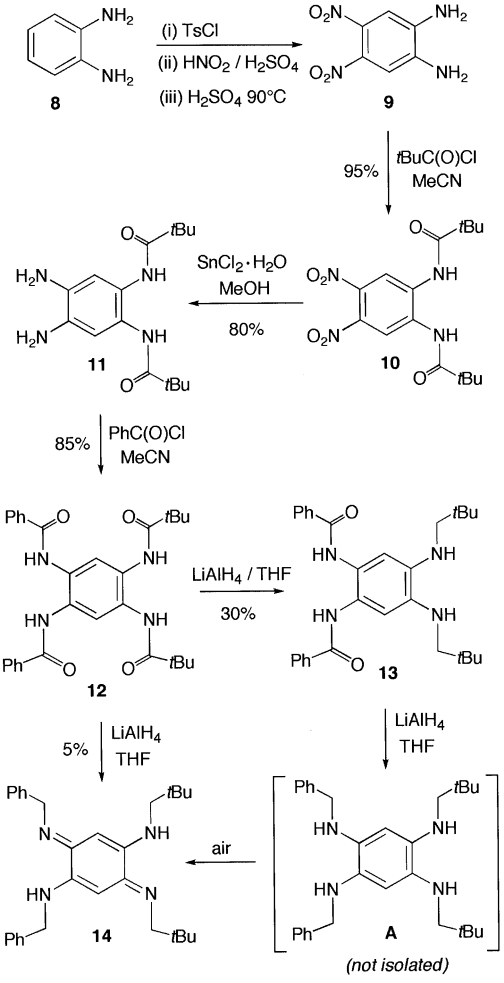
Results and Discussion

Nitration of 1,2-diaminobenzene **8** itself is not feasible and *N*,*N*′-protected derivatives have been used for the preparation of 1,2-diamino-4,5-dinitrobenzene **9** bearing two amino groups (Scheme 1).[37] After treatment of **9** with *t*BuC(O)Cl in MeCN in the presence of NEt_3, compound **10** was isolated in 95% yield. The reduction of the nitro groups was performed with $SnCl_2{\cdot}2H_2O$ in MeOH to afford **11** (80% yield), which was further treated with PhC(O)Cl in MeCN to give **12** in 85% yield (Scheme 1).



Scheme 1. Synthesis of molecules **13** and **14**.

The ^{1}H NMR spectrum of **12** revealed two NH resonances at δ = 9.03 and 9.98 ppm and a signal at δ = 7.84 ppm (aromatic C–H of the central ring), which is consistent with the structure drawn. This tetraamido compound appeared to be a key intermediate for the preparation of two new classes of organic systems. Reduction of **12** with $LiAlH_4$ in refluxing THF afforded **13** and **14** as the major (30% yield) and minor (5% yield) products, respectively.

The selective reduction of **12** with $LiAlH_4$ into 1,2-diamino-4,5-diamidobenzene **13** could be achieved as a result of the different reactivities of the carbonyl amides, which originates from the different steric and electronic effects of the alkyl and aryl substituents. However, the chemoselectivity in the reduction of **12** to **13** is limited, probably by the presence of competing reaction sites in the intermediates involved in the formation of **13** and **14**.

Direct reduction of the four amido functionalities of **12** results in the formation of the corresponding electron-rich tetraamino derivative **A** (not isolated), which in air sacrifices its aromatic character in favor of quinoid structure **14** (Scheme 1). Isolation of **A** should be possible under an atmosphere of nitrogen, as described for the symmetrical 1,2,4,5-tetrakis-*N*-*tert*-butylaminobenzene analog.[4] Despite difficult purifications due to its high solubility and its presence among a mixture of compounds with similar polarities, molecule **14** could be isolated pure as an orange solid. The use of a large excess of $LiAlH_4$ (18 equiv.) for the reduction of **12** led only to the formation of **14** with a similar yield (5%). The low yield may be due to partial decomposition of **14** during its isolation as a result of possible side reactions (hydrolysis, co-condensation), which lead to the presence of a large number of unidentified compounds (the remaining 65% of the reaction products). However, once isolated pure, **14** appears to be stable in solution or in the solid state for weeks. Note that access to **14** can also be achieved by reduction of **13** with $LiAlH_4$.

The ^{1}H NMR spectrum of **13** shows the presence of a signal at δ = 2.61 ppm, which is in agreement with the presence of a methylenic HN–CH_2–*t*Bu group (i.e., methylenic HN–CH_2–Ph groups are downfield shifted up to 4.30 ppm approx.). In addition, a broad signal at δ = 9.06 ppm is consistent with the presence of two equivalent amido N–H protons and confirms the selective reduction.

As a white powder, molecule **13** exhibits an expected absorption band in the UV region centered at 326 nm (ε = 5200 L mol^{-1} cm^{-1}) (Figure 1).

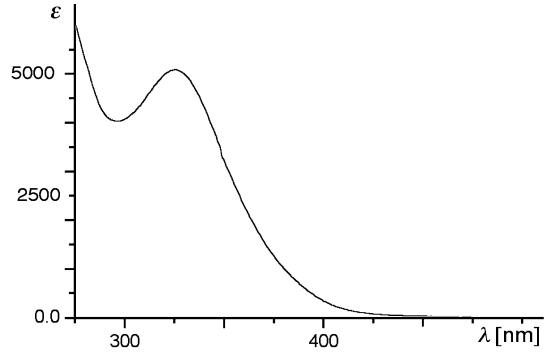


Figure 1. UV/Vis absorption spectrum of compound **13** in $CHCl_3$ at room temperature.

The cyclic voltammogram of **13** in anhydrous CH_2Cl_2 showed two poorly reversible waves (oxidative potentials at 0.54 and 0. 77 V vs. Ag/AgCl) resulting from two successive oxidation processes (Figure 2). When the cyclic voltammogram was recorded by starting in negative potentials, no reduction peak was observed. In contrast, three new reduction peaks appeared at –0.03, –0.69, and 0.83 V vs. Ag/

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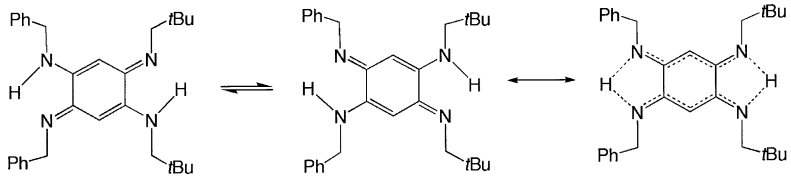


Scheme 2. Tautomeric equilibrium of **14** in solution.

AgCl when the experiment was started in positive potentials. This result is consistent with chemical evolution of the oxidized species as observed for aromatic amines.[38]

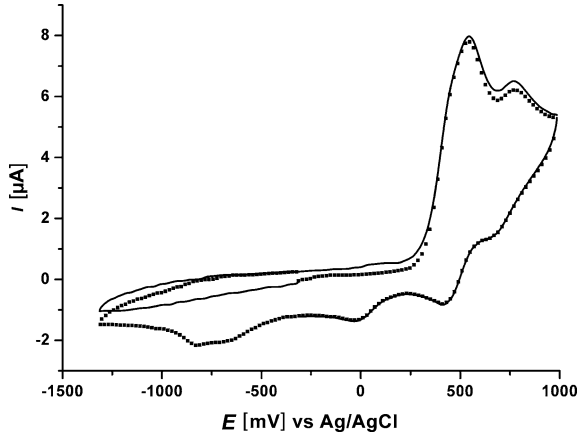
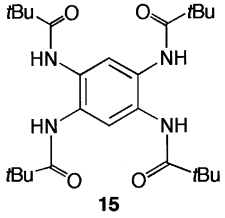


Figure 2. Cyclic voltammogram of compound **13** in CH_2Cl_2 [0.1 M $N(nBu)_4PF_6$] starting in oxidation (···) and in reduction (−).

The ^1H NMR spectrum of **14** showed two singlets at δ = 2.92 and 4.50 ppm, which is characteristic of the methylenic protons *N*–*CH*$_2$–*t*Bu and *N*–*CH*$_2$–Ph, respectively. The presence of two magnetically equivalent olefinic protons and neopentyl and benzyl groups is consistent with a fast intramolecular double proton transfer involving two tautomers and generating in solution an average structure of higher symmetry (Scheme 2). This phenomenon has been described previously but only for symmetrical quinonediimines.[5,11,39]

The poor solubility of **12** suggests the formation in the solid state of an H-bonded supramolecular network involving the four amido functionalities, as observed for symmetrical analog **15**.[5] The fact that diamino–diamido analog **13** is much more soluble in organic solvents supports the view that the four amido groups of **15** are involved in this H-bonded network.



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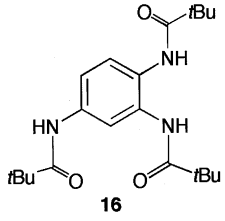

16

In order to confirm this hypothesis, we realized the synthesis of compound **16** by reaction of commercially available 1,2,4-triaminobenzene dihydrochloride with *t*BuC(O)Cl in MeCN in the presence of NEt_3. As expected, molecule **16** is well soluble in organic solvents such as acetone and CH_2Cl_2.

Conclusions

We described a rare example of selective reduction of carbonyl amides from key tetraamido intermediate **13**, which afforded unprecedented *N*-substituted 1,2-diamino-4,5-diamidobenzene **12** that might be used in different areas of chemistry. In addition, we could isolate the first member (**14**) of a new family of 12π-electron quinonediimines, for which a fine tuning of the *N*-substituents in the two different potentially chelating sites opens new opportunities in coordination chemistry.

Experimental Section

General: Commercial analytical-grade reagents were obtained from commercial suppliers and used directly without further purification. Solvents were distilled under an atmosphere of argon prior to use and dried by standard methods. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, [D_6]acetone, and [D_6]DMSO with a AC250 Bruker spectrometer operating at 250 MHz. Chemical shifts are reported in δ units in parts per million (ppm). Splitting patterns are designed as s, singlet; d, doublet; m, multiplet; br., broad. Elemental and MS analyses were performed by the Spectropole of Marseille. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Cyclic voltammetric (CV) data were acquired by using a BAS 100 Potentiostat (Bioanalytical Systems) and a PC computer containing BAS100W software (v2.3). A three-electrode system with a Pt working electrode (diameter 1.6 mm), a platinum counter electrode, and an Ag/AgCl (with 3 M NaCl filling solution) reference electrode was used. Tetrabutylammonium hexafluorophosphate (Fluka) was used as received. Anhydrous CH_2Cl_2 with electronic-grade purity was used. The compound was studied at 1×10^{-3} M in CH_2Cl_2/TBHP 0.1 M, and the cyclic voltammogram was recorded at a scan rate of 250 mV·s^{-1}. Ferrocene was used as an internal standard.

1,2-Bis(2,2-dimethylpropanamido)-4,5-dinitrobenzene (10): Triethylamine (1.4 mL, 4 equiv.) was added dropwise to a solution of 1,2-diamino-4,5-dinitrobenzene **9** (0.50 g, 2.53 mmol, 1 equiv.) in anhydrous acetonitrile (80 mL) under an atmosphere of argon at room temperature. The mixture was then stirred at room temperature for 5 min and trimethyl acetyl chloride (625 µL, 6.90 mmol, 2 equiv.) was added dropwise. The reaction mixture was heated under reflux for 6 h, and the reaction was monitored by TLC (cyclohexane/ethyl

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acetate, 5:5). The solvent was then evaporated under reduced pressure. The residue was taken up in water (50 mL), and the insoluble product was isolated by filtration. This latter was purified by chromatography on silica gel (cyclohexane/ethyl acetate, 8:2, 7:3, 6:4) to afford **10** (0.88 g, 95% yield) as a beige solid. ^{1}H NMR (250 MHz, [D$_6$]acetone): δ = 1.34 (s, 18 H, CH$_3$), 8.43 (s, 2 H, aromatic CH), 9.35 (br. s, 2 H, NH) ppm. ^{13}C{^{1}H} NMR (62 MHz, [D$_6$]acetone): δ = 27.5 (CH$_3$), 40.5 [-*C*(CH$_3$)$_3$], 122.3 (aromatic CH), 136.0, 139.6 (aromatic C), 178.9 (C=O) ppm. MS (ESI): *m*/*z* = 367 [M + H]$^+$. $C_{16}H_{22}N_4O_6$ (366.15): calcd. C 52.45, H 6.05, N 15.26; found C 52.18, H 6.03, N 15.09.

4,5-Diamino-1,2-bis(2,2-dimethylpropanamido)benzene (11): $SnCl_2 \cdot 2H_2O$ (12.00 g, 53.38 mmol, 14 equiv.) was quickly added to a solution of **10** (1.40 g, 3.82 mmol, 1 equiv.) in methyl alcohol (100 mL) under reflux. The solution was then stirred for 17 h in refluxing methyl alcohol. The end of the reaction was monitored by TLC (cyclohexane/ethyl acetate, 5:5). The solvent was evaporated under reduced pressure, and the residue was taken up in a mixture of EtOH/H$_2$O (20:50). The mixture was neutralized by the addition of a saturated solution of NaHCO$_3$. Tin salts were removed by filtration. The filtrate was then extracted by ethyl acetate. The organic layer was dried with anhydrous MgSO$_4$, filtered, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (ethyl acetate then ethyl acetate/methyl alcohol, 99:1, 98:2, 95:5, 90:10). Expected compound **11** (0.93 g, 80% yield) was obtained as an orange solid. ^{1}H NMR (250 MHz, [D$_6$]acetone): δ = 1.25 (s, 18 H, CH$_3$), 4.06 (br. s, 4 H, NH$_2$), 6.70 (s, 2 H, aromatic CH), 8.46 [br. s, 2 H, *NH*-C(O)] ppm. ^{13}C{^{1}H} NMR (62 MHz, [D$_6$]acetone): δ = 28.0 (CH$_3$); 39.7 [-*C*(CH$_3$)$_3$]; 105.3 (aromatic CH); 123.3, 139.2 (aromatic C); 177.1 (C=O) ppm. MS (ESI): *m*/*z* = 307 [M + H]$^+$. $C_{16}H_{26}N_4O_2$ (306.20): calcd. C 62.30, H 8.72, N 17.87; found C 62.50, H 8.75, N 17.92.

4,5-Dibenzamido-1,2-bis(2,2-dimethylpropanamido)benzene (12): Triethylamine (1 mL, 7.17 mmol, 4 equiv.) was added dropwise to a solution of **11** (0.56 g, 1.83 mmol, 1 equiv.) in acetonitrile (60 mL) under an atmosphere of argon at room temperature. The mixture was then stirred at room temperature for 5 min and benzoyl chloride (640 μL, 5.51 mmol, 3 equiv.) was added dropwise. The reaction mixture was heated under reflux for 26 h, and the reaction was monitored by TLC (cyclohexane/ethyl acetate, 5:5). The solution was cooled down to room temperature, and the white precipitate was isolated by filtration and washed with water to afford **12** (0.81 g, 85% yield) as a white solid. ^{1}H NMR (250 MHz, [D$_6$]acetone): δ = 1.33 (s, 18 H, CH$_3$), 7.55 (m, 6 H, aromatic CH), 7.84 (s, 2 H, aromatic CH), 8.06 (dd, J_{ortho} = 8.0 Hz, J_{meta} = 1.5 Hz, 4 H, aromatic CH), 9.03 [br. s, 2 H, *NH*-C(O)-*t*Bu], 9.98 [br. s, 2 H, *NH*-C(O)-Ph] ppm. ^{13}C{^{1}H} NMR spectroscopic data of compound **12** are not reported owing to its lack of solubility. MS (MALDI-TOF): *m*/*z* = 513 [M – H]$^+$. $C_{30}H_{34}N_4O_4$ (514.25): calcd. C 70.02, H 6.66, N 10.89; found C 69.71, H 6.72, N 10.92.

4,5-Dibenzamido-1,2-bis(neopentylamino)benzene (13): Compound **12** (0.21 g, 0.41 mmol, 1 equiv.) was added in small portions to a stirred suspension of LiAlH$_4$ (0.10 g, 2.63 mmol, 6 equiv.) in anhydrous THF (30 mL) under an atmosphere of argon. The reaction mixture was stirred in refluxing THF under an atmosphere of argon for 6 h. The total consumption of reactive **12** was monitored by TLC. The mixture was cooled down to room temperature and hydrolyzed with water/methyl alcohol (3:1, 8 mL). The solvents were evaporated under reduced pressure, and the residue was taken up in dichloromethane. The insoluble aluminate salts were removed by filtration, and the filtrate was washed with water, dried with anhydrous MgSO$_4$, filtered, and evaporated under reduced pressure. The crude product was then taken up in acetonitrile (2 mL). The solid in suspension was isolated by filtration and washed with diethyl ether (3 mL) to afford **13** (0.06 g, 30% yield) as a white solid. ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.91 (s, 18 H, CH$_3$), 2.61 (s, 4 H, N-*CH*$_2$-*t*Bu), 3.04 (br. s, 2 H, *H*N-CH$_2$-*t*Bu), 6.72 (s, 2 H, aromatic CH), 7.51 (t, J_{ortho} = 7.5 Hz, 6 H, aromatic CH), 8.02 (d, J_{ortho} = 7.5 Hz, 4 H, aromatic CH), 9.06 [s, 2 H, *HN*-C(O)Ph] ppm. ^{13}C{^{1}H} NMR (62 MHz, CDCl$_3$): δ = 27.8 (CH$_3$), 31.3 [-*C*-(CH$_3$)$_3$], 56.2 (N-*CH*$_2$-*t*Bu), 109.2, 122.5, 127.6, 128.6, 131.7, 134.3, 137.2 (aromatic CH), 166.1 (C=O) ppm. MS (MALDI-TOF+): *m*/*z* = 487 [M + H]$^+$, 509 [M + Na]$^+$. $C_{30}H_{38}N_4O_2 \cdot H_2O$ (504.31): calcd. C 71.40, H 7.99, N 11.10, found C 71.90, H 7.32, N 11.62.

***N*-Benzyl-2-(benzylamino)-*N*′-neopentyl-5-(neopentylamino)-1,4-benzoquinonediimine (14):** The filtrate obtained from the synthesis of **13** was evaporated under reduced pressure and taken up in pentane. The insoluble solid was then isolated by filtration and washed with pentane to afford compound **14** (0.01 g, 5% yield) as an orange amorphous solid. ^{1}H NMR (250 MHz, [D$_6$]acetone): δ = 0.97 (s, 18 H, CH$_3$), 2.92 (s, 4 H, N-*CH*$_2$-*t*Bu), 4.50 (s, 4 H, N-*CH*$_2$-Ph), 5.29 (s, 2 H, quinoid CH), 6.80 (br. s, 2 H, NH), 7.35 (m, 10 H, aromatic CH) ppm. HRMS (ESI): calcd. for $C_{30}H_{40}N_4$ [M + H]$^+$ 457.3326; found 457.3312.

1,2,4-Tris(2,2-dimethylpropanamido)benzene (16): Triethylamine (57 μL, 4.09 mmol, 3 equiv.) was added dropwise to a solution of 1,2,4-triaminobenzene dihydrochloride (0.21 g, 1.02 mmol, 1 equiv.) in anhydrous acetonitrile (30 mL) under an atmosphere of argon at room temperature. The mixture was then stirred at room temperature for 5 min and trimethyl acetyl chloride (38 μL, 3.09 mmol, 2 equiv.) was added dropwise. The reaction mixture was heated under reflux for 4 h, and the reaction was monitored by TLC (cyclohexane/ethyl acetate, 5:5). The solvent was then evaporated under reduced pressure. The residue was taken up in water (30 mL), and insoluble product **16** (0.34 g, 89% yield) was isolated by filtration as a purple solid. ^{1}H NMR (250 MHz, [D$_6$]acetone): δ = 1.29 (br. s, 27 H, CH$_3$), 7.31 (d, J_{ortho} = 8.5 Hz, 1 H, aromatic CH), 7.52 (dd, J_{ortho} = 8.5 Hz, J_{para} = 2.5 Hz, 1 H, aromatic CH), 7.75 (d, J_{para} = 2.5 Hz, 1 H), 8.74 (br. s, 1 H, NH), 8.82 (br. s, 1 H, NH), 8.88 (br. s, 1 H, NH) ppm. ^{13}C{^{1}H} NMR (62 MHz, [D$_6$]acetone): δ = 27.75, 27.76, 27.77 (CH$_3$); 39.48, 39.57, 39.62 [-*C*(CH$_3$)$_3$]; 117.17, 118.04, 125.39, 126.91, 131.31, 135.57 (aromatic CH); 177.07, 178.10, 178.24 (C=O) ppm. MS (ESI): *m*/*z* = 376 [M + H]$^+$. $C_{21}H_{33}N_3O_3 \cdot 1/2H_2O$ (384.25): calcd. C 65.81, H 8.80, N 11.29; found C 65.60, H 8.91, N 10.93.

Acknowledgments

This work in Marseille and Strasbourg was supported by the Centre National de la Recherche Scientifique, the Ministère de l'Enseignement Supérieur et de la Recherche, and the Provence Alpes Côte d'Azur Region (PhD grant of C. S.). We thank Dr. Hugues Brisset for fruitful discussions and electrochemical studies.

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Received: January 24, 2008
Published Online: May 8, 2008

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