PERKIN 2 COMMUNICATION

10,10′,10″-(Benzene-1,3,5-triyl)triphenothiazine trication

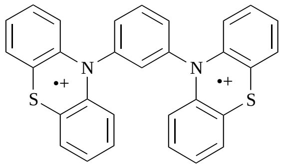
Keiji Okada,[a] Takaaki Imakura,[b] Masaji Oda,[b] Atsushi Kajiwara,[b] Mikiharu Kamachi,[b] Kazunobu Sato,[a] Daisuke Shiomi,[c] Takeji Takui,[a] Koichi Itoh,[c] Lileta Gherghel[d] and Martin Baumgarten[d]

[a] *Department of Chemistry, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan*
[b] *Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan*
[c] *Department of Material Science, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558, Japan*
[d] *Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany*

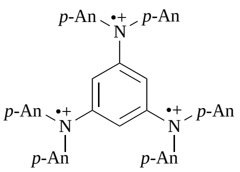
10,10′,10″-(Benzene-1,3,5-triyl)triphenothiazine trication has been prepared and its ground and nearby excited states were identified by use of EPR and EPTN techniques, showing that this species is in a doublet ground state with the doublet-quartet energy gap of *ca.* 3.8 × 10^2 J mol^{-1}.

Organic high-spin compounds have recently received intense attention in relation to materials science and basic understanding of spin alignment. It is well known as a topology rule in hydrocarbon high-spin molecules that *m*-xylylene-type linkers, *i.e. meta*- (or 1,3,5-) connection, give rise to high-spin ground states, whereas the *p*-xylylene types tend to be quinoid forms with low-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 singlet ground states.[1–5] Borden and co-workers have proposed that this may be attributed to the orbital interaction through σ bonds of the linker by *ab initio* calculations for the *m*-phenylene linked bisnitroxides which have large dihedral angles between the nodal plane of nitroxide and the linker plane.[6] We have shown that 10,10′-(*m*-phenylene)diphenothiazine dication (**1**$^{2+}$) is also singlet in the ground state.[4]

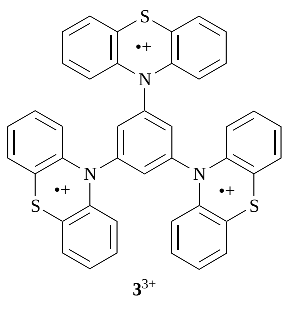
It is interesting to compare the results of **1**$^{2+}$ with those reported for the diphenylamine cation substituted derivatives.[7–9] Stickley and Blackstock have reported that hexa-*p*-anisyl-1,3,5-triaminobenzene trication (**2**$^{3+}$) is a stable quartet species.[7] More recently, Wienk and Janssen also reported that the related 1,3-substituted and 1,3,5-substituted derivatives are also high-spin species in their ground states.[8] It seems that there is a large difference in the ground state spin multiplicities between phenothiazine cation derivatives and diphenylamine cation derivatives. In order to clarify this point, we report the preparation and determination of spin multiplicities in the ground and nearby excited states for 10,10′,10″-(benzene-1,3,5-triyl)triphenothiazine trication (**3**$^{3+}$).



1^{2+}



2^{3+}



3^{3+}

The neutral compound **3** was synthesised in 23% yield by Ullmann arylation of phenothiazine with 1,3,5-triiodobenzene [at 200 °C for 72 h in the presence of K_2CO_3 (4.4 equiv.) and Cu powder (0.7 equiv.) without solvent]. The oxidation was achieved by dissolving the neutral compound **3** (*ca.* 1 mg) in concentrated sulfuric acid (1 cm^3, $\rho = 1.84$ g cm^{-3}). The electronic spectrum in sulfuric acid showed an absorption band (518 nm, $\varepsilon = 3.24 \times 10^4$ dm^3 mol^{-1} cm^{-1}, assuming clean conversion) similar to the 10-phenylphenothiazine cation (**4**$^+$) (515 nm, $\varepsilon = 1.31 \times 10^4$ dm^3 mol^{-1} cm^{-1}) except that the molar absorptivity of **3**$^{3+}$ is 2.5 times larger than that of **4**$^+$, suggesting trication formation.

The EPR spectrum in sulfuric acid at 123 K showed a fine structure pattern for random orientation of quartet state molecules with overlapping hyperfine structures on *x,y* components and on the central line [Fig. 1(*a*)].† The zero-field splitting parameter *D* was determined to be 3.26 mT, corresponding to the splitting of the outermost *z*-component signals of 13.04 mT. The splitting is close to the splitting (12.80 mT) for **1**$^{2+}$; therefore, one could also assume that the observed spectrum is a mixture of the triplet species and a monocation attributable to the central line. To obtain further insight into this point, the temperature-dependent EPR spectra was studied. When temperature decreases, the signal intensity of the *z* and *x,y* components decreases and that of the central line increases, giving an apparent appearance of isosbestic points [Fig. 1(*b*)]. This observation is indicative of the existence of an equilibrium between the quartet (*x,y,z* and the central line) and the doublet (the overlapping central line) states.

In order to identify clearly the observed species, a new pulsed EPR method called ‘FT Pulsed Electron Paramagnetic Transient Nutation (EPTN) spectroscopy’[10–12] is now applied. This method allows the direct determination of spin multiplicity of high-spin species even in non-oriented media.[12] The FT-pulsed EPTN spectrum (a frequency spectrum) was measured by monitoring the intensity of spin-echo while increasing the excitation pulse width. Fig. 2 shows 2D contour plots of the intensity of EPTN spectrum by varying the magnetic field (*y* axis).† Under weak microwave power, nutation frequency ω_N for EPR allowed transition $|S,m_s\rangle \leftrightarrow |S,m_{s'}\rangle$ is given by eqn. (1) where ω_1

$$\omega_N = [S(S+1) - m_s m_{s'}]^{\frac{1}{2}}\omega_1 \qquad (1)$$

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† The central signal appears at 326 mT in Fig. 1 and at 345 mT in Fig. 2 under the experimental conditions. The pulsed EPR experiments were performed on a Bruker ESP380E FTEPR spectrometer.

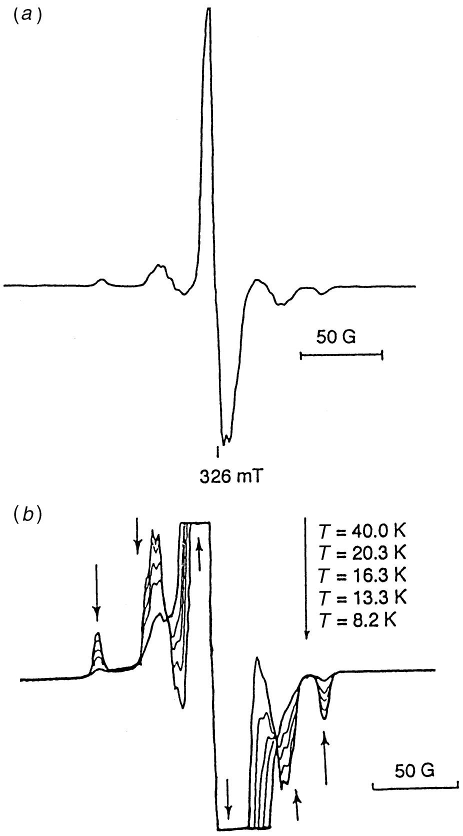

Fig. 1 (*a*) EPR spectrum of $\mathbf{3}^{3+}$ at 123 K in frozen sulfuric acid and (*b*) the spectral change as a function as temperature

is proportional to the microwave field strength. The nutation frequency ω_N at 345 mT is given by the absolute value of the outermost peak top(s) in a slice at 345 mT. Thus, the strong doublet signal due to the $|1/2, -1/2> \leftrightarrow |1/2, +1/2>$ transition at the central field (345 mT in Fig. 2)† at 3 K has a value of $\omega_N = 6.10$ MHz which, in turn, leads to the relation of $\omega_N = \omega_1 = 6.10$ MHz by eqn. (1). On the other hand, the signal at the central magnetic field (345 mT, $|S, -1/2> \leftrightarrow |S, +1/2>$) at 100 K has a value of 11.95 MHz, which allows estimation of S as $2.92/2 \approx 3/2$ (quartet) according to eqn. (1) with $\omega_1 = 6.10$ MHz. Similarly, the nutation frequencies ω_N for the x,y component signals at 342 and 348 mT give the S value as *ca.* 3/2.‡ Thus, the EPTN experiments unequivocally establish that the observed fine structure spectrum at 100 K is due to the thermally accessible quartet state above the doublet ground state. The energy difference between the doublet and quartet states can be estimated to be 3.8×10^2 J mol^{-1} by the simulation of the plots of the signal intensity *vs.* $1/T$.

It is interesting to compare these results with those reported for the above mentioned tris(diphenylamine) trication derivatives. The difference in spin multiplicities should be related to the presence of sulfur bridging. Triphenylamine cation has the largest spin density on the nitrogen atom (+0.61 by AM1-UHF),§ whereas 10-phenylphenothiazine cation ($\mathbf{4}^{+}$) has the largest spin density on the sulfur atom (+0.56) and a smaller spin density on the nitrogen atom (+0.26). Obviously, the delocalization of the sulfur lone pair electrons decreases the spin density of the nitrogen atom. For this reason, dynamic spin polarization[13] stabilizes the quartet states and destabilizes the doublet states in larger amounts for tris(diphenylamine) trication derivatives than for $\mathbf{3}^{3+}$. Furthermore, the sulfur bridging obviously changes the geometry. The phenothiazine cation is known to be a planar species[14] and $\mathbf{4}^{+}$ would have a large dihedral angle (*ca.* 90° by AM1-UHF)§ between the phenyl and phenothiazine planes. However, the triphenylamine cation has a much smaller dihedral angle (*ca.* 32° by AM1-UHF)§ between the plane (defined by three sp^2 carbons attached to the nitrogen atom) and one of the benzene rings. Thus, the phenothiazine trication $\mathbf{3}^{3+}$ has a larger dihedral angle than (benzene-1,3,5-triyl)tris(diphenylamine) trication derivatives. Therefore, the orbital interaction through the σ bonds of the linker[6] can be operative for $\mathbf{3}^{3+}$. These effects (dihedral angle effect and spin density effect) cooperatively place the doublet state lower than the quartet state for $\mathbf{3}^{3+}$.

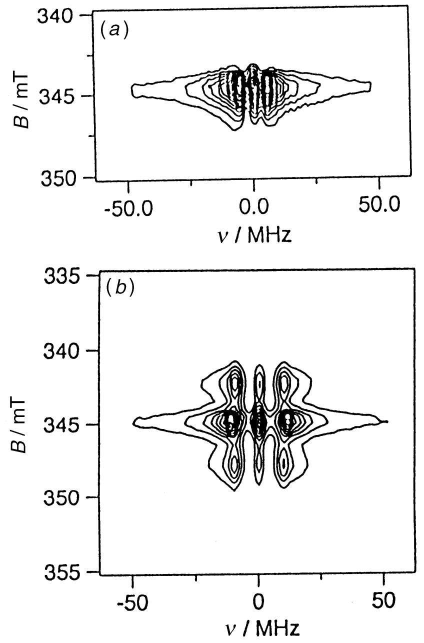

Fig. 2 2D Contour plots of nutation spectra at (*a*) 3 K and (*b*) 100 K for $\mathbf{3}^{3+}$

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‡ The nutation frequencies ω_N for the x,y component signals (10.37 MHz at 342 mT or 10.16 MHz at 348 mT due to $|S, -3/2> \leftrightarrow |S, -1/2>$ or $|S, +1/2> \leftrightarrow |S, +3/2>$ transitions) gives the S value as 2.94/2 or 2.88/2, respectively.

§ Geometries were fully optimised by AM1-UHF method with a keyword 'PRECISE'.