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### Invalidity of Simple Application of Spin-Prediction Topology Rule to Heteroatomic $\pi$ -Conjugated Systems: 10,10'-(M-Phenylene)Diphenothiazinedication and 10,&10', 10''-(1,3,5-Benzenetriyl)Triphenothiazine Trication

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INVALIDITY OF SIMPLE APPLICATION OF SPIN-PREDICTION  
TOPOLOGY RULE TO HETEROATOMIC  $\pi$ -CONJUGATED SYSTEMS:  
10,10'-(*m*-PHENYLENE)DIPHENOTHIAZINE DICATION AND 10,10',  
10''-(1,3,5-BENZENETRIYL)TRIPHENOTHIAZINE TRICATION

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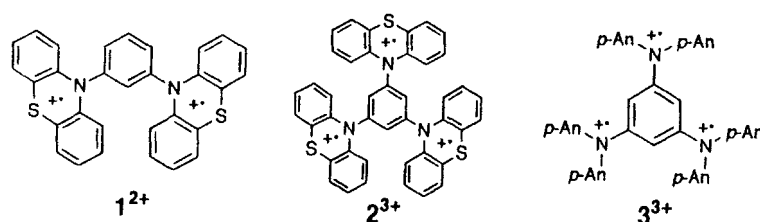
**Abstract** Invalidity of simple application of hydrocarbon spin-prediction  
topology rule to heteroatomic  $\pi$ -conjugated systems were exemplified for 10,  
10'-(*m*-phenylene)diphenothiazine dication and 10,10',10''-(1,3,5-benzene-  
triyl)triphenothiazine trication.

## INTRODUCTION

Organic high-spin compounds have recently attracted growing interest in relation to materials science as well as basic understanding of spin alignment. It has generally been accepted as a spin-prediction topology rule in hydrocarbon high-spin molecules that *m*-phenylene linkers, i.e., *meta*- or 1,3 5-connection, give rise to high-spin ground states. This rule has experimentally and theoretically been validated during the past decades. However, it has recently been found that some diradicals with *m*-topology give the low-spin ground states.<sup>1-5</sup> These low-spin diradicals have common features: 1) a large dihedral angle between the nodal plane of spin sources and the linker plane, as Borden and co-workers pointed out in terms of the orbital interaction through the  $\sigma$ -bond of the linker,<sup>6</sup> and 2) the presence of heteroatoms in  $\pi$ -conjugated systems.

Among aniline derived cations, phenothiazine cation has a unique heteroatomic  $\pi$ -conjugated nature: diphenylamine cation has a relatively large spin density on the nitrogen atom, whereas phenothiazine cation has a large positive spin density not only on the nitrogen atom but also on the sulfur atom, so that phenothiazine cation does not

benefit from alternating spin polarization which underlies the topology rule in homoatomic  $\pi$ -conjugation systems. There may be a large difference in the spin multiplicity in the ground states between diphenylamine based polycations and phenothiazine based polycations. Stickley and Blackstock recently reported that hexaanisyl-1,3,5-triaminobenzene trication ( $3^{3+}$ ) is a stable quartet species.<sup>7</sup> More recently, the related 1,3-diaminobenzene dication was shown to be triplet in the ground state.<sup>8,9</sup> We report low-spin ground states of the titled dication ( $1^{2+}$ ) and the trication ( $2^{3+}$ ).<sup>10</sup>



## RESULTS AND DISCUSSION

The neutral compounds **1** and **2** were synthesized in 50 and 23% yield by Ullmann arylation of phenothiazine with *m*-diiodo- or 1,3,5-triiodobenzene [at 200 °C for 60–72 h in the presence of  $K_2CO_3$  (3–4.4 equiv.) and Cu-powder (0.4–0.7 equiv.) without solvent]. The oxidation was achieved by dissolving the neutral compound **1** and **2** (ca. 1 mg) in concentrated sulfuric acid (1 cm<sup>3</sup>,  $d=1.84$  g cm<sup>-3</sup>). The electronic spectrum in sulfuric acid showed an absorption band (516 nm,  $\epsilon = 2.50 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> for  $1^{2+}$ , 518 nm,  $\epsilon = 3.24 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> for  $2^{3+}$ , assuming clean conversion) similar to 10-phenylphenothiazine cation ( $4^+$ ) (515 nm,  $\epsilon = 1.31 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>). The molar absorptivity of  $1^{2+}$  and  $2^{3+}$  is 1.9 and 2.5 times larger than of  $4^+$ , suggesting the dication and trication formation, respectively.

The ESR spectrum of  $1^{2+}$  observed at 135 K in the frozen sulfuric acid showed a fine structure pattern due to randomly oriented triplet species with overlapping hyperfine structures on X and Y components (FIGURE 1). The zero-field splitting parameter  $D$  was determined to be 6.40 mT. The triplet state of  $1^{2+}$  was shown to be an excited state by measuring the temperature dependence of the signal ( $\Delta m_s = \pm 2$ ) intensity. The singlet-triplet energy gap was determined to be  $1.2 \times 10^2$  J mol<sup>-1</sup>.

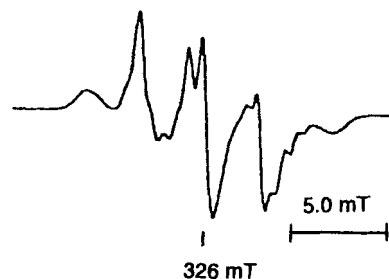


FIGURE 1. ESR spectrum of  $1^{2+}$  at 135 K in frozen sulfuric acid.

The trisubstituted compound **2** showed an apparent quartet-state pattern in the frozen sulfuric acid (FIGURE 2). The zero-field splitting parameter  $D$  was determined to be 3.26 mT that corresponds to the splitting of the Z-component signals of 13.04 mT. The total splitting is close to the splitting (12.80 mT) for  $1^{2+}$ ; therefore, one could also assume that the observed spectrum for the oxidation of **2** is a mixture of the triplet species and a monocation attributable to the central line. To obtain an insight into this point, the temperature dependence of the ESR spectrum was studied. When temperature decreased, the signal intensity of the Z and X,Y components decreased while that of the central line increased, giving an apparent appearance of isosbestic points (FIGURE 3). This observation is indicative of the existence of equilibrium between the quartet (X, Y, Z and the central line) and the doublet (the overlapping central line) states.

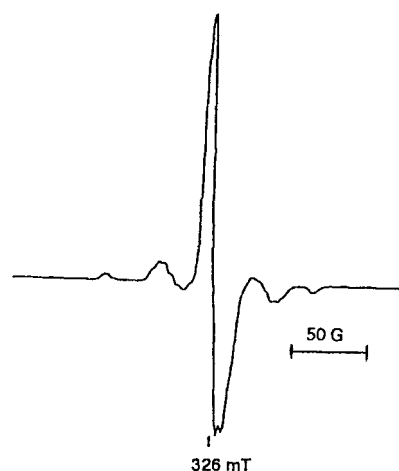


FIGURE 2. ESR spectrum of  $2^{3+}$  at 123 K in frozen sulfuric acid.

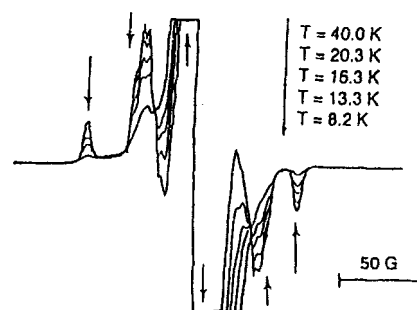


FIGURE 3. The temperature dependence of the ESR spectrum of  $2^{3+}$  in frozen sulfuric acid at 123 K.

In order to rule out any possibility of the doublet signal due to by-products, a new pulsed ESR method called "FT Pulsed Electron Spin Transient Nutation (ESTN) spectroscopy"<sup>11-13</sup> was applied. This method allows the direct and unequivocal determination of spin multiplicity of high-spin species even in non-oriented media.<sup>13</sup> The FT-pulsed ESTN spectrum (a frequency spectrum) was obtained by Fourier transforming spin-echo based time domain signals observed while increasing the excitation microwave pulse width. FIGURE 4 (top at 3 K, bottom at 100 K for  $2^{3+}$ ) shows 2D contour plots of the magnetic field swept ESTN spectrum. In the weak

extream limit of the microwave excitation, the nutation frequency  $\omega_N$  for ESR allowed transition  $|S, m_s\rangle \leftrightarrow |S, m_s'\rangle$  is given by the equation (1) in non-vanishing fine structure terms, where  $\omega_1$  is proportional to microwave field strength;

$$\omega_N = [S(S+1) - m_s m_s']^{1/2} \omega_1 \quad (1)$$

This equation predicts  $\omega_N = \omega_1$  for the doublet  $|1/2, -1/2\rangle \leftrightarrow |1/2, +1/2\rangle$  transition,  $\omega_N = 2^{1/2} \omega_1$  for the triplet  $|1, +1\rangle \leftrightarrow |1, 0\rangle$  or  $|1, -1\rangle \leftrightarrow |1, 0\rangle$  transition, and  $\omega_N = 2\omega_1$  for the quartet  $|3/2, -1/2\rangle \leftrightarrow |3/2, +1/2\rangle$  corresponding to the central absorption peak and  $\omega_N = 3^{1/2} \omega_1$   $|3/2, +1/2\rangle \leftrightarrow |3/2, +3/2\rangle$  or  $|3/2, -1/2\rangle \leftrightarrow |3/2, -3/2\rangle$  to the side peaks.

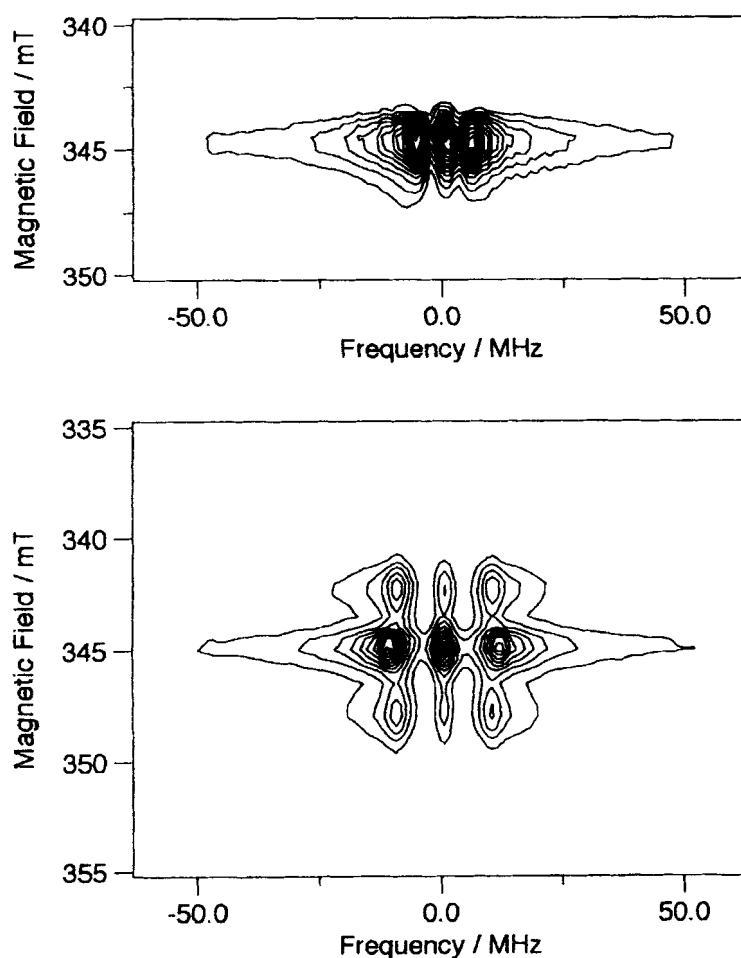


FIGURE 4. 2D-Contour plots of nutation spectra of  $2^{3+}$  at 3 K (top) and at 100 K (bottom).

The nutation frequency  $\omega_N$  is given by the absolute value of the outermost peak top(s) in a slice at the given magnetic field. Thus, the strong doublet signal at the central field (345 mT in FIGURE 4)<sup>14</sup> at 3 K has a value of  $\omega_N = 6.10$  MHz. On the other hand, the signal at the central magnetic field (345 mT) at 100 K has a value of 11.95 MHz. The ratio of the nutation frequency  $11.95/6.10 \approx 2$  indicates that the central signal at 100 K is due to the quartet state according to the above prediction. Similarly, the nutation frequencies  $\omega_N$  for the side peaks (X and Y components) at 342 and 348 mT give  $\omega_N = 10.37$  at 342 mT or  $\omega_N = 10.16$  at 348 mT. These values are close to  $3^{1/2} \times 6.10$ , again indicating that the side signals belong to the quartet species. Thus, the ESTN experiments unequivocally establish that the observed fine structure spectrum at 100 K is due to the thermally excited quartet state. The energy difference between the doublet and the quartet states was estimated to be  $3.8 \times 10^2 \text{ J mol}^{-1}$ .

It is interesting to compare these results with those reported for  $3^{3+}$  and its derivatives. The difference between the two systems obviously relates to the sulfur bridging. Triphenylamine cation has the largest spin density on the nitrogen atom (+0.61 by AM1-UHF calculation), whereas 10-phenylphenothiazine cation ( $4^+$ ) has the largest spin density on the sulfur atom (+0.56) and a smaller spin density on the nitrogen atom (+0.26). The delocalization of the sulfur lone pair electrons diffuses the spin density of the nitrogen atom. Therefore, the dynamic spin polarization<sup>15</sup> through the *m*-phenylene or 1,3,5-benzenetriyl linker stabilizes the high-spin state and destabilizes the low-spin state in smaller amounts in phenothiazine derivatives. Furthermore, the sulfur bridging obviously changes the geometry. Phenothiazine cation is known to be a planar species<sup>16</sup> and  $4^+$  would have a large dihedral angle (ca.  $90^\circ$  by AM1-UHF calculation)<sup>17</sup> between the phenyl and phenothiazine planes. However, triphenylamine cation has a much smaller dihedral angle (ca.  $32^\circ$  by AM1-UHF calculation)<sup>16</sup> between the plane (defined by three  $sp^2$  carbons attached to the nitrogen atom) and one of the benzene rings. Therefore, according to Borden's interpretation, the orbital interaction through the  $\sigma$ -bonds of the linker<sup>6</sup> can be operative for  $1^{2+}$  and  $2^{3+}$ . Both the spin density and dihedral angle effects place these phenothiazine cations in the low-spin ground state.

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