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Published in:
Journal of the American Chemical Society

DOI:
10.1021/ja9616591

Published: 01/01/1996

Citation for published version (APA):
Stable Triplet-State Di(Cation Radicals) of a Meta—Para Aniline Oligomer by “Acid Doping”

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Received May 17, 1996

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-(phenylimino)phenyl]-1,3-benzediamine (1) and \( N,N'\)-bis[4-(phenylimino)cyclohexa-2,5-diénylene]-1,3-benzediamidine (2). In this reaction 1 is oxidized, while protonated 2 is reduced, both yielding the same di(cation radical) \( 1^{2+2} \). The di(cation radical) is characterized with UV/visible/near-IR and ESR spectroscopy \( (D = 118 \text{ MHz}; E \approx 0 \text{ MHz}) \). Variable-temperature ESR measurements are consistent with a triplet ground state for \( 1^{2+2} \). The high stability of \( 1^{2+2} \) 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 \( p \)-quinodimine and fully reduced \( p \)-phenylene-1,4-benzenediamine 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 unit to a \( p \)-quinodiminium 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 oligoanilides prepared by oxidation of arylamines have been described.\(^4\) Recently, we have shown that oxidation of a meta-...
tetraimine is reduced to the corresponding di(cation radical), tetraamine for a high-spin molecule. Unambiguous proof for a high-spin
110 K (Figure 2), reveals the zero-field splitting characteristic
of the absorptions of
N,N-diphenyl-1,4-benzenediamine. 6 Apparently, up to four
electrons can be removed reversibly from oligoaniline 1 under acidic conditions.

When equimolar amounts of tetraamine 1 and tetraimine 2 are dissolved in acetonitrile, no reaction occurs. The UV/visible/
shorter IR spectrum changes completely. The initial absorption bands disappear and two new peaks at
1.75 and 3.17 eV emerge, attributed to singly oxidized
1,4-benzenediamine and its monocation radical. This suggests that the non-

resonant m-phenylene ring effectively separates the electronic transitions in 1 and 122+.

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)
122+, 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),

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

Scheme 2

![Scheme 2](image)

Figure 2. X-Band ESR spectrum of 122+ in CH3Cl2/TFA recorded at
110 K. The central line is due to some doublet impurity. Inset: \( \Delta M_s = \pm 1 \) transition recorded at 4.0 K.

122+, while at the same time the tetraamine 1 is oxidized to exactly the same species. In acidic solution this triplet-state
di(cation radical) 122+ is stable at room temperature for several days. Reduction of 122+ with hydrazine monohydrate generates
1 in quantitative yield, as evidenced from the UV/visible/
shorter 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 (\( D = 118 \text{ MHz}; E \approx 0 \text{ MHz} \)) 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, \( D = 118 \text{ MHz} \)
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 122+, 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.3 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) 122+ has also been prepared by chemical oxidation of tetraamine 1 in dichloromethane/tetrafluoroacetic
acid (1:1), using thianthrenium perchlorate9 or phenylidyne-
(III) bis(trifluoracetate)10 as oxidizing agent. Addition of <1 equiv of oxidant affords monocation radical 1+**, a being a mixed-valence molecule.11 The ESR spectrum of 1+** at room temperature exhibits a well-resolved complex pattern dominated by hyperfine interaction with two 14N nuclei and two amine
protons. The isotropic couplings of \( A_{iso}(N) = 5.5 \text{ G} \) and

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1993, 55–57, 1521.

(7) The optical absorption spectra of neutral tetraamine 1 and its
dication radical) 122+ are found to be identical to those of \( \lambda \)-N,N-diphenyl-
1,4-benzenediamine and its monocation radical. This suggests that the non-

m-phenylene ring effectively separates the electronic transitions in 1 and 122+.

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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 1H and 13C NMR spectra. Cyclic voltammograms were obtained with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte using a Potentiostan Wenking POS73 potentiostat.

N-Phenyl-N,N',1,4-phenylenebis(acetamide) (3). Acetic anhydride (3.6 mL, 40 mmol) was added slowly to N-phenyl-1,4-benzendiamine (3.68 g, 20 mmol) in acetic acid (20 mL). After the addition was complete, the reaction mixture 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 EtOAc (1:1) provided 3 (3.83 g, 87%) as a white crystalline solid: mp 137 °C.1H NMR (300 K, CDCl3) 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-5) 7.30 (1H, bs, N-H), 7.33 (2H, dd, J = 8.4 Hz and 6.9 Hz, H-3 and H-5), 7.43 (2H, bd, J = 8.7 Hz, H-3 and H-5); 13C NMR (300 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′), 126.70 (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′), 186.73 (CO), 170.53 (CO). Anal. Calcd for C13H14N2O2: 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) were heated at 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.13C NMR (300 K, CDCl3) δ 198 (6H, s, CH3), 199 (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′), 3.75 (4H, t, J = 7.7 Hz, H-3′ and H-5′); 13C 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 C32H26N4O4: C, 73.74; H, 5.61; N, 9.17. Found: C, 73.70; H, 4.89; N, 9.39.

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 38–100 K. Saturation of the ESR signal during variable temperature experiments on the ΔM = ±1 and ΔM = ±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.