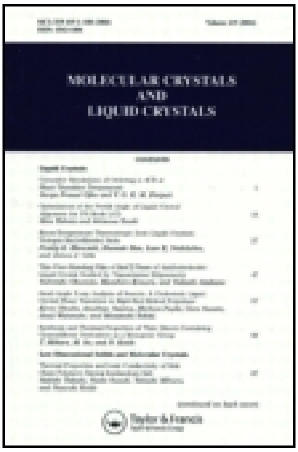

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High-Spin Polycations of a Trlaminobenzene

Kurt R. Stickley [a] & Silas C. Blackstock [a]
[a] Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235, USA

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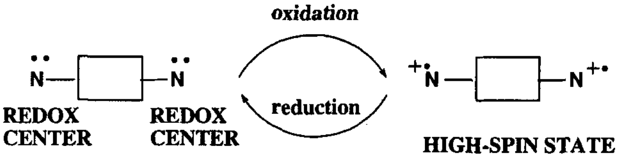
HIGH-SPIN POLYCATIONS OF A TRIAMINOBENZENE

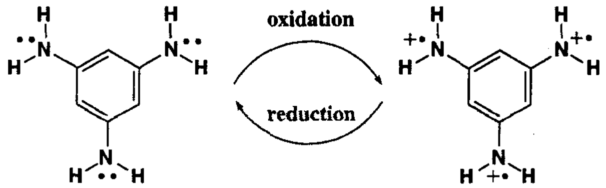
KURT R. STICKLEY AND SILAS C. BLACKSTOCK*
Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235
USA

Abstract Organic poly radical ions are molecular spin units which could be used in the construction of magnetic materials. They possess the feature of redox activation / deactivation, a potential means of reversibly controlling the molecular spin state of the unit, thus imparting a magnetic switch function. Here, we describe the prospect of preparing *tris* arylamines suitably structured to yield long-lived cation, dication, and trication states of successively higher spin mutiplicity. The preparation and oxidation of N,N,N',N',N",N"-hexa-*p*-anisyl-1,3,5-triaminobenzene (HATAB) are discussed, along with the ESR spectra of the HATAB higher oxidation states. The HATAB^{2+} and HATAB^{3+} ESR signals are assigned to triplet and quartet states respectively which, on the basis of cursory Curie-Weiss data, are tentatively assigned as the ground states of these poly cations, consistent with calculational results (AM1/UHF) on the unsubstituted system, 1,3,5-triaminobenzene dication and trication.

INTRODUCTION

The development of magnets composed of organic molecules constitutes a major contemporary research aim for organic chemists and has spawned interest in organic radicals as building blocks for the construction of such materials.[1-4] One potential class of molecular building block for such a purpose is the organic radical ion. Radical ions possess the useful feature of being spin activated or deactivated by a simple redox process. This means that no covalent change in molecular structure is necessary to alter the spin state of the molecule and that the spin "status" of the molecular unit (or assembly) is thus redox switchable. One can assume that such electron-transfer switching of spin states should be inherently reversible, as long as the accessible oxidation states of the units are kinetically stable. In addition, kinetic barriers to electron-transfer are generally small so that the desired spin level (magnetism) of the unit will be a function of only the applied potential. Because it is easy to count electrons with modern electrochemical instrumentation, it should be possible to know precisely the amount of charge imparted to a molecule or molecular assembly and therefore know the amount of possible net spin. If substrates can be designed which possess the requisite kinetically stable multiple oxidation states (no trivial requirement for organic structures), and the redox-active sites can be appropriately positioned for ferromagnetic interaction (also no trivial matter), then redox mediation of molecular magnetism (and perhaps someday of bulk magnetism) should be achievable. Our approach to the development of this concept has been to utilize nitrogen lone pair functions (amines in this case) as redox-active spin-bearing units and use the neutral-to-cation radical redox motif to generate high-spin units as shown diagrammatically below. Here, we discuss our work on triaminobenzenes employed as precursors to new high-spin organic molecules.



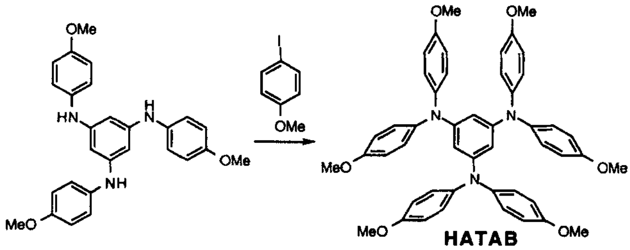


TAB

RESULTS AND DISCUSSION

Knowledge gained from several decades of research on the relation of spin-state preference to molecular structure for organic π biradicals now allows the rationale design of organic high-spin π coupling units which might suitably be used to ferromagnetically link redox-active groups.[5] For example, Ovchinnikov's rules[6] can be used to ascertain the ground state spin multiplicity of alternant π-systems. These rules predict the ground state spin quantum number S to be $(n^* - n)/2$ for alternant hydrocarbons where n^* is defined as the number of "starred" and n as the number of "unstarred" atoms in the conjugated system, such that $n^* > n$. By this rational, it is predicted that the non-Kekulé structure *m*-quinodimethane (MQDM) will be a ground state triplet molecule as has been experimentally documented.[7] Application of these rules also predicts a ground state quartet for 1,3,5-trimethylenebenzene (TMB). Isoelectronic with TMB, but containing charged heteroatoms, is the trication of 1,3,5-triaminobenzene (TAB). We and others have carried out quantum mechanical calculations on the oxidized forms of TAB which predict a ground state triplet for TAB^{2+} and a quartet ground state of TAB^{3+}.[8] While unsubstituted TAB itself is not expected to be a practically useful substrate because its oxidized forms will be too short-lived for study, *p*-substituted hexaaryl TAB derivatives are considered potentially good precursors for the generation of stable high-spin polyradical cations. Of the tris triarylamino compounds we have so far prepared, N,N,N',N',N",N"-hexa-*p*-anisyl-1,3,5-triaminobenzene (HATAB) has the most promising oxidation properties and its chemistry is the focus of this presentation.[9]

Neutral HATAB is prepared as shown in Equation 1. An iodine catalyzed condensation between phloroglucinol dihydrate and *p*-anisidine affords the *tris* secondary arylamine[10] which is further reacted by an Ullmann coupling with *p*-iodoanisol to give HATAB in 45% yield.



(1)

Cyclic voltammetry[11] (CV) analysis of HATAB at -78 °C in CH_2Cl_2 shows three chemically reversible oxidation waves ($E^{\circ\prime}$ 0.65, 0.88, and 1.04 V vs. SCE) (Figure 1). This result suggests that the cation, dication, and trication states of HATAB have lifetimes of at least seconds in cold solution.

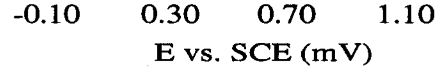


FIGURE 1. Oxidation cyclic voltammetry of HATAB in CH_2Cl_2 (0.1 M nBu_4NClO_4) at -78 °C.

Chemical oxidation of HATAB by 1 molar equiv of thianthrenium perchlorate[12,13] ($TH^+ClO_4^-$) in CH_2Cl_2 at -78 °C gives a blue solution which shows a 10-line ESR spectrum (Figure 2). We assign this spectrum to $HATAB^{+\cdot}$ and propose the hyperfine to derive from a(3N) ≈ a(3H) (central ring) ≈ 3 G. We have simulated the spectrum using a(3N) = 3.4 G, a(3H) 2.6 G, and $\nu_{1/2}$ = 2.1 G.

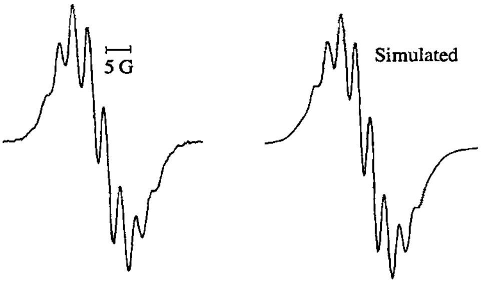
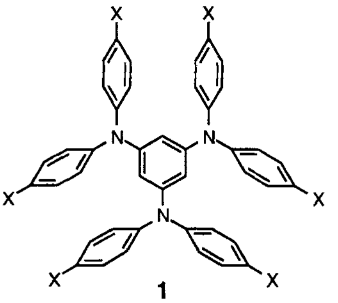


FIGURE 2. Observed and simulated ESR spectra of $HATAB^{+\cdot}$ in CH_2Cl_2 at -65 °C.

The ESR spectrum for $HATAB^{+\cdot}$ suggests that the spin is delocalized over three chemically equivalent N atoms or that electron exchange between the nitrogens is fast enough on the ESR timescale at -78 °C to give an averaged structure. Similar 10-line ESR spectra are observed for two other *p*-substituted aryl TAB cation radicals which we have prepared (**1b**$^{+\cdot}$ and **1c**$^{+\cdot}$) as would be expected.[14] Interestingly, **1a**$^{+\cdot}$ shows only a the broad singlet by ESR, presumably because a small, unresolved a(18H) splitting due to the methyl protons effectively broadens all the lines to the point that 3 G resolution is lost.



1

X = CH_3, (**1a**)
X = t-Bu, (**1b**)
X = OBn, (**1c**)

When HATAB is treated with 2 molar equiv of $TH^+ClO_4^-$ at -90 °C in butyronitrile in a quartz ESR tube under an N_2 atmosphere, a resultant broad singlet ESR spectrum is observed in fluid solution at -90 °C. When this sample is frozen in liquid nitrogen and is reanalyzed, a six line ESR spectrum is observed which we assign to triplet $HATAB^{2+}$. The observed $|D|/hc$ and $|E|/hc$ values for $HATAB^{2+}$ are 0.0065 cm^{-1} and 0.0011 cm^{-1}, respectively. A cursory Curie-Weiss plot over the limited temperature range of 98 - 140 K is linear, consistent with a tentative assignment of a triplet ground state for this dication.[15] The HATAB trication can be prepared similarly at -90 °C and is stable for minutes in solution at this temperature. In frozen solution at -180 °C, a 5-line ESR signal with a weak transition ($\Delta m_s = 2$) ~1622 G is observed and is assigned to the quartet state of HATAB^{3+}. Again, a preliminary Curie-Weiss analysis from 98 - 140 K is linear, suggesting that this trication has a quartet ground state.[15] The quarter field transition for HATAB^{3+} has not been observed and is expected to be quite weak.[16] The $|D|/hc$ value for HATAB^{3+} is 0.0046 cm^{-1}.

In summary, we have shown that HATAB possesses solution stable cation, dication, and trication oxidation states at low temperature and that the dication and trication forms have observable triplet and quartet spin states respectively. Thus, the prospect of preparing stable neutral precursors for redox activation of intramolecular ferromagnetic interactions has been realized. It is also apparent that the polycationic oxidation states of HATAB are not as long-lived as might be expected by analogy to their triarylaminium cation counterparts which are isolably stable. Presently, we are investigating ways of achieving even greater polyion lifetimes.

ACKNOWLEDGMENT

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