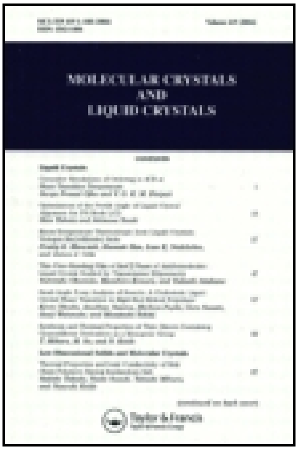

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# AN FT-PULSED ESR/ELECTRON SPIN TRANSIENT NUTATION STUDY OF HYPERBRANCHED π-ARYL STABLE TRIPLET AND QUARTET MOLECULES

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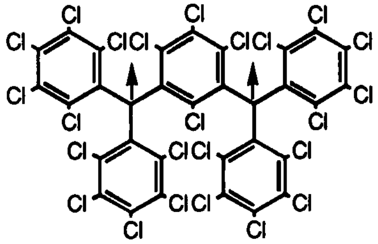
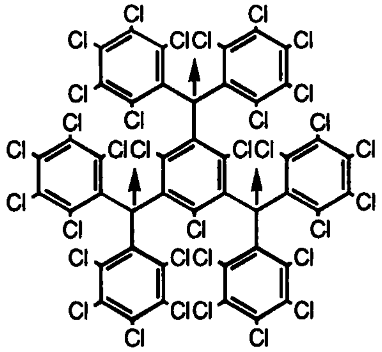
Abstract An electron spin transient nutation (ESTN) method based on FT-pulsed ESR spectroscopy was for the first time carried out for identifying the ground-state high spin multiplicities of stable π-aryl based molecules in organic glasses. The transient nutation frequencies ($\omega_n$) observed from the molecules in frozen toluene were interpreted using an equation, $\omega_n = \omega_1 \times [S(S+1)-M_S(M_S-1)]^{1/2}$, expected for an $|S, M_S-1> \leftrightarrow |S, M_S>$ single transition in the weak microwave irradiation limit. $\omega_1$ is a frequency that depends on the strength of an irradiated microwave pulse field. The observed nutation frequencies clearly depended on the S and $M_S$, identifying directly that the ground states of the molecules were triplet and quartet from the viewpoint of quantum spin nutation phenomena. The usefulness of the ESTN spectroscopy for the identification of spin multiplicity was illustrated to be a complement of cw-ESR spectroscopy.

## INTRODUCTION

Recently, organic molecular based magnetic materials have attracted increasing interest in pure and applied science.[1,2,3,4] Purely organic molecules with high-spin states in the ground or low-lying excited state have been designed and studied as models for organic ferro-, ferri-, and superpara-magnet. Spin identification and discrimination between different spin multiplicities are an increasingly important issue in the research field of organic magnetism and spin chemistry. An electron spin transient nutation (ESTN) method[5,6,7] based on FT-pulsed ESR spectroscopy is a useful and powerful tool for the above purposes, being complementary to continuous-wave ESR spectroscopy. This paper deals with the identification of the ground-state spin multiplicities of stable π-aryl based triplet and quartet molecules (**1** and **2**)[8,9] by ESTN spectroscopy, showing the usefulness of the transient nutation method. The present work has been the first reporting a successful application of the ESTN method to high-spin systems in organic rigid glasses.



**1**



**2**

## EXPERIMENTAL AND ANALYSIS

Transient nutation occurs when an irradiated field is suddenly applied to a spin system in a static magnetic field on (near) resonance. Then an effective spin , which has been aligned to the direction of the static field, precesses around a new effective field which is formed by the static and suddenly applied fields. This precession around the effective field is treated as dynamics of the fictitious spin of the two level system corresponding to a resonance transition in the rotating frame.

The transient nutation phenomena for both **1** and **2** diluted in frozen toluene were measured at liquid helium temperature by monitoring the peak of a 2-pulse (Hahn) echo while increasing the length of a first excitation pulse. Pulsed ESR experiments were performed on a Bruker ESP380E FT-ESR spectrometer with a dielectric resonator and a 1kW TWT amplifier. The nutation frequencies ($\omega_n$) observed from **1** and **2** were interpreted using an equation,

$$\omega_n=\omega_1 \times [S(S+1)-M_S(M_S-1)]^{1/2}, \qquad (1)$$

expected for an $|S, M_S-1\rangle \leftrightarrow |S, M_S\rangle$ single transition in the weak microwave irradiation limit.[1,2,3] $\omega_1$ is a frequency that depends on the strength of an irradiated microwave pulse field.

## RESULTS AND DISCUSSION

Figure 1 shows an echo-detected field-swept ESR spectrum of **2**. The spectrum indicates that the observed ESR signals consist of widely distributed ESR transitions over about 10 mT for **2**, which are corresponding to the ESR absorptions due to randomly oriented multiplets.

Figure 2 shows the nutation spectra for **2** observed at three magnetic fields (a-c) denoted in Figure 1. The nutation frequency observed at the central magnetic field, 347.29 mT, and those at the magnetic fields, 341.36 mT and 352.77 mT, were 32.72 MHz and 28.32 MHz, respectively, when the irradiated-microwave attenuation was 5dB. This finding is interpretable by considering a quartet spin state. The nutation frequencies for an $|S=3/2, M_S=-1/2\rangle \leftrightarrow |3/2, 1/2\rangle$ ESR transition in the quartet state and that for a $|3/2, -3/2\rangle \leftrightarrow |3/2, -1/2\rangle$ or $|3/2, 1/2\rangle \leftrightarrow |3/2, 3/2\rangle$ ESR transition are $2\omega_1$ and $3^{1/2}\omega_1$, respectively. The ratio of the observed nutation frequencies (32.72MHz : 28.32MHz) corresponds to that of the expected nutation frequencies for

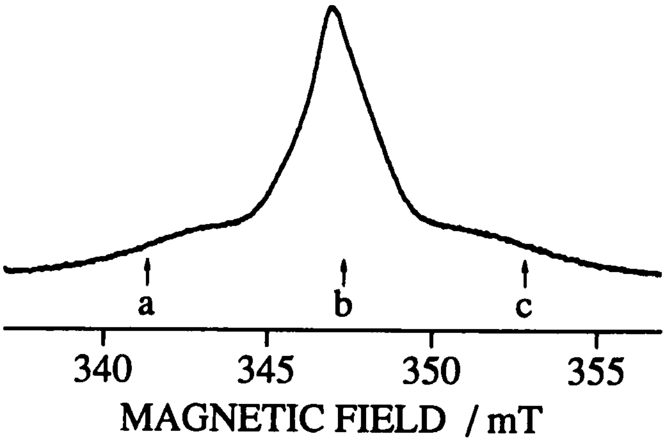


FIGURE 1. Echo-detected field swept ESR spectrum of **2**.

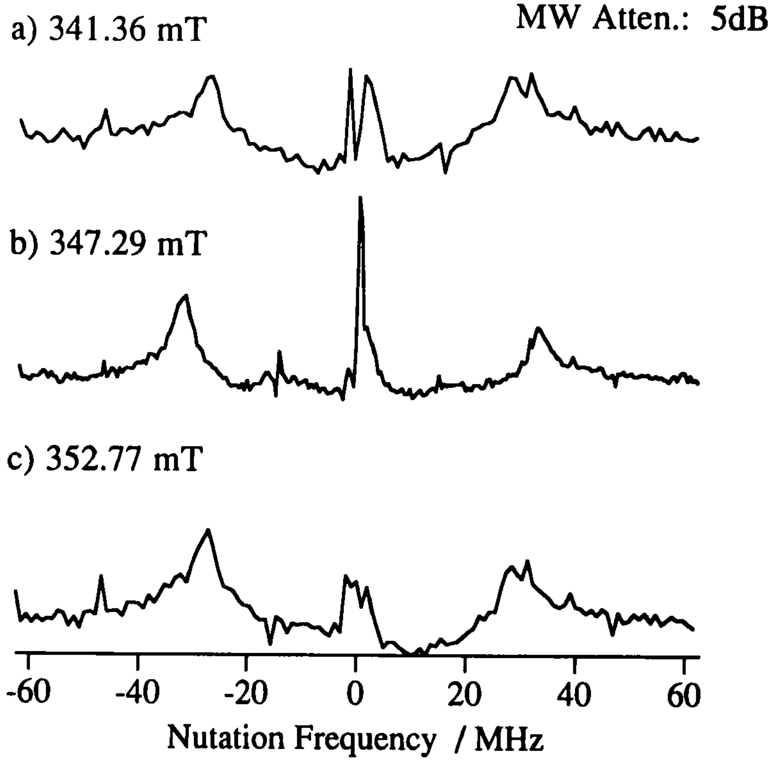


FIGURE 2. Observed nutation spectra of **2**.

the ESR transitions in the quartet spin state (2 : $3^{1/2}$), unequivocally identifying the spin state of **2** to be quartet.

The nutation spectra for **1** were observed at five magnetic fields. All the observed nutation frequencies indicated the same values which are nearly $2^{1/2}$ times larger than that for the doublet state of 1,1-diphenyl-2-picrylhydrazyl (DPPH) used as a standard reference. Equation (1) states that the nutation frequency for the ESR transition between doublet sublevels is $\omega_1$ and that for the $|1, -1\rangle \leftrightarrow |1, 0\rangle$ or $|1, 0\rangle \leftrightarrow |1, 1\rangle$ ESR transition in a triplet state is $2^{1/2}\omega_1$. The relationship between the observed nutation frequencies for **1** and DPPH, therefore, identifies the spin state of **1** to be triplet.

The microwave power ($\omega_1$) dependence of the nutation frequencies for **1**, **2**, and DPPH is summarized in Figure 3. The solid line stands for the nutation frequency for DPPH (S=1/2), the broken line the nutation frequency for **1** (S=1), and the dot-dashed

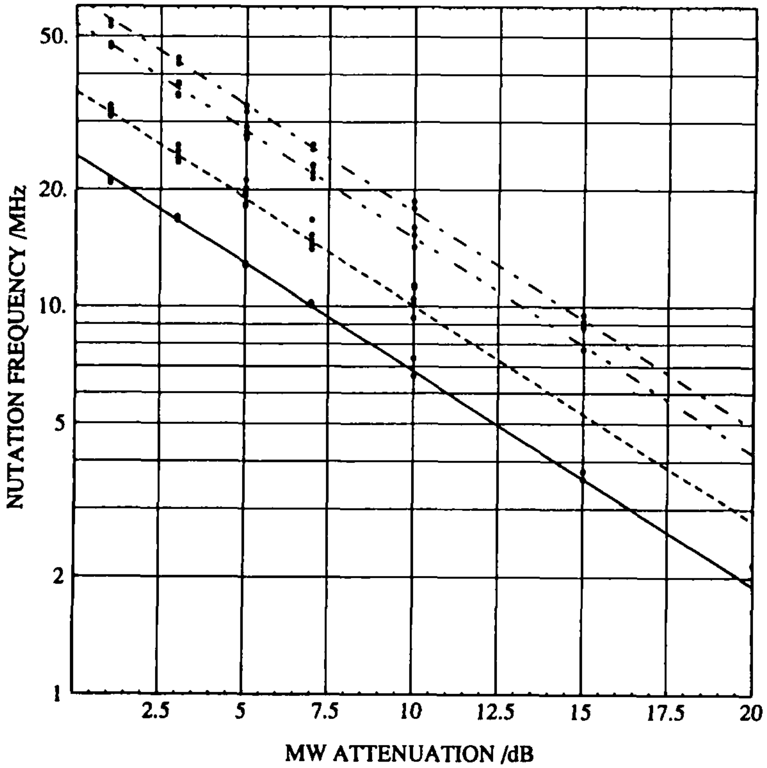


FIGURE 3. Microwave power dependence of the nutation frequencies for DPPH, **1**, and **2**. The solid line stands for DPPH(S=1/2), the broken line for **1** (S=1), and both the dot-dashed and the double dot -dashed lines for **2** (S=3/2), respectively.

and the double dot-dashed lines the nutation frequencies for **2** (S=3/2). The nutation frequencies clearly depend on the S and $M_S$ of the monitoring ESR transitions, indicating the usefulness of the ESTN spectroscopy for the identification and discrimination of spin multiplicities in the complex mixtures of high-spin assemblages.

The structures of these hyperbranched molecules are distorted because of their steric hindrance. In spite that the π-spin system is extremely twisted from a planar form, the ground-state spin multiplicities of the molecules are unaffected. This finding indicates that the delocalized π-spin system constructs a robust π-spin polarization network and that a very high-spin molecule with a dendmeric structure is possible by extending its π-spin network.

In conclusion, we have applied the ESTN spectroscopy to the hyperbranched π-aryl molecules in organic glasses in order to determine their spin multiplicities independently of a cw-ESR spectroscopy. The nutation frequencies for the molecules depended on the S and $M_S$ of the monitoring ESR transitions, allowing us to determine the spin multiplicities. The ESTN spectroscopy has especially great advantages for the identification and discrimination of spin multiplicities in the complex mixtures of high-spin assemblages. The present study shows that these can be done without making spectral simulation in randomly oriented ESR spectroscopy.

## ACKNOWLEDGMENTS

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