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Macrocyclic Poly Arylamines for Rigid Connection of Poly Radical Cation Spins

Trent D. Selby and Silas C. Blackstock*

Department of Chemistry, The University of Alabama,
Tuscaloosa, Alabama 35487-0336

blackstock@ua.edu

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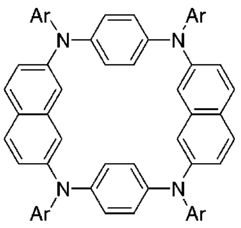
ABSTRACT



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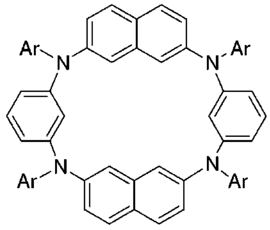

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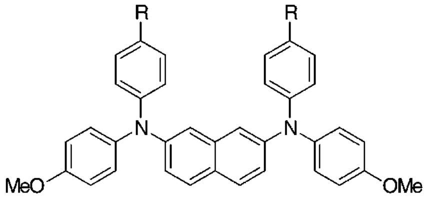
The synthesis of macrocyclic arylamines 3 and 4 is reported. These structures yield conformationally rigid polyradical cations for investigation of their electron spin properties. Dication 3^{2+} has dual N and N′ connection of its *p*-phenylenediamine radical cation units via 2,7-naphthalene bridges. By ESR and NMR analysis, 3^{2+} is found to possess a populated, low-lying triplet excited state. Macrocycle 4 undergoes multielectron oxidation as observed by cyclic voltammetry to yield polycations with more limited kinetic stability.

Arylamine poly radical cations have gained attention as useful spin units for preparing and testing new electron spin-coupling modes in organic polyradicals.[1] Convenient radical site generation by electron removal from neutral polyamines and kinetic stability of the resulting polyradical ions make this approach to multispin organic molecules a fruitful one. However, control of the conformational relationship between the spin-bearing functions can be problematic, yet it surely influences spin coupling. One way to limit conformational freedom in the polyradical is by cyclization. An added benefit of cyclization is the reinforcement of spin−spin interactions at the cycle closure junction. Rajca et al. have used this strategy to make cyclic arylmethane spin clusters.[2]



1, R = OMe
2, R = N(p-anisyl)$_2$

Recently, we showed that 2,7-bis(arylamino)naphthalenes **1** and **2** have stable triplet dication states.[3] Here, we report the preparation of cyclic analogues **3** and **4** for evaluation of their redox chemistry and polycation spin multiplicity preferences.

Macrocycles **3** and **4** were prepared by Ullmann coupling of 2,7-diaminonaphthalene (**5**) with 1,4-diiodobenzene or 1,3-diiodobenzene, respectively (Schemes 1 and 2). One-pot synthesis of the macrocycles was also successful, but with overall yields lower than those for the two-step method. Most recently, Hartwig and co-workers have shown Pd-mediated N-arylation reactions can be used to prepare macrocyclic arylamines in good yield.[4]

The conformational structure of macrocycle **3** has been investigated by AM1 calculations and by single-crystal X-ray diffraction analysis. The crystal structure shows alternating canting of the phenyl and naphthyl rings along the cyclo-

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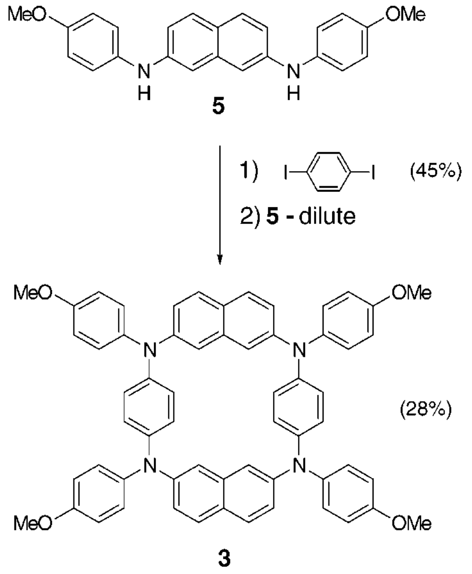
(1) For a review see: Blackstock, S. C.; Selby, T. D. Polyradical Cations of High Spin. In *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999; pp 165−78.
(2) Rajca, A.; Rajca, S.; Desai, S. R. *J. Am. Chem. Soc.* **1995**, *117*, 806.
(3) Selby, T. D.; Blackstock, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 7152.
(4) Hauck, S. I.; Lakshmi, K. V.; Hartwig, J. F. Submitted manuscript.

10.1021/ol991040e CCC: $18.00

Scheme 1



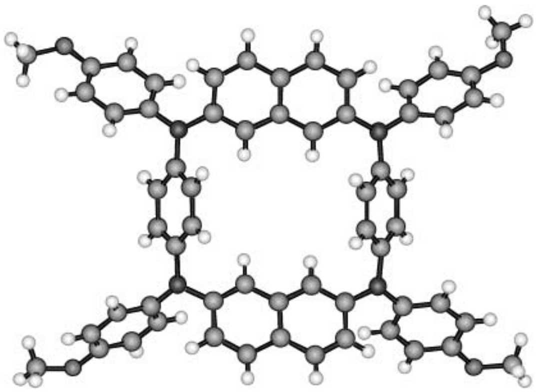
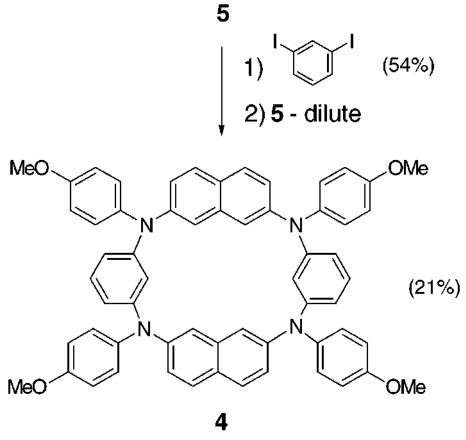


Figure 1. X-ray crystal structure of **3**. Solvent molecules at the core of the macrocycle have been omitted from this picture.

phane rim in **3** (Figure 1), and this conformational trend is also qualitatively reproduced by AM1 calculation of the tetra-NH (H for anisyl) analogue. Disorder of included nitrobenzene solvent molecules at the core of **3** has resulted in a loss of some resolution in the crystal structure, but the macrocyclic component is clearly refined from the diffraction data.

Electrochemical oxidation of **3** by cyclic voltammetry (CV) shows four chemically reversible waves with $E°'(1) \approx 0.59$, $E°'(2) \approx 0.64$, $E°'(3) \approx 1.00$, $E°'(4) \approx 1.09$ (Figure 2). These potentials are slightly anodic of those observed for acyclic analogue **2** whose $E°'(1)$ and $E°'(2)$ values are 0.50 and 0.59 V.[3] Loss of *N*-anisyl substitution in **3** vs **2** explains the shift. In addition, the relative ease of oxidation of **3** suggests that there is not large torsional strain associated with oxidation of the *p*-phenylenediamine groups within the macrocycle. The smaller $\Delta E°'(1,2)$ for **3** than for **2** could indicate a weaker interaction between redox groups in the macrocycle.

Scheme 2



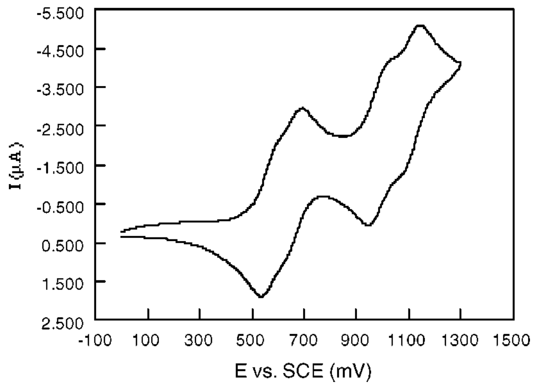


Figure 2. Voltammogram of **3** (1.0 mM) at 298 K in CH_2Cl_2 (0.1 M Bu_4NBF_4) with scan rate of 20 mV s^{-1}.

Oxidation of macrocycle **4** by CV shows a single chemically reversible wave at 0.85 V vs SCE (Figure 3). Both

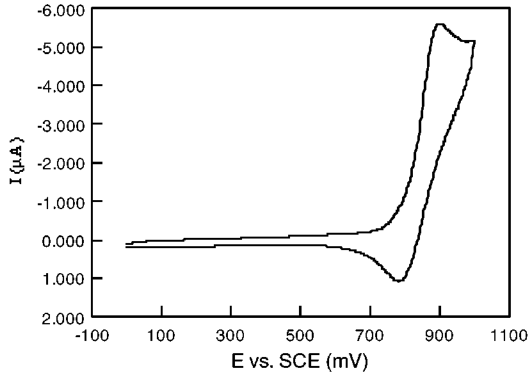


Figure 3. Voltammogram of **4** (1.0 mM) at 298 K in CH_2Cl_2 (0.1 M Bu_4NBF_4) with scan rate of 20 mV s^{-1}.

voltammograms of **3** and **4** were run under identical conditions. The significantly larger current response observed for the latter suggests that it undergoes multielectron oxidation. Controlled potential coulometry at $E = 0.87$ V suggests that removal of more than one electron from **4** occurs at this potential. Nevertheless, a broad five-line ESR signal assigned as $a(2N) = 5.5$ G of $\mathbf{4}^{+\cdot}$ is observed when **4** is treated with 1 mol equiv of thianthrenium perchlorate[5] ($TH^+ClO_4^-$) in CH_2Cl_2. The higher order polycation states of **4** are less stable than those of **3** and will need to be further evaluated at low temperature to gain definitive ESR data.

Oxidation of **3** by 1 or 2 mol equiv of $TH^+ClO_4^-$ yields stable solutions of $\mathbf{3}^+$ and $\mathbf{3}^{2+}$ at 298 K. No fine structure is observed in the ESR spectrum of $\mathbf{3}^+\cdot ClO_4^-$ in CH_2Cl_2 over a large concentration and temperature range, so we have been unable to evaluate its spin distribution. The dication diradical $\mathbf{3}^{2+}\cdot(ClO_4^-)_2$ shows a triplet ESR signal (Figure 4) with a D value of 0.0027 cm^{-1} and no well-resolved E value. This D value is close to that observed by Bushby et al.[6] for $\mathbf{6}^{2+}$, which has a similar average spin−spin distance. Acyclic analogue $\mathbf{2}^{2+}$ did not show an observable D splitting in its matrix ESR spectrum[3] probably because its D value is smaller (and hence unresolved) than that for $\mathbf{3}^{2+}$ due to $\mathbf{2}^{2+}$'s extended conformation of *p*-phenyelenediamine groups.

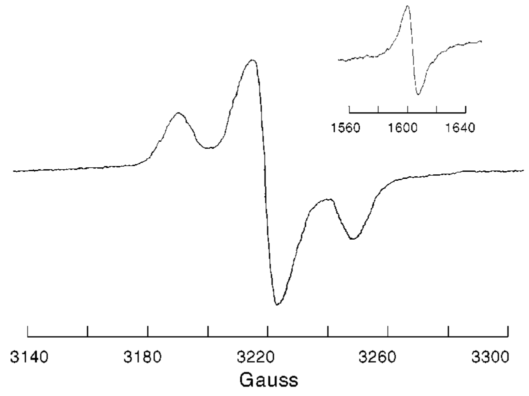
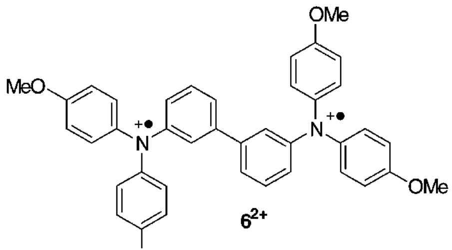


Figure 4. ESR spectrum of $\mathbf{3}^{2+}$ in PrCN at 100 K.



$\mathbf{6}^{2+}$

D = 0.0029 cm^{-1}

Over the limited temperature range of 113−83 K, the intensity of the half-field signal of triplet $\mathbf{3}^{2+}$ obeys the Curie−Weiss law. However, measurement of the solution magnetic susceptibility of $\mathbf{3}^+$ and $\mathbf{3}^{2+}$ in $CDCl_3$ at 298 K by NMR shift analysis[7] gives μ_{eff} values of 1.74 ± 0.01 and 2.18 ± 0.04, respectively. Theoretical values for doublet and triplet molecules are 1.73 and 2.83. Thus, it appears that $\mathbf{3}^{2+}$ is a mixture of singlet and triplet states at room temperature. If so, then $(\mu_{eff})^2/(2.83)^2$ gives the mole fraction of triplet $\mathbf{3}^{2+}$ as 60% in this case. Degenerate singlet and triplet states yield a 75% triplet solution because of the 3:1 triplet:singlet statistical bias. Therefore, we conclude that $\mathbf{3}^{2+}$ is a thermally populated triplet dication with a singlet ground state in $CDCl_3$ solution at 298 K with $\Delta E_{S,T} \approx 0.4$ kcal mol^{-1}.

Despite the conformational rigidity imposed by the macrocyclic skeleton and the dual *N*,*N′*-2,7-naphthyl coupling of the *p*-phenylenediamine radical cations in $\mathbf{3}^{2+}$, a low-spin ground state prevails in this diradical. Of course, the acyclic analogue $\mathbf{2}^{2+}$ did not show a strong triplet preference, having essentially degenerate singlet and triplet states.[3] Furthermore, it is certain that the $\mathbf{3}^{2+}$ conformation, while fairly rigid, is also not perfectly planar and so both spin dilution at nitrogen (over the *p*-phenylenediamine unit) coupled with a degree of deconjugative twisting at the 2,7-naphthalene connections may combine to diminish the preference for spin alignment in the $\mathbf{3}^{2+}$ diradical and ultimately result in a singlet ground state. Further work on cyclic arylamines is underway to better address the issues of spin coupling between amine-based radical cations within rigid macrocyclic frameworks.

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Supporting Information Available: X-ray structure tables, description of synthetic procedures, and compound spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Caution! Thianthrenium perchlorate is a shock-sensitive explosive solid that should be handled only on a small scale and with due care. For preparation and properties see: Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.

(6) Bushby, R. J.; McGill, D. R.; Ng, K. M.; Taylor, N. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1405.

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