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# Polycationic High-Spin States of One- And Two-Dimensional (Diarylamino)Benzenes as Studied By Pulsed Esr/Electron Spin Transient Nutation (Estn) Spectroscopy

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# POLYCATIONIC HIGH-SPIN STATES OF ONE- AND TWO-DIMENSIONAL (DIARYLAMINO)BENZENES AS STUDIED BY PULSED ESR/ELECTRON SPIN TRANSIENT NUTATION (ESTN) SPECTROSCOPY

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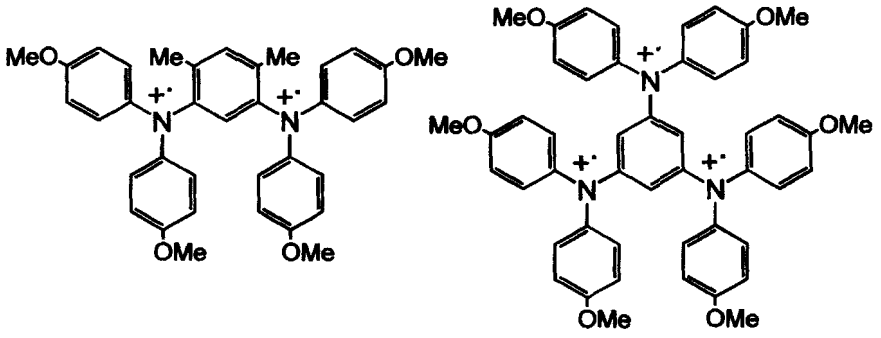
**Abstract** Polycationic high-spin states of star-burst molecules based on (diarylamino)benzenes have been studied by cw and pulsed ESR spectroscopy. An electron spin transient nutation (ESTN) method based on pulsed ESR spectroscopy was applied to the dicationic and tricationic high-spin states of *N,N,N',N'*-tetra(4-anisyl)-2,4-dimethyl-1,5-phenylenediamine and *N,N,N',N',N'',N''*-hexa(4-anisyl)-1,3,5-triaminobenzene, respectively, in order to identify the spin multiplicity of the polycationic states. The observed 2D nutation spectra of the dicationic and tricationic states unequivocally showed that the dicationic and tricationic states are ground-state triplet and quartet, respectively.

## INTRODUCTION

Recently, organic molecular based magnetism has been attracting wide interest in the pure and applied sciences. Stable polyionic magnetic materials are the focus of current topics as models for multifunctionality molecule-based magnetic materials. Organic heteroatomic high-spin molecules with multi-charge are designed by the use of topological quasi-degeneracy of HOMOs or LUMOs which are close to a zero energy (non-bonding) level. This feature is quite different from the case of neutral homoatomic high-spin molecules in which topological complete degeneracy plays an important role in generating high-spin states. A study of electronic structures of the heteroatomic high-spin molecules with multi-charge is of fundamental importance for examining relations




$\mathbf{1}^{2+}$ $\mathbf{2}^{3+}$

between spin polarization and charge fluctuation in organic molecular systems.

We have studied polycationic high-spin states of star-burst molecules based on (diarylamino)benzenes[1,2,3] using pulsed/cw ESR spectroscopy, emphasizing the unequivocal magnetic characterization of the high-spin states. An electron spin transient nutation (ESTN) method based on pulsed ESR spectroscopy[4,5,6] was applied to the polycationic high-spin states of *N,N,N',N'*-tetra(4-anisyl)-2,4-dimethyl-1,5-phenylenediamine **1** and *N,N,N',N',N'',N''*-hexa(4-anisyl)-1,3,5-triaminobenzene[7] **2** in order to examine the molecular spin quantum numbers of the cationic states. The methyl and methoxyl groups were introduced for increasing the chemical stability of the polycationic high-spin states. This paper deals with the identification of the molecular spin quantum number by the ESTN method.

## EXPERIMENTAL AND ANALYSIS

The polycationic high-spin molecules, $\mathbf{1}^{2+}$ and $\mathbf{2}^{3+}$, were generated by chemical oxidation of the parent molecules, **1** and **2**, in dichrolomethane containing tetra-*n*-buthylammonium tetrafluoroborate, *n*-$Bu_4NBF_4$, by lead tetraacetate. A small amount of trifluoroacetic anhydride was also dropped to the dichrolomethane solution with *n*-$Bu_4NBF_4$ for performing the chemical oxidation process for generating the polycations as shown in the previous literature[8].

X-band cw-ESR measurements were carried out on JEOL JES-FE2XG and Bruker ESP300 spectrometers. Pulsed ESR measurements were carried out on a Bruker ESP380 FT-EPR spectrometer with a dielectric resonator and a 1kW traveling wave tube

microwave amplifier.

The electron spin transient nutation (ESTN) experiments were performed by a three pulse sequence which consisted of nutation (microwave excitation) and $\pi/2$-$\pi$ (detection) pulses. We applied a 4-step phase cycling, monitoring the peak of a 2-pulse Hahn echo after the nutation pulse with different pulse length ($t_1$). Two-dimensional (2D) ESTN spectra were constructed by sweeping the static magnetic field. The nutation frequency ($\omega_n$) for an $|S,M_S\rangle \leftrightarrow |S,M_S\text{-}1\rangle$ allowed transition is given by

$$\omega_n = \sqrt{S(S+1) - M_S(M_S-1)} \times \omega_1 \qquad (1)$$

in the weak extreme limit of the microwave irradiation ($\omega_D >> \omega_1$ where $\omega_D$ is a fine structure coupling in a frequency unit)[4,5,6]. $\omega_1 (\approx \gamma B_1)$ corresponds to the strength of a microwave irradiation field.

## RESULTS AND DISCUSSION

The powder pattern ESR spectrum of a polycationic state of **1** observed at 7K is shown in Figure 1. It indicated five inhomogeneously broad lines in an allowed ESR transition region, not allowing one to characterize the polycationic spin state of **1** unequivocally.

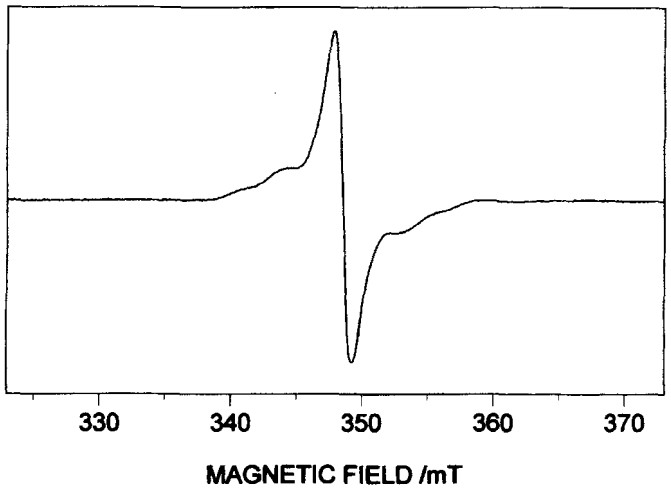



FIGURE 1 Powder pattern ESR spectrum observed by chemical oxidation of **1**.

In order to clarify the polycationic spin state of **1** we have measured the ESTN phenomena using the pulsed ESR technique. Figure 2 shows a 2D ESTN spectrum observed at 5K. The spectrum indicated that the nutation frequencies observed at 348.0mT and both sides of the field were 15.3MHz and 23.1MHz, respectively. The nutation frequency expected for $|1,0\rangle \leftrightarrow |1,\pm1\rangle$ transitions of a triplet state is $\sqrt{2}\omega_1$ from Eq.(1). At the central field in which both ESR transitions are excited at the same time, the frequency is expected to be $\omega_1$ because of a complete excitation. A Ratio of the frequencies (23.1/15.3) corresponds to that ($\sqrt{2}/1$) expected for a triplet state from Eq.(1). The intensity of the peak observed at 348.0mT was much stronger than that expected for the triplet state, indicating that signals due to radical impurities were overlapped. The powder pattern ESR spectrum, therefore, consists of the triplet and doublet species which were attributed to the dication of **1** and the radical impurities including a monocation of **1**, respectively. For the triplet dication, the fine-structure parameter $|D|$ was determined to be about 0.007cm$^{-1}$ from a splitting between the Z transitions in the ESR spectrum. The $|D|$ value is very close to those (0.0064 ~ 0.0079 cm$^{-1}$) of neutral high-spin molecules with the similar electric spin structure which have been reported so far[9,10,11,12,13], indicating that the charge fluctuation does not affect spin polarization mechanism pronouncedly.

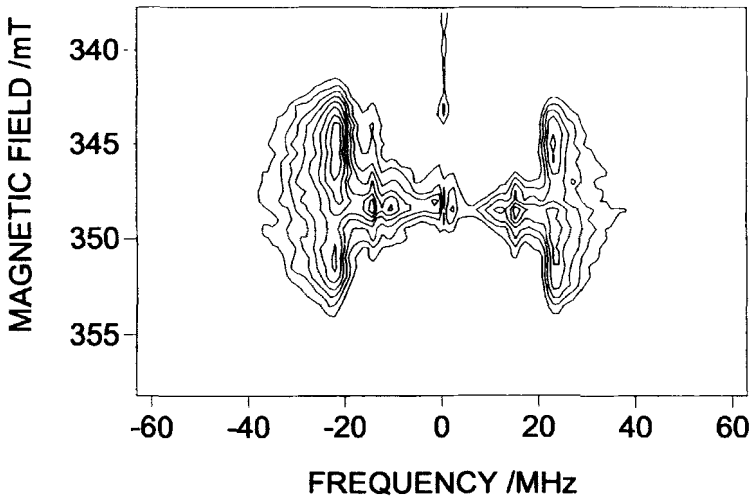



FIGURE 2 2D ESTN spectrum observed by chemical oxidation of **1**.

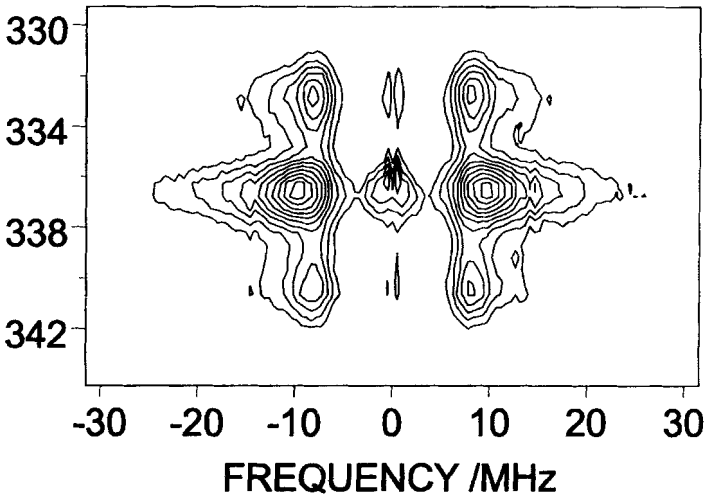



FIGURE 3 2D ESTN spectrum observed by chemical oxidation of **2**. $\omega_1$ corresponds to ~5MHz in this case.

Figure 3 shows a 2D-ESTN spectrum of $\mathbf{2}^{3+}$ observed at 6K. The nutation frequencies ($\omega_n$'s) observed at the central magnetic field and both sides of the field are 10.08MHz and 8.12MHz, respectively. A ratio of the observed nutation frequencies, 10.08/8.12, agrees with that ($2/\sqrt{3}$) expected for a quartet spin state by Eq.(1). We can, therefore, assign the central and side ESR transitions to |3/2,1/2> ↔ |3/2,-1/2> and |3/2,±3/2> ↔ |3/2, ±1/2> allowed transitions, respectively. In the ESTN spectrum any peaks were not observed at 5MHz region. This assures that the quartet state is a ground state. If the quartet state is an excited one, the frequency component arising from a doublet ground state has to be observed. The determined $|D|$ value of the quartet state is 0.0040cm$^{-1}$, which is also close to that of a neutral quartet molecule with hyperbranched diaryl-based spin structures[14].

## CONCLUSIONS

The ESTN method based on pulsed ESR spectroscopy was applied to the polycationic high-spin molecules, unequivocally determining the spin multiplicities of those molecules. The 2D ESTN spectroscopy was a powerful tool for spin identification and

discrimination between different spin multiplicities even in non-oriented systems. π-Topology-mediated molecular design for heteroatomic molecules is workable for generating pluricationic high-spin models for organomagnetic synthetic metals.

## ACKNOWLEDGMENTS

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