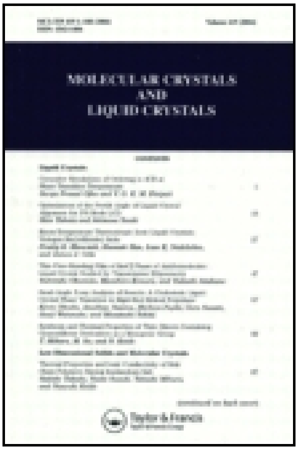

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Exchange Interaction of Some Thianthrene-Derived Dications

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Exchange Interaction of Some Thianthrene-Derived Dications

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Tribenzohexathiatriphenylene dication derivatives and 2,2-bisthian-threnenyl dication derivatives are an interesting species because of their unique spin distribution patterns. The exchange interaction of these species was investigated.

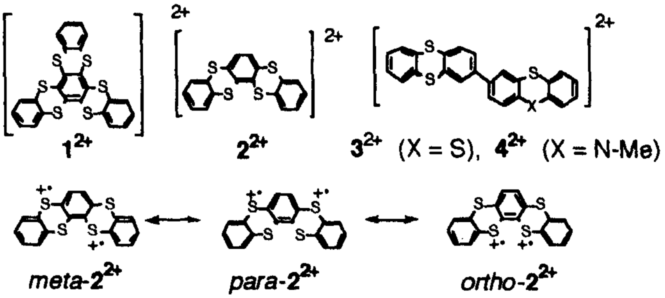
Keywords: exchange interaction; thianthrene cation; esr; high-spin; low-spin

INTRODUCTION

In alternant hydrocarbon high-spin molecules, it has generally been accepted that *m*-phenylene type linkers give rise to a high-spin ground state[1]. However, some systems containing non-carbon elements, such as nitrogen[2-4] and sulfur[5-7] atoms, have been recently found not to obey this *m*-phenylene linkage rule. The delocalization of lone-pair electrons of these elements[5-7] as well as the large dihedral angles[8] between the spin sources and their linker may underlie this anomaly.

Thianthrene cation is an interesting species because of its nonalternate spin distribution pattern. We describe two types (type I and II) of thianthrene cation-derivatives; type I includes almost planar tribenzohexathiatriphenylene (1^{2+}) or dibenzotetrathiaphenanthrene dications (2^{2+}), whereas type II relates to two thianthrene cations directly bound without a spacer, 2,2-bisthianthrenyl dication (3^{2+}) and its analogue (4^{2+}). These species have common interesting features as follows. Thianthrene has an electron-rich center due to its 8π-dithine structure, so that its cation radical has a large spin density on the sulfur atoms. For instance, 2^{2+} may be expressed by the resonance of a series of VB canonical structures whose spins are localized on the two *meta-*, *para-* or *ortho-* sulfur atoms (Scheme 1). Spin polarization via the nearest π-network may suggest triplet, singlet, and singlet states for these structures, respectively. A similar argument is possible for 1^{2+}, 3^{2+}, and 4^{2+}. Therefore, the spin-prediction of the ground state for these heteroatomic systems is not easy. We report an experimental approach to these species.

SCHEME 1



RESULTS AND DISCUSSION

Type I Compounds

The neutral compounds **1** and **2** are sparingly soluble in sulfuric acid. However, the suspension becomes an intense blue after a suitable time of oxidation (ca. 1 day for **1** and a few hrs for **2** at 30 °C). The ESR spectrum of the blue species in frozen sulfuric acid at -150 °C showed a triplet pattern besides a strong signal due to the monocation for both cases [Fig. 1 upper for $\mathbf{1}^{2+}$, lower for $\mathbf{2}^{2+}$].

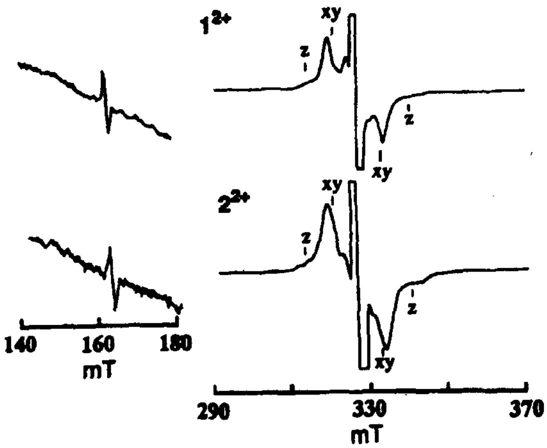


FIGURE 1 ESR spectra of $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$ in frozen H_2SO_4 at -150 °C. The microwave frequencies were 9.18324 GHz and 9.18180 GHz, respectively.

The zero-field splitting parameters were determined to be D = 0.012 cm^{-1}, $E \approx 0.00$ cm^{-1}. The calculated averaged distance [6.0 Å by $D = (-3/2)g^2\beta^2 r^{-3}$] between the two spin centers is in a range between the *para*-sulfur atoms (6.4 Å) and the *meta*-sulfur atoms (5.5 Å). A weak forbidden signal due to the Δm_S = ±2 transition was also observed in the half-magnetic field region. A similar triplet pattern was observed for the oxidation of **2** ($D = 0.012$ cm^{-1}, $E \approx 0.00$ cm^{-1}) [Fig. 1 (lower)].

Fig. 2 (left) shows Curie plots using the Δm_S = ±2 signal. The plots for $\mathbf{1}^{2+}$ gave a straight line in the temperature range between 3.5 and 20 K, indicating a triplet ground state. However, similar plots for $\mathbf{2}^{2+}$ gave a curvature which indicates a singlet ground state (Fig. 2, right). The energy gap between the singlet and triplet states was determined to be -35 J/mol.

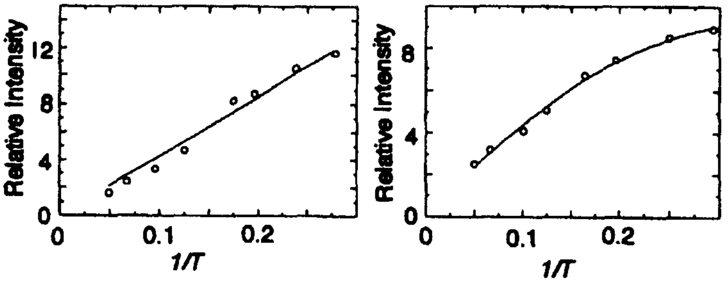
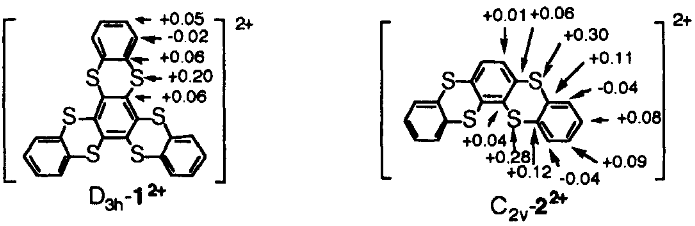


FIGURE 2 Curie plots for $\mathbf{1}^{2+}$ (left) and $\mathbf{2}^{2+}$ (right).

The triplet nature of $\mathbf{1}^{2+}$ is not surprising since some triphenylene-derived dications (D_{3h}) are known to be a triplet species[9,10]. In contrast to the previous triphenylene dications ($D = 0.022 \sim 0.038$ cm^{-1}) , the dication $\mathbf{1}^{2+}$ has a considerably smaller D-value (0.012 cm^{-1}). This is probably due to the difference in the electronic structure between these dications; $\mathbf{1}^{2+}$ has cation centers on the 8π-dithine rings, whereas the previous triphenylene dications receive a large contribution of the benzene dication on the central benzene ring.

The low-spin ground state of $\mathbf{2}^{2+}$ is interesting. This result suggests that the exchange interaction of thianthrene-based dications (even for $\mathbf{1}^{2+}$) is not large and is dependent on a subtle structural change. The low-spin nature of $\mathbf{2}^{2+}$ may be rationalized by either or both of the following factors. Firstly, the ground state nature is dependent on the molecular symmetry. The dication $\mathbf{1}^{2+}$ has D_{3h} symmetry, provided that the two spins are well delocalized. Then, the two higher molecular orbitals (two SOMOs) of $\mathbf{1}^{2+}$ degenerate, leading to the triplet ground state. However, the dication $\mathbf{2}^{2+}$ has C_{2v} symmetry, where the two SOMOs do not degenerate. The resulting energy gap between the two SOMOs may favor the singlet ground state. Secondly, the ground state nature is also dependent on the spin density pattern of these dications. The calculations were achieved using the DFT (B3LYP/6-31G**//3-21G in Gaussian 94 program method for D_{3h} symmetry for $\mathbf{1}^{2+}$ and C2v-symmetry for $\mathbf{2}^{2+}$, respectively (see D_{3h}-$\mathbf{1}^{2+}$ and C_{2v}-$\mathbf{2}^{2+}$). Obviously, the six sulfur atoms of $\mathbf{1}^{2+}$ are equivalent and have the same spin density (+0.20). For $\mathbf{2}^{2+}$, however, two sulfur atoms in the *para*-relation have a larger spin density (+0.30) than those in the *ortho*-relation (+0.28). Provided that $\mathbf{2}^{2+}$ has a pure *meta*-structure (Scheme 1), the spin density of the four sulfur atoms

SCHEME 2



should be equal. The calculated larger sulfur spin density at the *para*-positions would be due to the larger contribution of the *para*-$\mathbf{2}^{2+}$ structure (Scheme 1) where the destabilizing spin polarization through *p*-phenylene linkage is predominant in the triplet state. This consideration accords with the singlet ground state of $\mathbf{2}^{2+}$.

Type II Compounds

2,2'-Bithianthrenyl (**3**) was prepared in 41% yield by the Pd(0)-mediated cross coupling (in THF, 7 days) of 2-bromothianthrene with 2-trimethylstannylthianthrene. The compound $\mathbf{4}^{2+}$ was similarly prepared by the coupling of 2-bromo-10-methylphenothiazine with 2-trimethylstannylthianthrene in lower yield (13%). The oxidation of **3** and **4** was best achieved by dissolving in concentrated sulfuric acid.

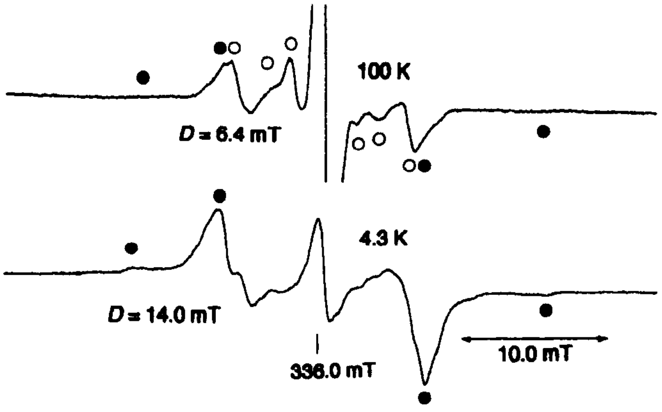


FIGURE 3 ESR spectrum for the oxidation of $\mathbf{3}^{2+}$ measured at 100 K (upper) and at 5 K (lower) in frozen sulfuric acid. The microwave frequencies were 9.45149 GHz and 9.45154 GHz, respectively.

Fig. 3 shows the ESR spectrum for the oxidation of **3** measured at two different temperatures (upper, 100 K; lower, 4 K) in frozen sulfuric acid. Obviously, two sets of triplet signals, denoted by solid (D = 0.013 cm^{-1}) and open (D = 0.006 cm^{-1}) circles, were observed at 100 K. At 4 K, only the triplet with the larger D was seen.

The relative intensity of these signals at 100 K did not vary with the concentration or the oxidation period. Furthermore, quenching the oxidized species by adding water and the subsequent extraction with dichloromethane recovered the starting material (**3**). These results indicate that the observed two sets of triplet signals are ascribable to the conformational isomers of $\mathbf{3}^{2+}$[11].

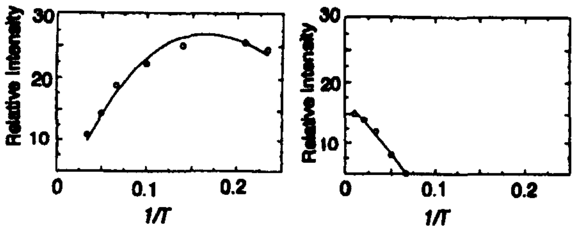
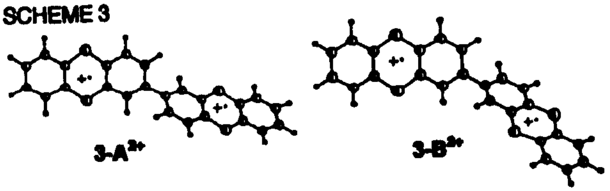


FIGURE 4 Curie plots for the signals ($\Delta m_s = \pm 1$) of solid circle (left) and open circle (right) denoted in Figure 1.

Fig. 4 shows the temperature dependence of these signals. When temperature decreases, the open circle signals almost disappear at about 15 K (Fig. 4, right). On the other hand, the intensity of the solid-circle signals gradually increases with decreasing temperature down to 10 K and approaches a plateau in the range between 10 to 5 K (Fig. 4, left). The S-T energy gap for the solid-circle species was determined as -80 J/mol by a simulation with the S-T model. These results in combination with the above consideration suggest that **3**$^{2+}$ has conformers and one of the conformers (D = 0.013 cm^{-1}) has a considerably low lying triplet state, although the ground state is a singlet state. The Curie plots using Δm_s = ±2 signal were similar to those using Δm_s = ±1 signal.

Although the assignment of these triplet species is not clear at present, inspection of the molecular models suggests that there should be two conformers **3-A**$^{2+}$ and **3-B**$^{2+}$ (Scheme 3). Geometry optimization for these conformers was carried out by the AM1-UHF method. The energy values were obtained by the AM1-CI method at the UHF geometry. In both cases, the thianthrene rings are almost planar. The obtained Hf (heat of formation) values and torsion angles are 489.48 kcal/mol with θ = 45° for **3-A**$^{2+}$ and 489.85 kcal/mol with θ = 48° for **3-B**$^{2+}$. The isomer **3-A**$^{2+}$ was suggested to be the predominant isomer.

SCHEME 3



3-A^{2+} **3-B**$^{2+}$

Similar ESR behavior was observed for the oxidation of **4**$^{2+}$. Two different triplet patterns were clearly seen at 123 K. However, only one component (with larger D-value = 0.015 cm^{-1}) was observed at 3.3 K (Fig. 5). Interestingly, the signal intensity using Δm_s = ±2 signal gave a straight line, indicating that **4**$^{2+}$ has a conformer whose ground state is a triplet state or a singlet state with a nearly degenerate triplet state.

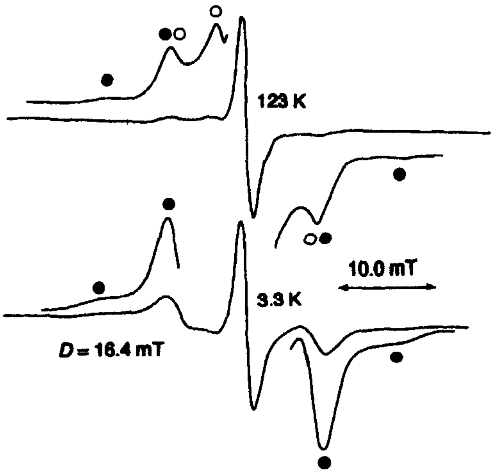


FIGURE 5 ESR spectrum of 4^{2+} measured at 123 K (upper) and at 3.3 K (lower) in frozen sulfuric acid. The microwave frequencies were 9.45295 GHz and 9.45301 GHz, respectively.

CONCLUSION

The ground state of the phenothiazine dications (1^{2+} ~ 4^{2+}) was found to be altered by a subtle change in the molecular structure. The exchange interaction of these systems is probably not large even in the case of 1^{2+} and 4^{2+}. The small energy gap seems to be characteristic of these systems and would be related to the following electronic nature of phenothiazine. Firstly, the spin density of phenothiazine cations is mainly localized on the sulfur atoms, so that 1^{2+} and 2^{2+}, for instance, receive a small contribution of the benzene dication which leads to large exchange interaction because of two electrons in the smaller space. Secondly, both sulfur atoms of the phenothiazine cation have up-spins (α), so that the spin distribution cannot be arranged in alternate fashion and would be described by the resonance of several VB canonical structures. When more than two phenothiazine cations are linked or connected (directly or through spacers), the spins (α) on the sulfur atoms in the inter-phenothiazines are lined through either spin-alternate or -nonalternate π-networks depending on the positions of the sulfur atoms. Therefore, identification of the spin-controlling sulfur atoms seems to be essential in these systems.

Acknowledgments

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