

Naphthylidiamine Diradical Dications. Triplet Dications of 2,7-Bis(amino)naphthalene and 2,7-Bis(phenylenediamino)naphthalene

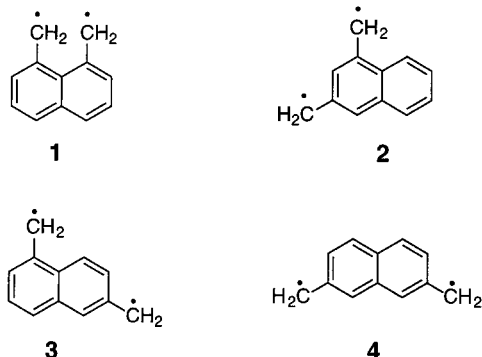
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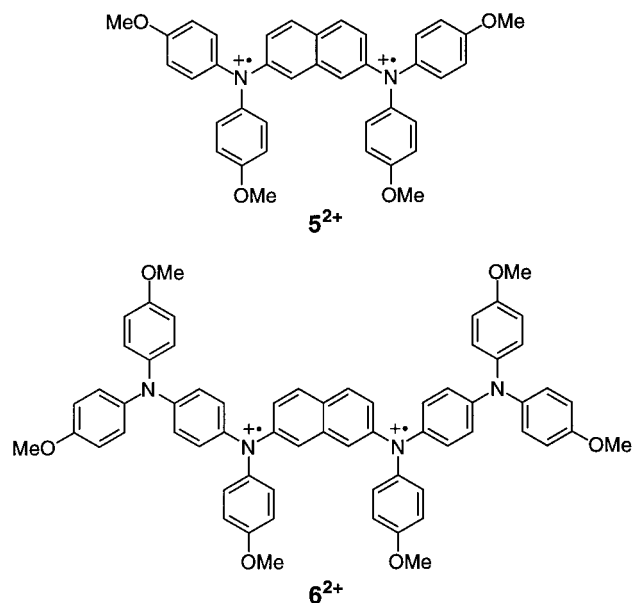
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As part of an effort to construct and characterize redox-switchable high-spin organic molecules,¹ we have begun a study of diamionaphthalene diradical dications isoelectronic with the non-Kekulé dimethylenenaphthalene structures **1–4**. The 1,8-



naphthyl diyl^{2,3} (**1**) and its alkyl derivatives^{4,5} have been previously observed by matrix ESR and fluorescence spectroscopy⁶ and assigned as *ground-state* triplet diradicals. Naphthyl diyls **2–4** have been prepared by matrix photolysis of the corresponding dichlorides and were also assigned as triplet diyls on the basis of their fluorescence spectra.⁷ Here, we report on 2,7-diamionaphthalene diradical dications **5²⁺** and **6²⁺** which are found to be solution-stable triplets.



Substrates **5** and **6** were prepared by condensation⁸ of *p*-anisidine with 2,7-dihydroxynaphthalene followed by Ullmann

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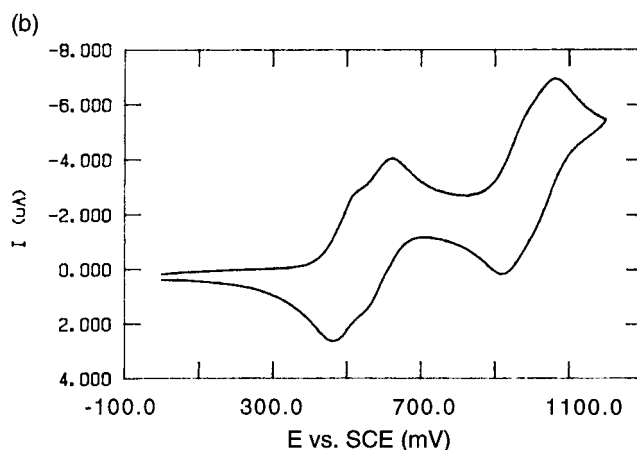
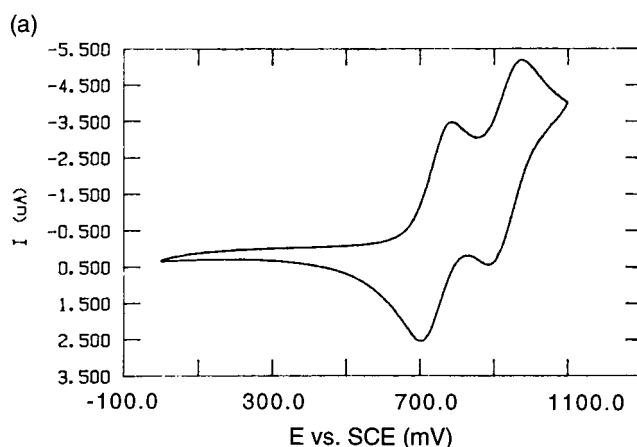
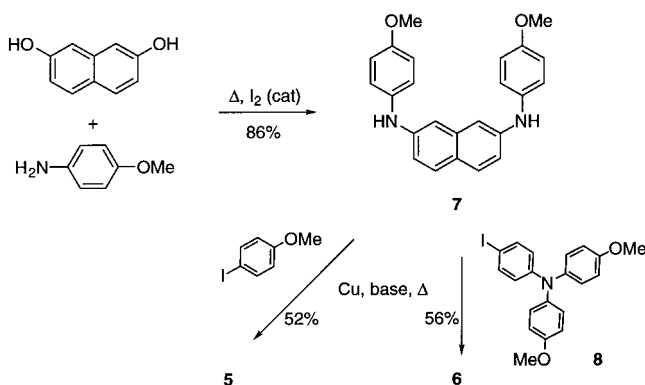


Figure 1. Cyclic voltammogram in CH₂Cl₂ (0.1 M Bu₄NBF₄) at 20 mV s⁻¹ scan rate at 298 K of (a) 1.0 mM **5** (b) 1.0 mM **6**.

coupling of the resulting diamine **7** with *p*-iodoanisole or di-*p*-anisyl-*p*-iodophenylamine (**8**) as shown below. Iodoamine **8** was made by Ullmann coupling of di-*p*-anisylamine with excess 1,4-diiodobenzene.



Oxidation of **5** by cyclic voltammetry (CV) shows two chemically reversible waves (Figure 1a) yielding $E^{\circ'}$ values of (*n*,+) 0.74 and (+,2+) 0.93 V vs SCE. CV oxidation of **6** shows

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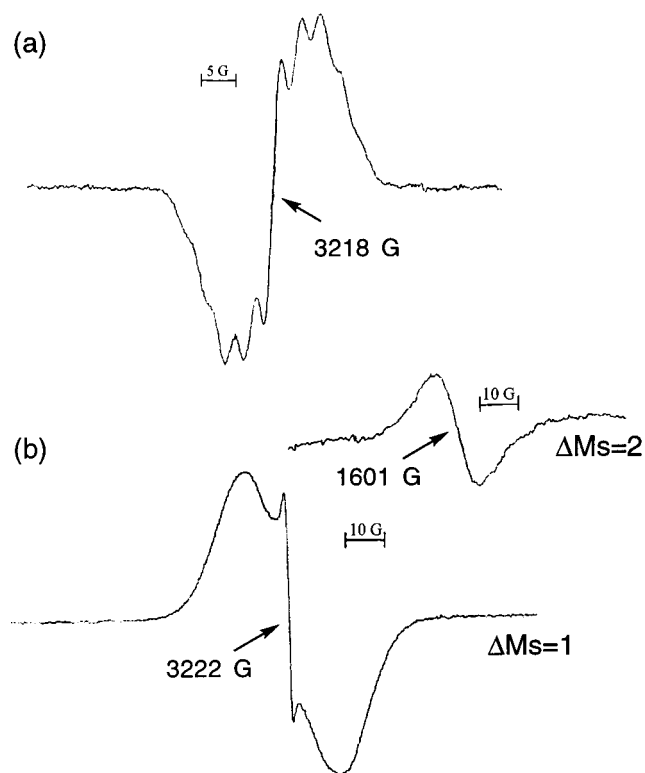


Figure 2. ESR spectra of (a) 0.5 mM $6^+PF_6^-$ in fluid CH_2Cl_2 at 298 K and (b) 0.5 mM $6^{2+}(PF_6^-)_2$ in solid PrCN at 90 K.

four chemically reversible waves (Figure 1b), with E° values of ($n,+$) 0.50, (+,2+) 0.59, (2+,3+) \sim 0.97, and (3+,4+) \sim 1.02 V vs SCE. The mono- and dication hexafluorophosphate salts of **6** are isolable and have been prepared by NOPF₆ oxidation of **6** in CH_2Cl_2 solutions.⁹

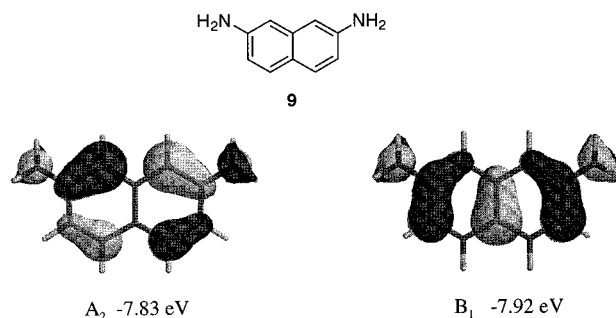
Oxidation of **5** and **6** by 1 or 2 molar equiv of thianthrenium (TH^+) perchlorate¹⁰ yields ESR-active solutions. The ESR spectrum of 5^+ in CH_2Cl_2 at 25 °C is a broad 5-line spectrum with overlaid fine structure (presumably due to multiple small hydrogen splittings). The 5-line splitting of \sim 4.6 G is assigned as the $a(2N)$ coupling due to two equivalent nitrogens. The dication 5^{2+} in frozen PrCN shows a broad signal in the $\Delta m_s = 1$ region with a signal width of \sim 95 G and a strong half-field $\Delta m_s = 2$ absorption centered at 1600 G. For 6^+ in CH_2Cl_2 at 25 °C, a broad, apparent 9-line spectrum (Figure 2a) is observed. The apparent splitting is consistent with nearly equal spin density on all four nitrogens of 6^+ with a splitting constant of \sim 3.0 G. For 6^{2+} in frozen PrCN, a $\Delta m_s = 1$ signal is observed with a

signal width of \sim 73 G along with a half-field $\Delta m_s = 2$ absorption centered at 1601 G that verifies the triplet nature of this dication (Figure 2b).

The half-field ESR signal intensities for 5^{2+} and for 6^{2+} obey the Curie law and increase linearly from 120 to 90 K which suggests that their triplet populations are not changing detectably in this limited temperature range. This observation is consistent with (a) triplet ground states and singlet/triplet energy gaps ($\Delta E_{S,T}$) greater than RT (i.e., >250 cal mol⁻¹) or (b) with $\Delta E_{S,T}$ values $\ll RT$ and either singlet or triplet ground states for these dications.

The solution stability of 5^{2+} and 6^{2+} allows the determination of their solution magnetic susceptibility by the Evans¹¹ NMR shift method. The effective magnetic moments (μ_{eff}) measured for 5^+ and 5^{2+} (prepared by TH^+ oxidation in CF_3CO_2D) were 1.75 ± 0.04 and 2.64 ± 0.04 , respectively. For $6^+PF_6^-$ and $6^{2+}(PF_6^-)_2$ dissolved in $CDCl_3$,¹² μ_{eff} values were measured to be 1.73 ± 0.04 and 2.40 ± 0.03 , respectively. Theoretical μ_{eff} values for doublet and triplet molecules are 1.73 and 2.83, respectively. The μ_{eff} values of 5^{2+} and 6^{2+} solutions suggests that they are singlet/triplet mixtures at 301 K. Assuming a weighted admixture of singlet ($\mu_{eff} = 0$) and triplet ($\mu_{eff} = 2.83$) states for these dication solutions yields populations of 87% triplet, 13% singlet for 5^{2+} and 72% triplet, 28% singlet for 6^{2+} . After correction for the 3:1 statistical triplet:singlet state preference, the data implies a triplet ground state for 5^{2+} with $\Delta E_{S,T}$ 0.48 kcal mol⁻¹ in CF_3CO_2D at 301 K and nearly degenerate singlet and triplet states with a possible singlet ground state for 6^{2+} in $CDCl_3$ at 301 K.

A high-spin ground state for 5^{2+} is consistent with AM1 calculations that predict a strong triplet preference for 2,7-diaminonaphthalene dication (9^{2+}) (UHF, 13.5 and π -CI, 14.9 kcal mol⁻¹). Although 2,7-aza substitution of the perinaphthalene nucleus alters the π MO structure from that calculated for the non-Kekulé hydrocarbon, the nondisjoint¹³ nature of the (nearly) degenerate singly occupied frontier MOs is preserved and thus so is also the energetic preference for spin alignment of the diyl electrons. The two highest energy occupied MOs of **9** (C_{2v}) are shown below. Spin dilution at α -nitrogens in 5^{2+} and 6^{2+} will diminish $\Delta E_{S,T}$ relative to that for 9^{2+} ; however, enough of an spin alignment preference apparently remains in the former to yield a triplet ground state structure.



(6) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216.

(7) Biewer, M. C.; Biehn, C. R.; Platz, M. S.; Després, A.; Migirdicyan, E. *J. Am. Chem. Soc.* **1991**, *113*, 616.

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(9) Anal. Calcd (%) for $6^{2+}(PF_6^-)_2$: C, 60.67; H, 4.46; N, 4.42. Found: C, 60.90; H, 4.38; N, 4.56.

(10) Caution! Thianthrenium perchlorate ($TH^+ClO_4^-$) is a shock-sensitive explosive solid and should be handled with due care. For preparation and properties see Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.

(11) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791.

(12) These solutions are normally stabilized with up to 5% trifluoroacetic acid and 5% trifluoroacetic anhydride. However, runs in the absence of these additives were checked and gave unaltered μ_{eff} values for the cations and dications.

(13) Borden, W. T. *Diradicals*; Wiley: New York, 1982; Chapter 1.

(14) For a potential application of 2,7-naphthyl-connected polyarylamine polymers as dopable high-spin cluster materials see: Bushby, R. J.; Gooding, D. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1069.

In summary, we conclude that 2,7-bis(amino)naphthalene substrates are a viable structural unit for preparing redox-activated stable diradical dication triplets.¹⁴ Further work to investigate other patterns of polyradical polycation spin-coupling about a naphthalene nucleus is in progress.

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Supporting Information Available: Synthesis and spectroscopic analysis of **5** and **6** and experimental details for ESR and NMR shift measurements (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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