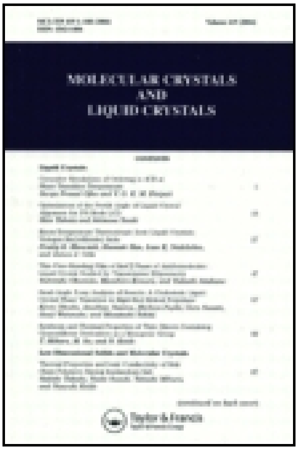

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2D-Electron Spin Transient Nutation (2D-ESTN) Study of a Stable High- Spin Carbene (S=3)

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2D-Electron Spin Transient Nutation (2D-ESTN) Study of a Stable High- Spin Carbene (S=3)

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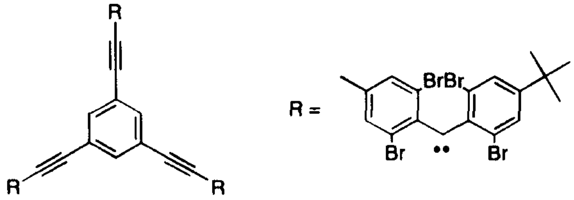
Stable high-spin polycarbene, polybrominated 1,3,5-tris[4-(phenylcarbeno)-phenylethynyl]benzene in a glass matrix was studied by Electron Spin Transient Nutation (ESTN) spectroscopy. 2D-ESTN spectra of the polycarbene were measured in order to identify a molecular spin multiplicity of the high-spin ground state. The observed nutation frequencies were assigned to those arising from the allowed ESR transitions of the septet ground state (S=3). It indicates that the high-spin state is generated by ferromagnetic interaction between stable bromo-substituted diphenylmethylenes (S=1) through a 2D topological spin coupling unit with C_3 symmetry, 1,3,5-tris(ethynyl)benzene. The observed fine-structure parameters of the septet state, $D = -0.040\ cm^{-1}$ and $|E| = 0.007\ cm^{-1}$, were well interpreted in terms of an intramolecular spin-spin interaction model. The observed small and negative D value was shown to arise from the C_3 symmetric molecular structure. The high-spin polycarbene has survived after annealing of the glass matrix. The stable triplet carbene unit is supposed to serve as a useful building block for extended super high-spin molecular systems and organic superparamagnets.

Keywords: transient nutation; pulsed ESR; high-spin carbene; intramolecular spin-spin interaction

INTRODUCTION

Organic molecular magnetic materials have been attracting continuous interest in the pure and applied sciences. We have been studying organic high-spin



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molecules using topological symmetry in a π-conjugation system and identifying molecular spin multiplicity of them using an electron spin transient nutation (ESTN) method[1-4] based on pulsed ESR spectroscopy. Topological nature in the π-conjugation system has been well-established in the field of purely organic magnetics so far. We designed a highly symmetric high-spin polycarbene, 1,3,5-tris[4-(4-*tert*-butyl-2,6-dibromophenylcarbeno)-3,5-dibromophenylethynyl]benzene **1**. The polybrominated diphenylmethylene unit is a persistent triplet carbene in solid[5] and is applicable as stable spin units. This paper presents spin characterization of the tricarbene **1** by ESR and ESTN spectroscopy applied to non-oriented systems[3,4]. Two-dimensional field-swept ESTN spectra of the polycarbene were measured in order to identify the molecular spin multiplicity of the high-spin ground state unequivocally. We also discuss the thermal stability and molecular and electronic structures of **1** based on the experimentally determined fine-structure parameters.

EXPERIMENTAL AND ANALYSIS

The tricarbene **1** was generated in a 2-methyltetrahydrofuran (2-MTHF) organic glass at liquid helium temperature by irradiation of a diazo precursor of **1** with a SAN-EI UVF-351S 300W high-pressure mercury lamp. X-band cw and pulsed ESR measurements were carried out on Bruker ESP300 and ESP380 spectrometers with a dielectric resonator and a 1kW traveling wave tube amplifier, respectively.

The electron spin transient nutation (ESTN) experiments were performed by monitoring the peak of a 2-pulse Hahn echo after a microwave excitation pulse with different pulse length (t_1). We constructed two-dimensional (2D) ESTN spectra by sweeping the static magnetic field. The nutation frequency (ω_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 ($\omega_l \ll \omega_D$ where ω_D is a fine structure coupling in units of frequency). $\omega_l(\approx\gamma B_l)$ corresponds to the strength of a microwave irradiation field.

RESULTS AND DISCUSSION

ESR and 2D-ESTN Spectra of the Tricarbene 1

Fig. 1 shows a fine-structure ESR spectrum of **1** observed at 2.6 K. The fine-structure ESR spectrum indicated asymmetrical broad lines in a wide range of magnetic field from 0.1 T to 0.6 T. Salient features of organic high-spin molecules apparently failed to show up in the observed spectrum. Canonical peaks dominate in the g≈2 region and key-peaks appearing in the wings away from g≈2 region are only vague.

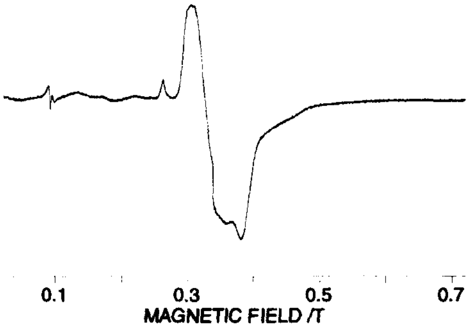

FIGURE 1 Fine-structure ESR spectrum of **1** observed at 2.6 K.

Fig. 2 shows the contour plot of field-swept 2D-ESTN spectra of **1** observed at 5K. On the right, an electron spin-echo detected ESR spectrum is given, which corresponds to the conventional fine-structure ESR spectrum in an integrated mode. Six typical slices of the nutation spectra in the range 200-350 mT are shown in Fig. 3. Three dominant peaks are discriminated at 22.0, 27.5, and 29.5 MHz which are denoted by a, b, and c, respectively. The observed ratio of 22.0:27.5:29.5 uniquely agrees well with the theoretical one of $\sqrt{6}:\sqrt{10}:2\sqrt{3}$ expected by Eq. (1) for M_S = 3, 2, 1 (S=3). These

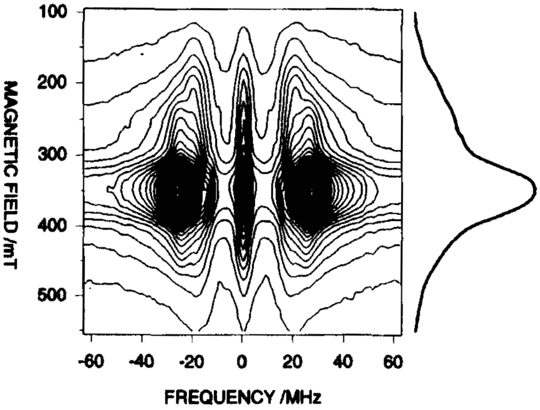

FIGURE 2 Contour plot of field-swept 2D-ESTN spectra of **1**.

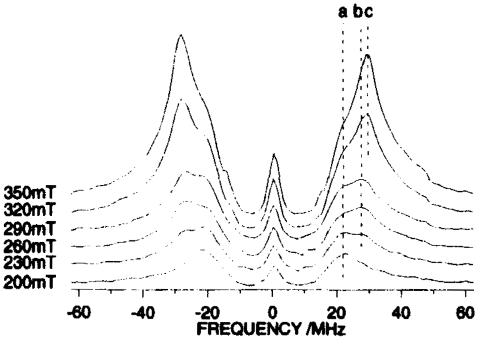

FIGURE 3 Typical slices of the 2D-ESTN spectra of **1**.

theoretical frequency values correspond straightforwardly to the allowed ESR transitions for septet states, unequivocally identifying that the observed fine-structure spectrum is due to a spin-septet state. Up to 90 K from 2.6 K, no other nutation peaks attributable to lower spin multiplet states were observed, showing the septet state to be the ground state with the excited low-spin states located above 300 *cm*$^{-1}$.

Thermal Stability of 1

A nutation peak arising from any doublet species of by-products was not detected in the whole ESTN measurement, showing a remarkable chemical stability of the tricarbene. A thermal stability of **1** also manifested itself during the annealing process shown below. A significant change in the shape of ESR signal was observed when the matrix temperature was raised above 140K and kept at the temperature for 15 min. The ESR spectrum observed after the annealing process is shown in Fig. 4. New fine-structure signals were irreversible with temperature, and they were characteristic of the small fine-structure constants. They were also identified to originate in a septet ground state by 2D-ESTN spectroscopy. This is in a contrast with that observed in a ground state septet carbene 1,3,5-tris[4-(phenylcarbeno)phenyl]benzene, which

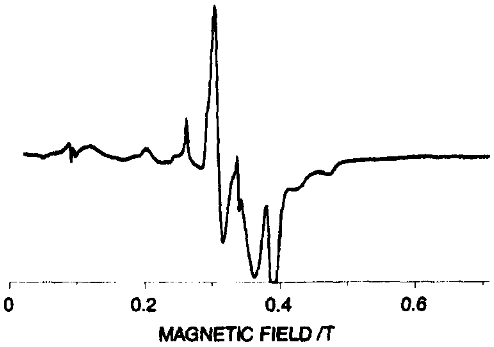

FIGURE 4 Fine-structure ESR spectrum of **1** observed at 3.1 K after annealing.

has been shown to be stable only 180 K in the crystalline state[6,7] and up to 85[6] and 50 K[8] in rigid glasses. It is noted that the polybrominated diphenylcarbene (S=1) is shown to be stable even up to 160 K in a glassy solution. Significant decrease in the thermal stability on going from the prototype monomeric carbene to the tricarbene must result from the ethynyl groups at the *para* positions, since it has been suggested that sterically congested diarylcarbenes are forced to decay also by undergoing reactions at the *para* positions of the aromatic rings, where unpaired spins can be delocalized.

Molecular and Electronic Structures of the Tricarbene

Fine-structure parameters of **1** were determined by a spectral simulation for the spectrum after annealing. The spectral simulation was numerically carried out using the eigenfield method.[9,10] Best-fit spin-Hamiltonian parameters obtained are summarized in Table I. The experimentally obtained fine-structure parameters for **1** before annealing were close to those after annealing but erroneous because of the line broadening. The broadening is presumably due to statistical fluctuation of molecular conformations of the diphenylcarbenes around the cylindrical triple-bond axis of the ethynyl group.

TABLE I Best-fit spin-Hamiltonian parameters for **1** after annealing.

S	3
g	2.003
D	-0.040 cm^{-1}
$\|E\|$	0.007 cm^{-1}

A semiempirical calculation for the fine-structure parameters was made in order to discuss molecular and electronic structures of **1**. The calculation was based on the assumption that the septet state is composed of intramolecular spin-spin interactions among the three triplet spin units, 4-(4-*tert*-butyl-2,6-dibromophenylcarbeno)-3,5-dibromophenylethynyl, denoted by fine-structure tensors $\underline{\underline{D}}_i$ (i =1, 2, 3). Then, the fine-structure tensor $\underline{\underline{D}}_{S=3}$ for the septet state is given by tensorial addition of the three $\underline{\underline{D}}_i$'s as well as interaction tensors $\underline{\underline{D}}_{jk}$ as

$$\begin{aligned}\underline{\underline{D}}_{S=3} &= \frac{1}{15}\left(\underline{\underline{D}}_1 + \underline{\underline{D}}_2 + \underline{\underline{D}}_3\right) + \frac{1}{15}\left(\underline{\underline{D}}_{12} + \underline{\underline{D}}_{23} + \underline{\underline{D}}_{31}\right) \\ &\approx \frac{1}{15}\left(\underline{\underline{D}}_1 + \underline{\underline{D}}_2 + \underline{\underline{D}}_3\right) \qquad (2)\end{aligned}$$

where $\underline{\underline{D}}_{jk}$ stands for the interaction between the two of three triplet spins and $\underline{\underline{D}}_{jk} \ll \underline{\underline{D}}_i$ is established since one-center n-π spin-spin interactions dominate in the triplet carbene units[6,7,11]. In Eq. (2) unitary transformations from local coordinate systems describing $\underline{\underline{D}}_i$ or $\underline{\underline{D}}_{jk}$ to a coordinate system spanned in the molecular frame of **1** are abbreviated. Empirical D and E values for the triplet tensor $\underline{\underline{D}}_i$ were evaluated from a fine structure spectrum of 4-(4-*tert*-butyl-2,6-dibromophenylcarbeno)-3,5-dibromophenylacetylene observed in a 2-MTHF glass. The calculation predicts a negative D value and vanishing E value for an axially C_3-symmetric structure and a positive D value and a large E value for a non-axially symmetric one. The Z axis corresponding to the largest principal value of the $\underline{\underline{D}}_{S=3}$ tensor is perpendicular to the molecular plane of **1** for the axially symmetric structure. On the other hand, the Z axis lies in the plane for the non-axially symmetric one. The molecular structure of **1** with the negative D value is, therefore, expected to be nearly C_3 symmetric. The non-vanishing E value of **1** may be due to subtle departure from the C_3 symmetry of the molecular structure by any distortion of the spin coupling unit, 1,3,5-tris(ethynyl)phenyl.

CONCLUSIONS

We have demonstrated using the field-swept 2D-ESTN spectroscopy that the tricarbene, where the persistent triplet carbenes were linked through ethynylphenyl π-cross conjugated frameworks, is in the spin-septet ground state and stable up to 140 K in a 2M-THF glass. It was indicated that the field-swept 2D-ESTN spectroscopy provides a spectroscopic resolution enhancement for unresolved fine-structure spectra characteristic of large spin quantum numbers and small fine-structure constants due to the high geometrical symmetry. The observed fine-structure parameters of the septet state were well interpreted in terms of the intramolecular spin-spin interaction model. The small and negative D value observed was shown to arise from the nearly C_3 symmetric molecular structure.

Acknowledgments

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