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10,10′-(*m*- and *p*-Phenylene)diphenothiazine Dications: Violation of a Topology Rule in Heterocyclic High-Spin π-Systems

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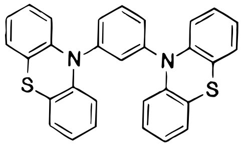
In the field of organic-based magnets and ferromagnetic materials,[1] high-spin organic molecules have recently received intense attention. It is well-known that in hydrocarbon high-spin molecules *m*-xylylene type hydrocarbons (non-Kekulé hydrocarbons) are triplet species, whereas *p*-xylylene type hydrocarbons (Kekulé hydrocarbons) tend to be in quinoid form with singlet ground states.[2] This topology rule has been supported by several theories[3] and many experiments demonstrating high-spin ground states in non-Kekulé hydrocarbons,[1a−d] although exceptions, i.e., singlet ground states in non-Kekulé systems, have recently been reported.[1e−h] In addition to this topological strategy, a different method toward high-spin states by orthogonal alignment of the spin-carrying π-systems has also been studied.[4] Although this approach certainly allows the detection of higher spin states, the ground states so far observed are of lower spin multiplicity.

In contrast to the information known for hydrocarbon high-spin compounds, relatively little is known for high-spin heterocyclic π-systems.[1a,c,d,5] 1,4-Thiazine has 8π electrons, and 2π electrons are obviously accommodated in a nonbonding level orbital; the oxidation gives a singly occupied orbital (SOMO) in such a level (Hückel MO). Interestingly, energy levels of such orbitals are rather insensitive to the structure of spacers and differ only slightly even when two thiazine cations are introduced in *p*-phenylene moieties. As a result, the orbital energy difference (ΔE) between the two SOMOs of 4,4′-(*p*-phenylene)bis(1,4-thiazine) dication ($\Delta E = 0.14\beta$) is considerably smaller than that of *p*-terphenyl dication ($\Delta E = 0.41\beta$), *p*-xylylene ($\Delta E = 0.62\beta$), and Thiele's hydrocarbon ($\Delta E = 0.31\beta$). Nonplanar geometries with large dihedral angles between the cation moieties and the spacer would give much smaller energy gaps and might produce stable high-spin states.



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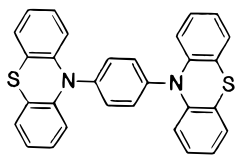

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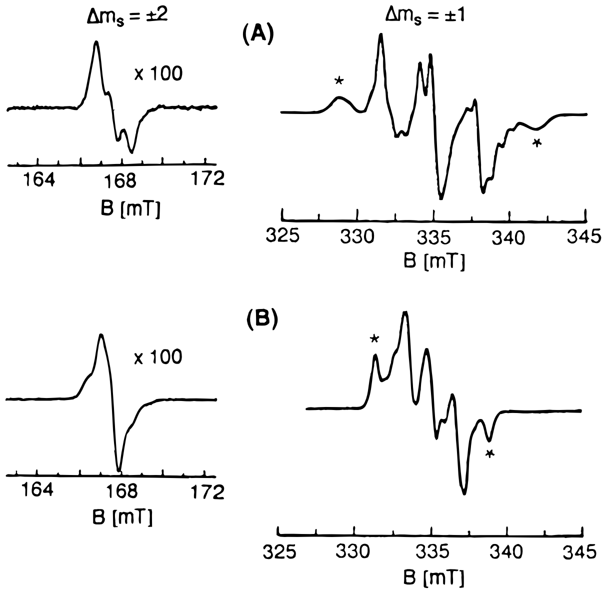

Figure 1. ESR spectra of 1^{2+} (A) and 2^{2+} (B) in frozen sulfuric acid at 135 K. The triplet lines of the axis components are marked by asterisks.

Phenothiazine radical cation is known to be a stable and (almost) planar species, although the neutral molecule has a slightly puckered conformation.[6] We report the first set of experimental evidence of violation of the above topology rule: a singlet ground state in *m*-phenylenediphenothiazine dication and a triplet ground state in *p*-phenylenediphenothiazine dication.

The neutral compounds 10,10′-(*m*-phenylene)diphenothiazine **1** and the para isomer **2** were prepared in 50 and 28% yields by Ullmann arylation[7] of phenothiazine with *m*-diiodobenzene or *p*-diiodobenzene (at 200 °C for 60 h in the presence of K_2CO_3 (3 equiv) and Cu powder (0.4 equiv) without solvent; with 26 and 43% recovery of phenothiazines, respectively). The oxidation was achieved by dissolving **1** or **2** (ca. 1 mg) in concentrated sulfuric acid (1 mL, $d = 1.84$). The electronic spectra of the dicationic species have absorptions (516 nm for both $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$) similar to that of 10-phenylphenothiazine monocation ($\mathbf{3}^{+}$ (515 nm, $\epsilon = 1.31 \times 10^4$))[8] except that the molar absorptivities (assuming clean conversion) of $\mathbf{1}^{2+}$ ($\epsilon = 2.50 \times 10^4$) and $\mathbf{2}^{2+}$ ($\epsilon = 2.48 \times 10^4$) are nearly twice that of $\mathbf{3}^{+}$. The similarity of the electronic spectra of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ indicates that the electronic configurations should be comparable and suggests that the conceivable quinoid type structure is unlikely for the para dication $\mathbf{2}^{2+}$.

The ESR spectrum of the degassed sample of meta isomer $\mathbf{1}^{2+}$ at 135 K showed a randomly oriented triplet pattern with overlapping hyperfine coupling (hfc) on the perpendicular components (Figure 1A).[9] Triplet spectra with hfc are precedented in nitrogen-containing biradicals.[10] The zero-field splitting parameter D is determined to be 5.97×10^{-3} cm^{-1} and

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[9] The ENDOR analyses are in progress.

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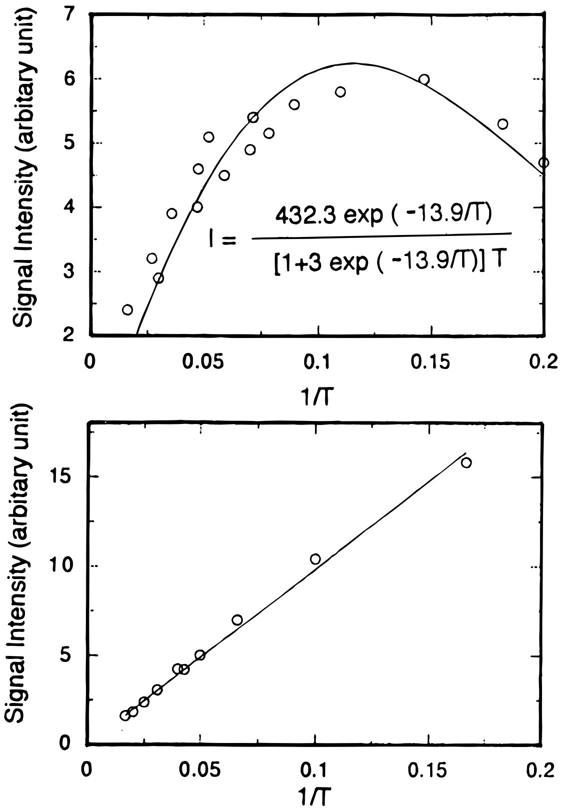

Figure 2. Temperature dependence of the signal intensity for $\Delta m_s = \pm 2$ transitions of $\mathbf{1}^{2+}$ (upper) and of $\mathbf{2}^{2+}$ (lower) in sulfuric acid.

corresponds to 7.6 Å as an averaged distance between the two spin centers by the point dipole approximation.[11] The calculated distance is in good agreement with the distances (ca. 7.4 Å) between the two phenothiazine centers around which averaged spin densities are likely located. Figure 1A also shows the forbidden $\Delta m_s = \pm 2$ transition signals which appear in the half magnetic field region and also have hyperfine coupling with nitrogen nuclei. These results establish the triplet nature of $\mathbf{1}^{2+}$. Similar triplet patterns ($\Delta m_s = \pm 1$ and ± 2 regions) were observed for the para isomer $\mathbf{2}^{2+}$ with a slightly smaller D of 4.39×10^{-3} cm^{-1} (Figure 1B),[9] corresponding to 8.4 Å, which is again close to the distance (ca. 8.6 Å) between the two phenothiazine centers.[11]

Figure 2 shows Curie plots using the highest signal of $\Delta m_s = \pm 2$ transitions for both $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$. The Curie plots for meta dication $\mathbf{1}^{2+}$ interestingly afford a convex curve, indicating that the triplet is a thermally excited state. The curve is best simulated (correlation coefficient = 0.91) by the equation shown in the figure, and the energy gap between the singlet and triplet states is determined to be about 28 cal/mol. On the contrary, the Curie plots of para dication $\mathbf{2}^{2+}$ surprisingly give a straight line in the temperature range between 50 and 6 K, indicating no thermal contribution in the triplet state. Therefore, the triplet of $\mathbf{2}^{2+}$ is a ground state or nearly degenerate with the singlet state within ±10 cal/mol.

Recently, Rassat et al.[1f] and Iwamura et al.[1g] reported that substituted analogues of *m*-phenylenebis(*t*-butyl nitroxide) are singlet in the ground states even though they are non-Kekulé compounds. These compounds have large dihedral angles between the nitroxides and the *m*-phenylene spacer. More recent *ab initio* calculations by Borden and co-workers indicate that the reason for the singlet is attributable to the orbital interaction through σ-bonds in the *m*-phenylene moiety.[1h] In these orbital interactions, the local radical orbitals (S and A) are destabilized through the mixing of σ-orbitals (S and A), giving the nondegenerate SOMOs.

In addition to their unique electronic nature, the dications $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ have large dihedral angles[12] between phenothiazine cations and the central benzene ring (ca. 88° for $\mathbf{1}^{2+}$ and 81° for $\mathbf{2}^{2+}$ by AM1 calculations), and therefore the energy gap between the two SOMOs would be further decreased in a π-orbital sense. However, in these geometries the local cation orbitals may be destabilized by the mixing of σ-orbitals of the central benzene ring as pointed out by Borden and co-workers.[1h] Since energy difference between the two σ-orbitals with different symmetries (S and A) is likely to be larger in the *m*-phenylene than in the *p*-phenylene framework simply because of the smaller number of σ-bonds in the *m*-phenylene structure, the resulting orbital energy splitting between the two SOMOs may be larger in the meta isomer than in the para isomer. The same conclusion is drawn in through-space orbital interaction between the two cations. Thus, the dication $\mathbf{2}^{2+}$ may have nearly degenerate SOMOs, whereas the dication $\mathbf{1}^{2+}$ may not.[13] These considerations and the nondisjoint[14] nature of $\mathbf{2}^{2+}$ would rationalize the observations.

The present results suggest that nondisjoint *p*-phenylene-bridged[13c] high-spin compounds may be stable if they have nearly degenerate SOMOs. Utility of nonbonding level orbitals in heterocyclic conjugated π-systems in combination with the large dihedral angle approach would provide an effective route for the design of novel high-spin molecules.

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(11) 10-Phenylphenothiazine **3** in sulfuric acid gave only monocation ESR absorption without zero-field splitting under the similar conditions. This result and the relatively low intensities of the monocation absorption (located at ca. 335.0 mT) in the spectra of Figure 1 indicate that the formation of ion pairs or intermolecular dications are not the source of the observed zero-field splitting.

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