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Triplet Dication and Quartet Trication of a Triaminobenzene

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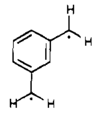
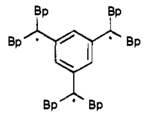
The prospect of synthesizing magnetic materials based on organic systems has led to continued interest in high-spin organic molecules which might serve as building blocks for the preparation of bulk magnetic materials.[1−4] Spin centers such as carbon radicals,[5−7] triplet carbenes,[8−11] and nitroxide radicals[12,13] have been "ferromagnetically" linked to give high-spin polyradical molecules. Our approach utilizes nitrogen cation radicals as the spin unit. This approach allows, in principle, molecular magnetism to be switched on or off and turned up or down by application of an external electric potential to control the redox state (and spin state) of a molecule or, ultimately, of a bulk material. To this end, we report the solution-stable cationic, dicationic, and tricationic states of *N,N,N′,N′,N″,N″*-hexaanisyl-1,3,5-triaminobenzene (HATAB) for which we observe doublet, triplet, and quartet spin states, respectively.

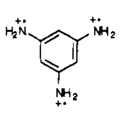
Several decades of fundamental research on the structural relationships that govern spin state preference in organic bi- and polyradicals have produced a coherent rationale for controlling the spin preference in organic π systems.[14,15] For example, Ovchinnikov's rule[16] can be used to predict, to a first order, the ground state spin multiplicity of alternant π systems. This rule specifies non-Kekulé structures such as *m*-quinodimethane (MQDM)[17] and tetraphenyl-*m*-quinodimethane[18,19] as ground state triplets, as is also known experimentally. Substitution of the third meta position on a benzene core with a third spin center leads to further propagation of high-spin preference in theory and also in practice. An example is the novel quartet triradical 1,3,5-tris[bis(*p*-biphenyl)methyl]benzene (TBPMB).[20] Similar to TBPMB, but containing charged heteroatoms, is the trication of 1,3,5-triaminobenzene (TAB^{3+}). Adopting the TAB structure motif, we have prepared a series of hexaaryl-TAB derivatives whose dications we predict to be triplets and trications to be quartets. Here, we report on the para-substituted anisyl derivative HATAB and its parent phenyl-substituted system, *N,N,N′,N′,N″,N″*-hexaphenyl-1,3,5-triaminobenzene (HPTAB).



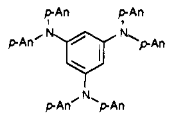
MQDM



TBPMB



TAB^{3+}



HATAB

Neutral HATAB is prepared in two steps, beginning with an iodine-catalyzed condensation between phloroglucinol dihydrate and *p*-anisidine.[21] The resulting tris secondary arylamine is then reacted with *p*-iodoanisol via a triple Ullmann coupling to give HATAB in 45% yield. HPTAB is prepared similarly.[22]

Cyclic voltammetry[23] (CV) on HATAB shows two chemically reversible oxidation waves at room temperature, and at −78 °C a third oxidation wave becomes reversible ($E^{\circ\prime}$ = 0.67, 0.87, and 0.98 V vs SCE) (Figure 1). Thus, the cation, dication, and trication states of HATAB all have solution lifetimes of ≥ 1 s in cold solution.

One-electron oxidation of HATAB (1 mM) by thianthrenium perchlorate[24,25] ($TH^+ClO_4^-$) in CH_2Cl_2 at −78 °C gives a blue solution which shows a 10-line ESR spectrum with a line separation of about 3.3 G. We assign this spectrum to HATAB$^{\bullet +}$ and propose the hyperfine splitting to derive from *a*(3N) ≈ *a*(3H) (central ring) ≈ 3 G.[26] The ESR spectrum for HATAB$^{\bullet +}$ is typical of those seen for other para-substituted aryl-TAB radical cations in which *a*(3N) and *a*(3H) dominate the hyperfine splitting of the ESR signal.[27]

Two-electron oxidation of HATAB at −90 °C in butyronitrile with $TH^+ClO_4^-$ gives a fluid solution which shows a broad singlet by ESR. When the solution is frozen in liquid nitrogen and reanalyzed at −175 °C, a six-line ESR spectrum is observed at 3140−3310 G, with a $\Delta m_s = 2$ (half-field) transition at ~1618 G (Figure 2). We assign this spectrum to triplet HATAB^{2+}. The observed $|D|/hc$ and $|E|/hc$ values are 0.0065 and 0.0011 cm^{-1}, respectively. This D value is smaller than that observed for MQDM (0.011),[17] presumably because of spin delocalization into the anisyl groups of HATAB^{2+}, but is close to that (0.0064 cm^{-1})[18] reported for tetraphenyl-MQDM (Schlenk's hydrocarbon), as expected. The detectable $|E|$ value for HATAB is perhaps surprising in view of its formal 3-fold symmetry. We hypothesize that this dication may prefer to exist with C_{2v} rather than D_{3h} symmetry for electronic reasons. Preliminary AM1/UHF[28] calculational results on TAB^{2+} show that restricting TAB^{2+} to C_{2v} symmetry does not increase the energy of either the singlet or the triplet state significantly above that derived from symmetry-unrestricted calculations.[29]

Oxidation of HATAB at −90 °C with 3 molar equiv of $TH^+ClO_4^-$ yields a fluorescent blue sample which gives a five-

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(23) Cyclic voltammograms are recorded in a three-electrode cell with a planar Pt disc working electrode, a Pt wire counter electrode, and a saturated calomel reference electrode (SCE). Substrate solutions were 1.0 mM in substrate and 0.1 M in tetra-*n*-butylammonium tetrafluoroborate electrolyte in dichloromethane or butyronitrile under a nitrogen atmosphere.

(24) ***Caution!*** Thianthrenium perchlorate ($TH^+ClO_4^-$) is a shock-sensitive explosive solid and should be handled with due care.

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(26) The spectrum has been simulated using *a*(3N) = 3.4 G, *a*(3H) = 2.6 G, and a line width of 2.1 G.

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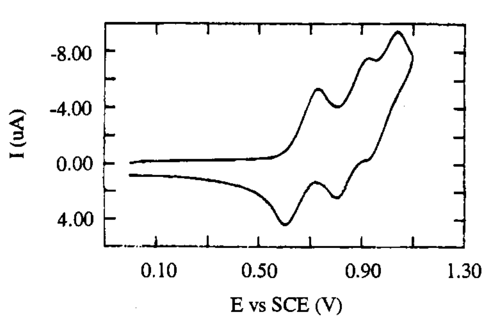

Figure 1. Cyclic voltammogram of HATAB in butyronitrile (0.1 M n-Bu_4NBF_4) at −78 °C and 200 mV/s scan rate.

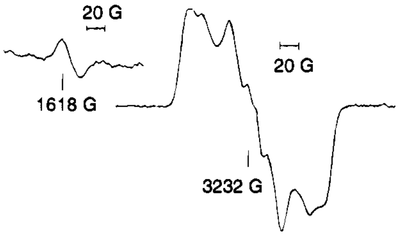

Figure 2. ESR spectrum of $HATAB^{2+}$ in butyronitrile at −175 °C.

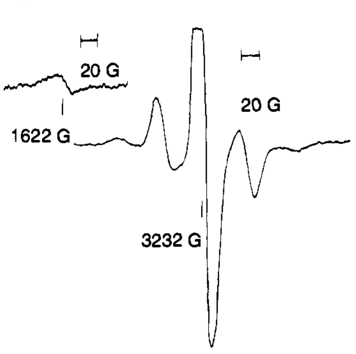

Figure 3. ESR spectrum of $HATAB^{3+}$ in butyronitrile at −180 °C.

line ESR signal with a line separation of ~50 G (Figure 3). A weak transition ($\Delta m_s = 2$) is observed at ~1622 G. This pattern is that expected for an axially symmetric quartet, and we assign it to $HATAB^{3+}$. The quarter field transition for this quartet has not been observed and will be quite difficult to see because of its expected low intensity.[30] The $|D|/hc$ value for this species is 0.0046 cm^{-1}. This trication is stable for minutes in solution at ≤−80 °C but decays rapidly at higher temperatures.

The intensities of the $HATAB^{2+}$ triplet and the $HATAB^{3+}$ quartet ESR signals increase with decreasing temperature from 140 to 90 K, in accord with the Curie–Weiss behavior expected for high-spin ground states of these polycations. This temperature dependence, however, does not rule out the possibility of degenerate or nearly degenerate singlet/triplet states for the dication or quartet/doublet states for the trication. Calculations of TAB^{2+} by AM1/UHF predict a triplet ground state for this unsubstituted species with a S/T splitting of 4.5 kcal mol^{-1}. These calculations predict an even stronger preference for the quartet state of the TAB^{3+} (D/Q splitting of 15 kcal mol^{-1}).[31]

Tanaka and co-workers[32] have performed calculations on TAB^{3+} which also suggest a strong preference for a quartet ground state for this species and, in addition, have recorded an ESR spectrum assigned to the solution-stable quartet trication of hexaphenyl-TAB, $HPTAB^{3+}$.[30,33] The putative trication is prepared by treatment of HPTAB with trifluoroacetic anhydride (TFAA) in CH_2Cl_2 containing n-Bu_4NBF_4. While we believe that the theoretical prediction of a quartet ground state for $HPTAB^{3+}$ is sound, we are surprised by both the apparent kinetic stability of this trication in solution and its ESR spectral properties. A number of comparisons to our work on HPTAB and HATAB are noteworthy.

First, the CV analysis of HPTAB shows clear chemical reversibility for only its first oxidation, in contrast to the three reversible oxidations seen for HATAB. Addition of trifluoroacetic acid or TFAA to the CV solution does not alter the chemical irreversibility of HPTAB dication or trication formation. Second, the five-line solution ESR signal previously observed[30,33] would appear to arise from a doublet species. This spectrum is not consistent with a $TAB^{\bullet+}$ derivative, which should show an a(3N) splitting, but could result from a radical cation of a benzidine-type structure, which will have a dominant a(2N) splitting. It is known that the triphenylamine radical cation undergoes facile self-reaction to form tetraphenylbenzidine,[34,35] and similar chemistry might occur for oxidized HPTAB. Earlier studies have shown that, when triphenylamine is treated with iodine, the ESR spectrum of the tetraphenylbenzidine radical cation is observed.[34] Upon treatment of HPTAB with 0.75 molar equiv of I_2 in CH_2Cl_2, we observe a strong five-line ESR signal with a splitting of 6 G, which we tentatively assign to the radical cation of the analogous benzidine-linked dimer of HPTAB.[36] Last, the $|D|/hc$ value of 0.0012 cm^{-1} for the putative $HPTAB^{3+}$ quartet observed by Tanaka and co-workers[30,33] is surprisingly low. The isoelectronic hydrocarbon quartet hexaphenyl-1,3,5-trimethylenebenzene has a $|D|/hc$ value of 0.0049 cm^{-1},[37] close to that found for $HATAB^{3+}$ but 4 times greater than the D value assigned to $HPTAB^{3+}$. In view of these results, we believe that the previously reported $HPTAB^{3+}$ structure assignment warrants further evaluation.

In conclusion, we have shown that HATAB possesses solution-stable cation, dication, and trication oxidation states at low temperature and that the dication and trication structures are ground state triplet and quartet molecules (or very nearly so)[38], respectively. The basic tenet of preparing stable neutral precursors for redox switching of molecular magnetic properties has been demonstrated.

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Supplementary Material Available: Synthesis of HATAB, ESR spectrum of $HATAB^{\bullet+}$, and ESR sample preparations of oxidized forms (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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