

Triamino-*s*-triazine Triradical Trications.

An Experimental Study of Triazine as a Magnetic Coupling Unit

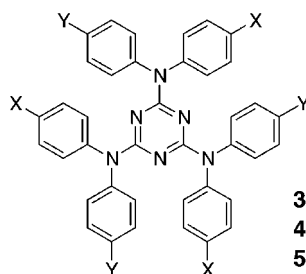
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ABSTRACT



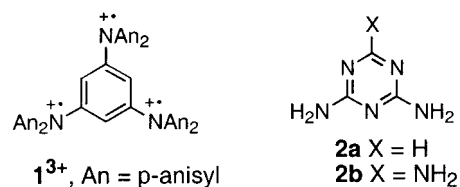
3a, X = Y = OCH₃
4, X = H, Y = N(phenyl)₂
5, X = OCH₃, Y = N(p-anisyl)₂

Triamino-*s*-triazine derivatives **3a**, **4**, and **5** have been prepared, and their cationic states have been analyzed electrochemically. At 298 K, **3a**⁺ has a limited lifetime in CH₂Cl₂ solution. However, **4**⁺ and **5**⁺ are long-lived under such conditions, and quartet states of **4**³⁺ and **5**³⁺ are observed by ESR spectroscopy. Variable-temperature ESR analysis and NMR shift susceptibility measurements indicate that **5**³⁺ is a doublet ground state with a populated quartet state.

Ferromagnetic coupling between electron spins in organic polyradicals is promoted by certain spin-connection geometries.¹ For example, *m*-phenylene connection of amino radical cations favors spin alignment, and 1,3,5-tris(di-*p*-anisylamino)benzene trication (**1**³⁺) has been shown to be a ground-state quartet triradical.²

In this report, we consider amino-type radical cations connected via an *s*-triazine nucleus. Theoretical predictions

have suggested that amino-substituted *s*-triazine polycations will prefer high-spin ground states. In 1989, Miller et al. proposed that diamino-*s*-triazines (**2a**) might have triplet



dication ground states.³ More recently, Yamabe et al.⁴ reported ab initio calculations that predicted a 12.5 kcal mol⁻¹ triplet ground-state preference for **2a**²⁺. These workers concluded *s*-triazine to be a strong ferromagnetic coupling unit for radicals derived from aza-substituted systems. Moreover, Baumgarten and Zhang⁵ have reported AM1-CI calculations of triamino-*s*-triazine trications **2b**³⁺ that suggest a 23 kcal mol⁻¹ quartet preference for this trication. Here,

(1) For reviews, see: (a) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999. (b) Rajca, A. *Chem. Rev.* **1994**, 94, 871. (c) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 385. (d) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, 26, 346. (e) Dougherty, D. A. *Acc. Chem. Res.* **1991**, 24, 88.

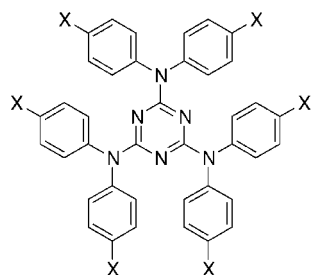
(2) (a) Stickley, K. R.; Blackstock, S. C. *J. Am. Chem. Soc.* **1994**, 116, 1441. (b) Sato, K.; Yano, M.; Furuichi, M.; Shiomi, D.; Takui, T.; Abe, K.; Itoh, K.; Higuchi, A.; Katsuma, K.; Shiota, Y. *J. Am. Chem. Soc.* **1997**, 119, 6607.

(3) Dixon, D. A.; Miller, J. S. *Mol. Cryst. Liq. Cryst.* **1989**, 176, 211. (4) Ito, A.; Miyajima, H.; Yoshizawa, K.; Tanaka, K.; Yamabe, T. *J. Org. Chem.* **1997**, 62, 38.

(5) Zhang, J.; Baumgarten, M. *Chem. Phys.* **1997**, 214, 291.

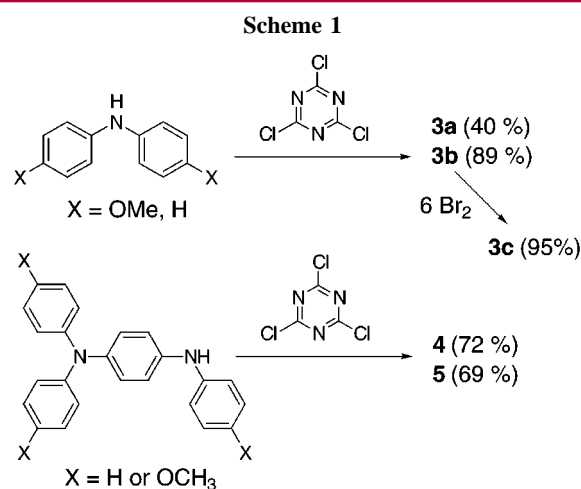
(6) For a report of triazinyl nitrenes, see: Nakai, T.; Sato, K.; Shiomi, D.; Itoh, K.; Kazaki, M.; Okada, K. *Synth. Met.* **1999**, 103, 2265.

we report preliminary experimental findings regarding amino-substituted triazine polyradical cations.⁶



3 (a X = OMe, b X = H, c X = Br)

Initially, a set of tris(aryl-amino) triazines (**3**) (Scheme 1) were prepared for study.⁷ Unfortunately, the polyradical



cations in this series were too short-lived for easy handling (lifetimes \leq seconds as determined electrochemically), and

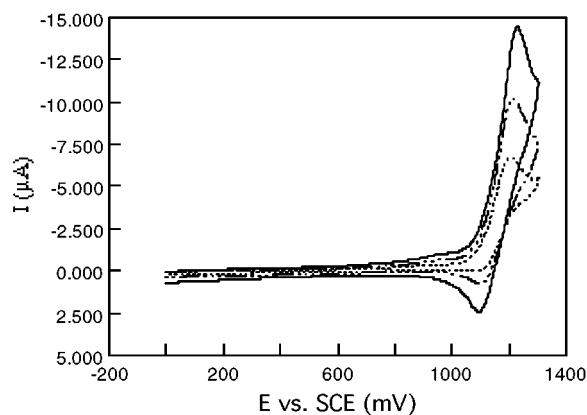
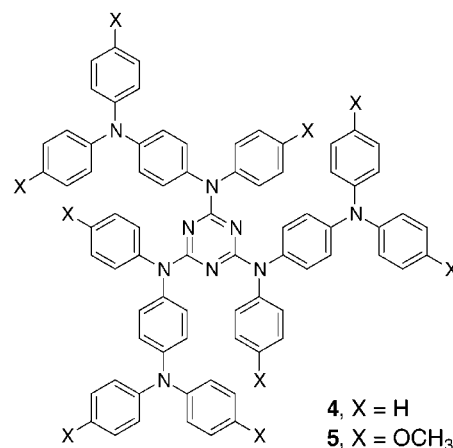


Figure 1. Voltammogram of **3a** (2.0 mM) at 298 K in CH_2Cl_2 (0.1 M Bu_4NBF_4) with scan rates of (solid) 100, (dash-dot) 50, and (dot) 20 mV s^{-1}

the high oxidation potentials made dication and trication generation difficult.

Figure 1 shows a cyclic voltammogram of **3a**. One-electron oxidation was quasi-reversible under ambient conditions. In cold CH_2Cl_2 , the first two oxidations became chemically reversible, yielding $E^\circ'(1) = 1.12$ and $E^\circ'(2) = 1.42$ V vs SCE. These values are 0.45 and 0.55 V higher than those for **1**.^{2a} In an attempt to improve the chemical stability of the aminotriazine cations and lower the E_{ox} values, we next prepared the corresponding *p*-phenylenediamine (*p*-PD) triazine analogues **4** and **5** (Scheme 1). As previously noted,⁸ substitution of arylamino groups by *p*-PD units generally lowers the oxidation potentials of the system and increases the stability of aryl-linked polyradical cations.



Electrochemical oxidation of **5** by cyclic voltammetry (CV) gave two chemically reversible waves at room temperature (Figure 2). Controlled potential coulometry at 0.90

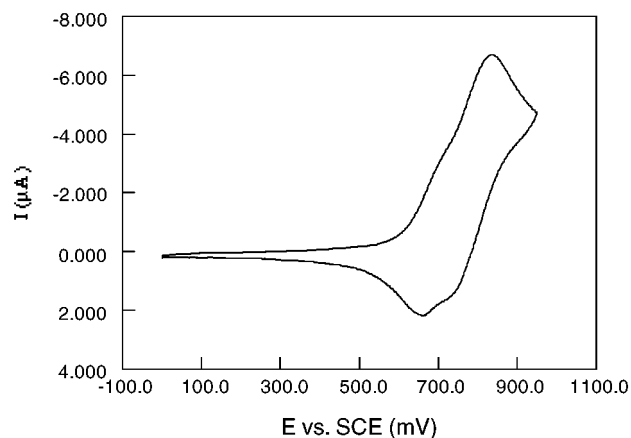


Figure 2. Voltammogram of **5** (1.0 mM) at 298 K in CH_2Cl_2 (0.1 M Bu_4NBF_4) with a scan rate of 20 mV s^{-1} .

V indicated that three electrons per molecule were removed at this potential (Figure 3). The associated formal oxidation potentials were assigned as $E^\circ'(1) \approx 0.71$, $E^\circ'(2) \approx E^\circ'(3) \approx 0.78$ V vs SCE. Oxidation of **4** showed a similar CV trace with $E^\circ'(1) \approx 0.90$, $E^\circ'(2) \approx E^\circ'(3) \approx 1.03$ V vs SCE.

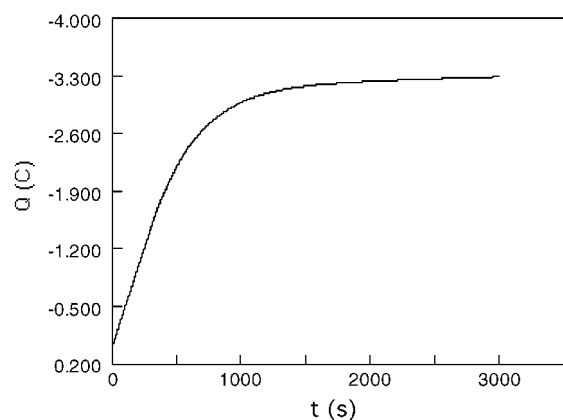


Figure 3. Controlled potential coulometry at 0.9 V vs SCE for **5** (0.0113 mmol) at 298 K in CH_2Cl_2 (0.1 M Bu_4NBF_4).

Oxidation of **4** or **5** by 1 molar equiv of thianthrenium perchlorate ($\text{TH}^+\text{ClO}_4^-$) gave green solutions of $\mathbf{4}^+$ or $\mathbf{5}^+$ that showed a single broad-line ESR spectrum. Presumably, no hyperfine coupling is observed in these spectra because of the numerous small splittings which effectively line broaden the signal.

Treatment of **4** with 3 molar equiv of $\text{TH}^+\text{ClO}_4^-$ in butyronitrile gave a $\mathbf{4}^{3+}$ solution that, when frozen, shows a quartet ESR spectrum at 100 K with a D value of 0.0023 cm^{-1} (Figure 4). This D value is close to that (0.0026 cm^{-1})

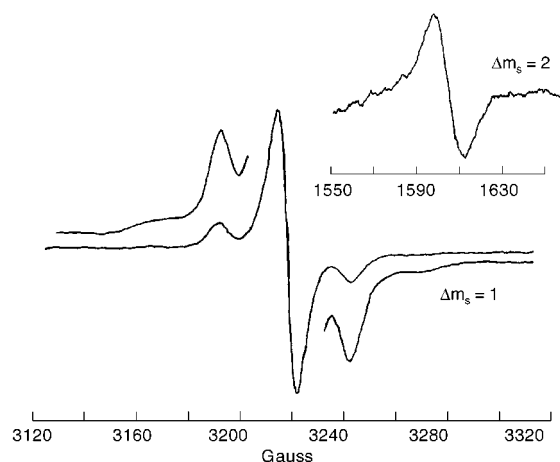


Figure 4. ESR spectrum of $\mathbf{5}^{3+}$ in frozen PrCN at 100 K.

observed for the *m*-phenylene analogue 1,3,5-tris(triphenyl-*p*-phenylenediamino)benzene triradical trication.⁸ Similarly

(7) Stickley, K. R. Ph.D. Dissertation, Vanderbilt University, Nashville, TN, 1996.

(8) Stickley, K. R.; Selby, T. D.; Blackstock, S. C. *J. Org. Chem.* **1997**, *62*, 448.

(9) **Caution!** Thianthrenium perchlorate is a shock-sensitive explosive solid that should be handled with due care. See: Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.

prepared, $\mathbf{5}^{3+}$ gave a quartet ESR signal with a D value of 0.0015 cm^{-1} . In frozen media, both $\mathbf{4}^{3+}$ and $\mathbf{5}^{3+}$ are quite stable, but in fluid solution $\mathbf{4}^{3+}$ decays in minutes at room temperature as deduced by ESR and NMR (vide infra) analyses.

To obtain the spin state ordering for $\mathbf{5}^{3+}$, its magnetic susceptibility was measured by the NMR shift method.¹⁰ (The solution instability of $\mathbf{4}^{3+}$ precluded its NMR analysis.) Measurements on $\mathbf{5}^+$ and $\mathbf{5}^{3+}$ in CDCl_3 at 298 K yielded μ_{eff} values of 1.72 ± 0.06 and $2.43 \pm 0.06\ \mu_{\text{B}}$, respectively. Theoretical μ_{eff} values for pure doublet and quartet species are 1.73 and $3.87\ \mu_{\text{B}}$, respectively. Therefore, we conclude $\mathbf{5}^{3+}$ to be a mixture of quartet and doublet states at 298 K with 24% quartet and 76% doublet, the latter being the ground state under these conditions.

This result is also consistent with the nonlinear temperature dependence found for the $\mathbf{5}^{3+}\ \Delta m_s = 2$ signal intensity measured by ESR in frozen butyronitrile over the range of 133–87 K (Figure 5). Here, a lower ESR signal intensity

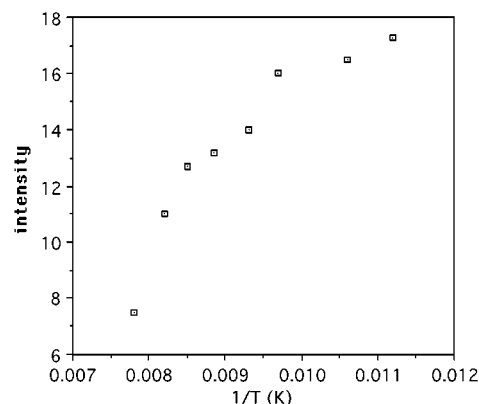


Figure 5. ESR $\Delta m_s = 2$ signal intensity for $\mathbf{5}^{3+}$ in frozen PrCN as a function of $1/T$.

than expected from linear Curie Law behavior is observed as the temperature is lowered in this range, indicating an increase in the doublet/quartet ratio.

In summary, we conclude that *p*-PD radical cations attached 1,3,5- to an *s*-triazine core have a slight energetic preference for spin pairing, yielding ground state doublet triradical trications with observable low-lying quartet excited states. Compared to the 1,3,5-phenyl-substituted tris(*p*-PD) structure, the triazine-core compound **5** is harder to oxidize ($\Delta E^\circ(1) = 0.3\text{ V}$), yields trications of lower chemical stability (the former are isoable, whereas the latter are not), and gives triradical trications with lower μ_{eff} values (2.43 vs 3.04). If deconjugation of the *p*-PD radical cations from the strongly electron-withdrawing *s*-triazine nucleus occurs in these polycations, then the apparent discrepancy between theoretical predictions of spin alignment in aminotriazine

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

polyradicals and the experimental observation of a low-spin ground state for 5^{3+} would be rationalized.

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Supporting Information Available: Description of synthetic procedures, compound spectral data, and NMR susceptibility data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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