Stable Triplet-State Di(Cation Radicals) of a *Meta−Para* Aniline Oligomer by "Acid Doping"

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Abstract: We describe the formation of a stable triplet-state oligoaniline di(cation radical) via a proton-triggered redox reaction between *N,N′*-bis[4-(phenylamino)phenyl]-1,3-benzenediamine (**1**) and *N,N′*-bis[4-(phenylimino)-cyclohexa-2,5-dienylidene]-1,3-benzenediamine (**2**). In this reaction **1** is oxidized, while protonated **2** is reduced, both yielding the same di(cation radical) **1²•²⁺**. The di(cation radical) is characterized with UV/visisble/near-IR and ESR spectroscopy ($D = 118$ MHz; $E \approx 0$ MHz). Variable-temperature ESR measurements are consistent with a triplet ground state for **1²•²⁺**. The high stability of **1²•²⁺** under ambient conditions demonstrates that alternating *meta* and *para* oligoanilines are interesting building blocks for future polaronic ferromagnets.

Introduction

A promising strategy toward high-spin polymers is that of a polaronic ferromagnetic chain, in which dopable segments are interlinked by ferromagnetic coupling units.[1] Doping of such a polymer may result in ferromagnetically coupled unpaired electrons, localized within these segments. A number of polymers have been prepared that demonstrate the feasibility of this strategy.[2] The concept of a polaronic ferromagnet bears a strong resemblance to the redox doping of conducting polymers. A special type of doping in conducting polymers is the "acid doping" of the emeraldine base of polyaniline to the conducting emeraldine salt.[3] The emeraldine base consists of an alternating sequence of fully oxidized *p*-quinodiimine and fully reduced *p*-phenylenediamine units linked via *p*-phenylenes. Protonation of the polyaniline emeraldine base at the imine nitrogen atoms induces an internal redox reaction in which one electron is transferred from each *p*-phenylenediamine to a *p*-quinodiiminium unit. In the resulting conducting emeraldine salt, all aniline units have the same intermediate oxidation state and all nitrogen atoms have become equivalent. This internal redox reaction produces one unpaired electron per two aniline units. In principle the same proton-induced spin unpairing can also be used to prepare high-spin polyanilines. Several high-spin oligoradicals prepared by oxidation of arylamines have been described.[4] Recently, we have shown that oxidation of a *meta−*

Scheme 1
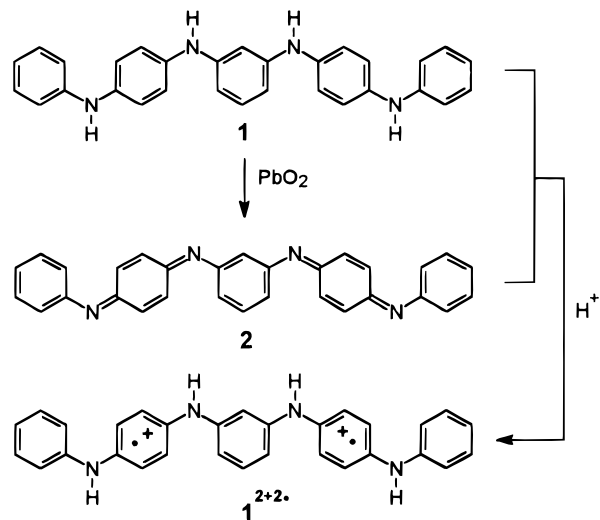
para aniline oligomer results in a triplet di(cation radical) that combines chemical stability from the *p*-phenylenediamine units with ferromagnetic interaction via a *m*-phenylene ring.[5] Here we demonstrate that the concept of acid doping can be used to prepare high-spin di(cation radical) oligoanilines. For this purpose we have prepared the fully reduced **1** and fully oxidized **2** forms of an oligoaniline, in which two *para*-substituted rings are linked by *m*-phenylene. A 1:1 mixture of **1** and **2** has the required overall oxidation state and by simply adding a drop of acid a redox reaction is initiated that produces a stable di(cation radical) as the single product (Scheme 1).

Results and Discussion

Tetraamine **1** was synthesized from *N*-phenyl-1,4-benzene-diamine as described in Scheme 2. Diacetylation with acetic anhydride and reaction with 0.5 equiv of 1,3-dibromobenzene in an Ullmann coupling with copper(I) iodide as a catalyst, afforded the tetra-*N*-acetyl oligomer, which was hydrolyzed to tetraamine **1**. Tetraimine **2** was prepared from **1** by oxidation with PbO₂ (Scheme 1).

Cyclic voltammetry of **1** under acid conditions (acetonitrile, 10^{-3} M perchloric acid, 0.1 M tetrabutylammonium hexafluo-

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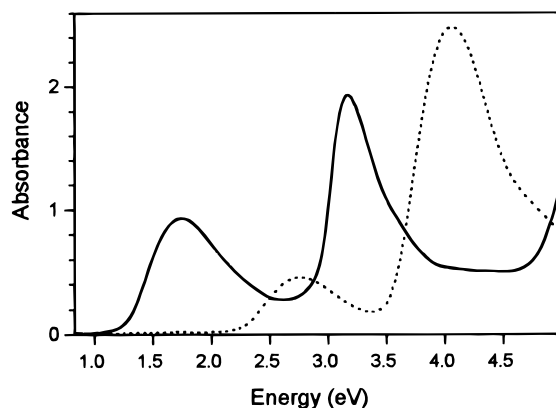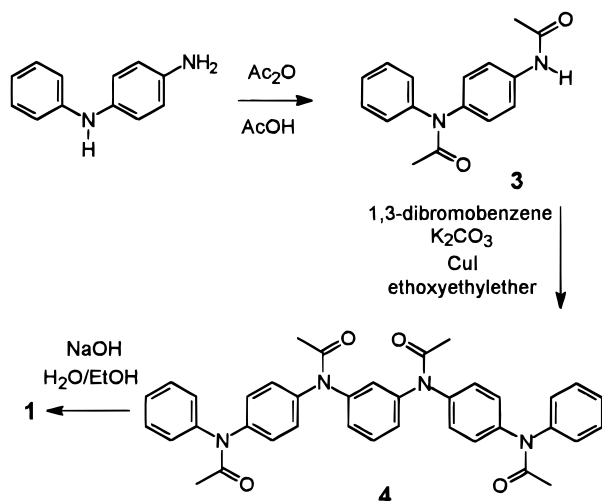(5) Wienk, M. M.; Janssen, R. A. J. *Chem. Commun.* **1996,** 267.

Figure 1. UV/visible/near-IR spectra of a 1:1 mixture of **1** and **2**: (···) in MeCN; (—) in MeCN/TFA (99:1).

Scheme 2

rophosphate as supporting electrolyte) reveals two chemically reversible two-electron oxidation/reductions at $E_1° = 0.63$ and $E_2° = 0.89$ V vs SCE. These values are similar to those reported for N,N'-diphenyl-1,4-benzenediamine.[6] Apparently, up to four electrons can be removed reversibly from oligoaniline **1** under acid conditions.

When equimolar amounts of tetraamine **1** and tetraimine **2** are dissolved in acetonitrile, no reaction occurs. The UV/visible/near-IR spectrum of the mixture (Figure 1) is a superposition of the absorptions of **1** (4.09 eV) and **2** (2.74 and 4.05 eV), and no ESR signal is observed. Upon addition of 1% (v/v) of trifluoroacetic acid the electronic spectrum changes completely. The initial absorption bands disappear and two new peaks at 1.75 and 3.17 eV emerge, attributed to singly oxidized p-phenylenediamine units.[6a,7]

The ESR spectrum of the acid-doped mixture, recorded at 110 K (Figure 2), reveals the zero-field splitting characteristic for a high-spin molecule. Unambiguous proof for a high-spin state is provided by a $\Delta M_s = \pm 2$ transition at half-field. These ESR signals are attributed to the triplet-state di(cation radical) $\mathbf{1^{2 \cdot 2+}}$ resulting from a proton-triggered redox reaction between tetraamine **1** and tetraimine **2**. In this process the protonated tetraimine is reduced to the corresponding di(cation radical),

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(7) The optical absorption spectra of neutral tetraamine **1** and its di-(cation radical) $\mathbf{1^{2 \cdot 2+}}$ are found to be identical to those of N,N'-diphenyl-1,4-benzenediamine and its monocation radical. This suggests that the non-resonant m-phenylene ring effectively separates the electronic transitions in **1** and $\mathbf{1^{2 \cdot 2+}}$.
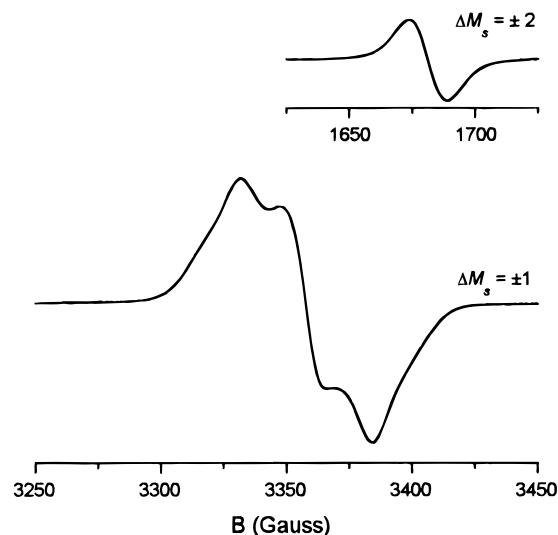
Figure 2. X-Band ESR spectrum of $\mathbf{1^{2 \cdot 2+}}$ in CH_2Cl_2/TFA recorded at 110 K. The central line is due to some doublet impurity. Inset: $\Delta M_s = \pm 2$ transition recorded at 4.0 K.

$\mathbf{1^{2 \cdot 2+}}$, while at the same time the tetraamine **1** is oxidized to exactly the same species. In acidic solution this triplet-state di(cation radical) $\mathbf{1^{2 \cdot 2+}}$ is stable at room temperature for several days. Reduction of $\mathbf{1^{2 \cdot 2+}}$ with hydrazine monohydrate regenerates **1** in quantitative yield, as evidenced from the UV/visible/near-IR spectrum showing the band of tetraamine **1** at 4.09 eV with double intensity as compared to the initial spectrum.

The zero-field splitting parameters ($D = 118$ MHz; $E \approx 0$ MHz) were determined by simulation of the $\Delta M_s = \pm 1$ transitions of the ESR spectrum. Assuming a point-dipole approximation for the zero-field splitting, $D = 118$ MHz corresponds to an average distance between the unpaired electrons of 8.7 Å. This is consistent with the separation of 9.8 Å between the centers of the two p-phenylenediamine units, as estimated from standard bond lengths, assuming a planar geometry.

In order to determine the ground state of $\mathbf{1^{2 \cdot 2+}}$, variable temperature ESR measurements were carried out. The signal intensity of the $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ transitions follows Curie's law ($I = C/T$) between 4 and 100 K and is completely reversible. The Curie behavior reveals that no extra population or depopulation of the triplet state occurs in this temperature region. This can be interpreted in two possible ways.[8] Either the triplet state is the ground state and separated from the singlet state by a substantial energy gap of a few hundreds of calories per mole or the singlet and triplet states are exactly degenerate. In either case, however, the triplet state corresponds to the lowest energy state.

Di(cation radical) $\mathbf{1^{2 \cdot 2+}}$ has also been prepared by chemical oxidation of tetraamine **1** in dichloromethane/tetrafluoroacetic acid (1:1), using thianthrenium perchlorate[9] or phenyliodine-(III) bis(trifluoroacetate)[10] as oxidizing agent. Addition of <1 equiv of oxidant affords monocation radical $\mathbf{1^{\cdot +}}$, being a mixed-valence molecule.[11] The ESR spectrum of $\mathbf{1^{\cdot +}}$ at room temperature exhibits a well-resolved complex pattern dominated by hyperfine interaction with two ^{14}N nuclei and two amine protons. The isotropic couplings of $A_{iso}(N) = 5.5$ G and

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$A_{iso}(H) = 6.5$ G are in good agreement with values reported for *N,N′*-diphenyl-1,4-benzenediamine.[6a] Hyperfine interaction with only two nitrogen nuclei demonstrates that the unpaired electron is localized within half of the molecule. Further oxidation of **1**[•+] leads to the formation of the di(cation radical) **1**[2•2+], with electronic and ESR spectra identical to those obtained in the acid doping experiment.

Conclusion

We have demonstrated that, in addition to redox doping, acid doping can be used to generate polaronic high-spin molecules. The chemical stability of the di(cation radical), **1**[2•2+] confirms the feasibility of alternating *meta* and *para* oligoanilines as building blocks for future polaronic ferromagnetic polymers.

Experimental Section

General Methods. Commercial grade reagents were used without further purification. Solvents were purified following standard procedures. NMR spectra were recorded on a Bruker AM-400 spectrometer, chemical shifts are relative to TMS for ^{1}H and ^{13}C NMR spectra. Cyclic voltammograms were obtained with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte using a Potentioscan Wenking POS73 potentiostat.

N-Phenyl-N,N′-1,4-phenylenebis(acetamide) (3). Acetic anhydride (3.8 mL, 40 mmol) was added slowly to *N*-phenyl-1,4-phenylenediamine (3.68 g, 20 mmol) in acetic acid (20 mL). After the addition was complete, the reaction mixtrure was heated to 70 °C for 2 h. The acetic acid was removed by distillation under reduced pressure. Column chromatography (SiO₂, EtOAc) and recrystallization from hexane/EtOAc (1:1) provided **3** (3.83 g, 87%) as a white crystalline solid: mp 137 °C; ^{1}H NMR (330 K, CDCl₃)[12] δ 2.09 (3H, s, CH₃), 2.16 (3H, s, CH₃), 7.18 (2H, d, *J* = 8.7 Hz, H-2 and H-6), 7.20−7.25 (3H, m, H-4′ and H-2′ + H-6′), 7.30 (1H, bs, N-H), 7.33 (2H, dd , *J* = 8.4 Hz and 6.9 Hz, H-3′ + H-5′), 7.43 (2H, bd, *J* = 8.7 Hz, H-3 + H-5); ^{13}C NMR (330 K, CDCl₃) δ 23.45 (CH₃), 23.86 (CH₃), 120.80 (C-3 + C-5), 126.87 (C-4′), 127.23 (C-2 + C-6 or C-2′ + C-6′), 127.60 (C-2 + C-6 or C-2′ + C-6′), 129.19 (C-3′ + C-5′), 137.4 (C-4), 138.61 (C-1), 143.15 (C-1′), 168.73 (CO), 170,53 (CO). Anal. Calcd for C₁₆H₁₆N₂O₂: C, 71.62; H, 6.01; N, 10.44. Found: C, 72.14; H, 5.94; N, 10.54.

N,N′-Bis[4-(N-phenylacetylamino)phenyl]-1,3-phenylenebis(acetamide) (4). Diamide **3** (2.69 g, 10 mmol), 1,3-dibromobenzene (1.18 g, 10 mmol), K₂CO₃ (1.38 g, 10 mmol), and CuI (0.05 g, 0.25 mmol) in ethoxyethyl ether (25 mL) were heated to reflux for 24 h. The hot reaction mixture was filtered over Hyflo and the filtrate thoroughly washed with EtOAc. The combined organic fractions were concentrated by vacuum distillation, and the crude product was purified by column chromatography (SiO₂, CHCl₃/MeOH 9:1) and recrystallization from hexane/EtOAc, providing **4** (3.11 g, 51%) as a white solid: mp 160−165 °C;[13] ^{1}H NMR (330 K, CDCl₃) δ 1.98 (6H, s, CH₃), 1.99 (6H, s, CH₃), 7.06 (2H, d, *J* = 8.1 Hz, H-4 and H-6), 7.16 (4H, d, *J* = 8.8 Hz, H-2″ and H-6″), 7.2−7.3 (12H, m, H-2, H-5, H-2′ + H-6′, H-3′ + H-5′, and H-4″), 7.35 (4H, t, *J* = 7.7 Hz, H-3″ + H-5″); ^{13}C NMR

(330K, CDCl₃) δ 23.74 (CH₃), 125.46 (C-4 + C-6), 126.65 (C-2), 127.44, 127.54, 127.87 and 128.06 (C-2′ + C-6′, C-3′ + C-5′, C-2″ + C-6″, and C-4″), 129.61 (C-3″ + C-5″), 129.91 (C-5), 140.72 and 141.86 (C-1′ + C-4′), 143.13 (C-1″), 143.83 (C-1 + C-3), 170.01 and 170.10 (CO). Anal. Calcd for C₃₀H₂₆N₄: C, 74.74; H, 5.61; N, 9.17. Found: C, 74.30; H, 4.89; N, 9.39.

N,N′-Bis[4-(phenylamino)phenyl]-1,3-benzenediamine (1). A solution of tetraamide **4** (1.22 g, 2 mmol) and sodium hydroxide (1.0 g, 40 mmol) in EtOH/H₂O (1:1, 40 mL) was heated under reflux for 48 h. During the reaction the initially homogeneous solution gave a liquid/liquid phase separation and a precipitate was formed. After cooling, the precipitate was filtered off, washed with water and dried under reduced pressure. Recrystallization from benzene gave pure **1** (0.73 g, 83%) as a white crystaline solid: mp 211 °C (dec); ^{1}H NMR (CDCl₃) δ 5.52 (2H, br s, NH), 5.56 (2H, br s, NH), 6.48 (2H, dd, *J* = 8.0 and 2.2 Hz, H-4 + H-6), 6.59 (1H, t, *J* = 2.2 Hz, H-2), 6.86 (2H, tt, *J* = 7.3 and 1.1 Hz, H-4″), 6.97 (4H, m, H-2″ + H-6″), 7.05 (8H, s, H-2′, H-3′, H-5′ + H-6′), 7.09 (1H, t, *J* = 8.0 Hz, H-5), 7.23 (4H, m, H-3″ + H-5″); ^{13}C NMR (CDCl₃) δ 103.75 (C-2), 108.29 (C-4 + C-6), 116.45 (C-2″ + C-6″), 120.15 (C-4″), 120.79 , 121.3 (C-2′ + C-6′ and C-3′ + C-5′), 129.34 (C-3′ + C-5′), 130.19 (C-5), 136.92 (C-1′ or C-4′), 137.25 (C-1′ or C-4′), 144.26 (C-1″), 145.58 (C-1 + C-5); ES− MS *m/z* (M⁺) calcd 442.2, obsd 442.4. Anal. Calcd for C₃₀H₂₆N₄: C, 81.42; H, 5.92; N, 12.66. Found: C, 81.54; H, 5.85; N, 12.71.

N,N′-Bis-[4-(phenylimino)-cyclohexa-2,5-dienylidene)]-1,3-benzenediamine (2). To tetraamine **1** (110 mg, 0.025 mmol) in chloroform (5 mL) was added PbO₂ (0.6 g, 2.5 mmol). The mixture was stirred at room temperature for 15 min. The dark red solution was filtered over silica, and the solvent was removed by evaporation. The product (98 mg, 90%) was isolated as a mixture of three *cis−trans* isomers (**2a, 2b, 2c**). These isomers could not be separated by column chromatography since during this process isomerization takes place: ^{1}H NMR (CDCl₃) δ 6.37, 6.41, 6.46 ((0.2 + 0.5 + 0.3)H, 3 t, *J* = 1.9 Hz, H-2**a**−**c**), 6.67 (0.4H, dd, *J* = 8.0 and 1.9 Hz, H-4**a** + H-6**a**), 6.69,6.70 (1H, 2 d, *J* = 8.0 H-4**b** and H-6**b**), 6.72 (0.6H, dd, *J* = 8.0 and 1.9 Hz, H-4**c** and H-6**c**), 6.75−7.15 (12H, m, H-2′, H-3′, H-5′, and H-6′), 7.20 (2H, m, H-4″), 7.31−7.43 (9H, m, H-5 and H-2″ + H-6″); ^{13}C NMR (CDCl₃) δ 112.22 (C-2), 117.09, 117.16, 117.19, 117.22 (C-4 + C-6), 120.49, 120.57 (C-2″ + C-6″), 124.45, 124.49, 124.72, 125.07, 125.11, 125.40 (*syn*-(C-2′ + C-3′ + C-5′ + C-6′)), 125.20, 125.23 (C-4″), 128.91, 128.95 (C-3″ + C-5″), 129.53, 129.58, 129.64 (C-5), 136.26, 136.30, 136.77, 137.44, 137.48, 137.98 (*anti*-(C-2′ + C-3′ + C-5′ + C-6′)), 149.92, 149.94 (C-1″), 150.74, 150.77, 150.82 (C-1 + C-3), 158.20, 158.22, 158.28, 158.31 (C-1′), 158.67, 158.74 (C-4′); ES− MS *m/z* (M + H⁺) calcd 239.2, obsd 239.4.

Electron Spin Resonance. ESR spectra were recorded using a Bruker ER200D SRC spectrometer, operating with an X-band standard cavity and interfaced to a Bruker Aspect 3000 data system. Temperature was controlled by a Bruker ER4111 variable-temperature unit between 100 K and room temperature or by an Oxford 3120 temperature controller combined with an ESR900 continuous flow cryostat in the range 3.8−100 K. Saturation of the ESR signal during variable temperature experiments on the $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ transition was avoided by using low microwave powers, well within the range where signal intensity is proportional to the square root of microwave power at 4.2 K.

UV/visible/near-IR Spectrometry. Absorption spectra in the UV/visible/near-IR region were recorded using a Perkin-Elmer Lambda 900 spectrophotometer with a sealed 10 mm cuvette.

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(12) The appearance of the ^{1}H NMR spectrum turned out to be very sensitive towards temperature and concentration.

(13) Between 160 and 165 °C a liquid crystalline phase was observed by polarization microscopy.