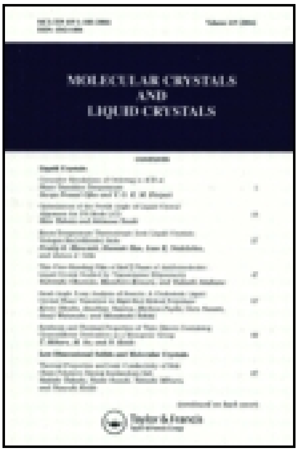

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Molecular and Electronic Spin Structures of High-Spin Polyphenylene-Based Oligonitrenes with High Symmetry; A Semiempirical Approach to Fine-Structure Tensors

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Molecular and Electronic Spin Structures of High-Spin Polyphenylene-Based Oligonitrenes with High Symmetry; A Semiempirical Approach to Fine-Structure Tensors

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Abstract: We have designed and synthesized highly symmetric polyphenylene-based oligonitrenes with quintet and septet spin multiplicity in their ground state. Their randomly oriented fine-structure ESR spectra were observed and analyzed by hybrid eigenfield method to obtain the accurate spin Hamiltonian parameters. From the semiempirical calculations of the fine-structure tensors for the oligonitrenes, their most probable molecular structures were determined and the interacting term of their fine-structure tensors were estimated to be negligible.

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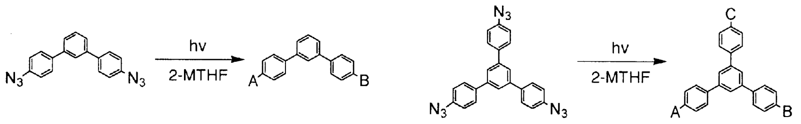
Keywords high-spin oligonitrene; polyphenylene; fine-structure calculation; molecular structure; ESR; hybrid eigenfield method.

INTRODUCTION

In recent years, super high-spin molecular systems have been materials challenges for synthetic chemistry[1]. Molecular design employed in high-spin chemistry is based on the use of the topological degeneracy of π-nonbonding MOs(π-NBMOs) which is underlain by dynamic π-spin polarization in the conjugated hydrocarbon[2]. The degree of the topological degeneracy is unlimited in contrast with group-theoretical orbital degeneracy. In high-spin chemistry, the electronic spin structures of high-spin molecular systems governed by the topological degeneracy have not been studied in group-theoretical terms. This study deals with highly symmetric high-spin molecular π-systems and interpretation of their electronic spin and molecular structures in terms of semiempirical calculations for their fine-structure tensors.

EXPERIMENTAL

The oligonitrenes shown in Figure 1 were generated by UV photolysis of corresponding azide precursors in 2-methyltetrahydrofuran (2-MTHF) rigid glasses at cryogenic temperatures. The detailed syntheses of the oligoazide precursors will be published elsewhere. ESR spectra were recorded on a Bruker ESP 300 X-band spectrometer equipped with an Oxford helium-gas flow temperature controller. The 2-MTHF rigid glass samples were prepared with freeze-pump-thaw method. The concentrations of the samples were ca. 10^{-4} M. The temperature



1 A = N_3 / B = N:
2 A = B = N_3

3 A = B = N_3 / C = N: **4a** A = B = N: / C = N_3
4b B = C = N: / A = N_3 **4c** C = A = N: / B = N_3
5 A = B = C = N:

FIGURE 1 The generation of oligonitrenes by UV photolysis.

dependencies of ESR signal intensities were measured from 3.0 K to 50.1 K.

RESULTS AND DISCUSSION

ESR Spectra of Oligonitrenes

Randomly oriented fine-structure ESR spectra of **2** and **5** were obtained by UV photolysis of the corresponding oligoazide precursor. The temperature dependencies of the ESR signal intensities showed that dinitrene **2** and trinitrene **5** are spin-quintet and septet in the ground state, respectively, demonstrating that robust π-spin polarizations are taking place in both oligonitrenes. The randomly oriented fine-structure ESR spectra were simulated by hybrid eigenfield method to obtain spin Hamiltonian parameters with high accuracy[3]. In Table 1 are summarized the spin Hamiltonian parameters.

Semiempirical Calculations of Fine-Structure Tensors

Molecular structural determination; neglecting the interacting term

In nitrene systems, the fine-structure terms are mainly due to one-center *n*-π spin-spin interactions on the nitrogen atoms. Thus, the spin Hamiltonian for the nitrene systems is described as shown below with neglecting the interacting term $H_{i,j}$;

TABLE 1 Observed and calculated spin Hamiltonian parameters of the high-spin oligonitrenes ($g = 2.003$).

Nitrene		D / cm^{-1}		E / cm^{-1}	
		Observed	Calculated	Observed	Calculated
1	($S = 1$)	0.9290	N/A	0.0016	N/A
2	($S = 2$)	0.2009	+ 0.2008	0.0358	+ 0.0358
3	($S = 1$)	0.9312	N/A	0.0012	N/A
4a	($S = 2$)	0.2123	+ 0.2123	0.0326	+ 0.0326
4b	($S = 2$)	0.1942	+ 0.1942	0.0385	+ 0.0385
4c	($S = 2$)	0.1751	+ 0.1751	0.0448	+ 0.0448
5	($S = 3$)	0.0912	- 0.0912	0.0039	- 0.0039

$$\mathrm{H}_{S=n} = \sum_i \mathrm{H}_i + \sum_{i,j} \mathrm{H}_{i,j} \approx \sum_i \mathrm{H}_i$$

where $\mathrm{H}_{S=n}$ and H_i are the spin Hamiltonian of the oligonitrene and that of the mononitrene which have the similar molecular frame, respectively. The directions of the C-N bonds of phenyl nitrenes and the Z axes of the fine-structure tensors are assumed to be colinear. The local tensors of the constituent mononitrenes are transformed to those in the molecular principal-axis coordinate system by using Euler angles (θ, ϕ, ψ). Thus, the fine-structure tensors of the oligonitrenes can be expressed as functions of molecular structural parameters

$$\mathbf{D}_{S=n} = f(\mathbf{D}_i, \theta, \phi, \psi).$$

In the case of dinitrene **2** and trinitrene **5**, considering the projection factors of the spin component, $\mathbf{D}_{S=2}$ and $\mathbf{D}_{S=3}$ are calculated as follows, respectively;

$$\mathbf{D}_{S=2} = \frac{1}{6}\mathbf{D}_A + \frac{1}{6}\mathbf{D}_B\ ,\quad \mathbf{D}_{S=3} = \frac{1}{15}\mathbf{D}_A + \frac{1}{15}\mathbf{D}_B + \frac{1}{15}\mathbf{D}_C$$

where $\mathbf{D}_A$, $\mathbf{D}_B$ and $\mathbf{D}_C$ correspond to the local fine-structure tensors of the mononitrenes. Figure 2(a) and 2(b) show the best fitted molecular structure for dinitrene **2** and trinitrene **5**, respectively. The calculated fine-structure parameters of the corresponding molecular structure satisfactorily reproduce the observed fine-structure parameters within

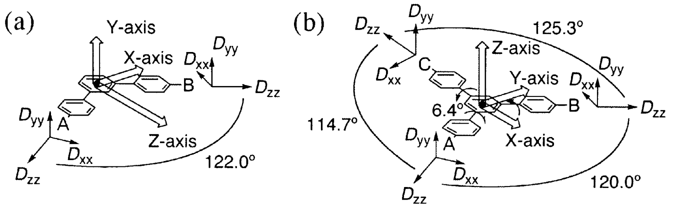


FIGURE 2 The probable molecular structures and theoretically obtained principal axes of (a) dinitrene **2** and (b) trinitrene **5**.

the error of ± 0.02 %.

Estimation of interacting fine-structure tensors

The spin Hamiltonian of the oligonitrene system is written as

$$\mathrm{H}_{S=n} = \sum_{i} \mathrm{H}_{i} + \sum_{i,j} \mathrm{H}_{i,j}$$

where the interacting terms between the mononitrene moieties are considered. The principal values of the $\mathbf{D}_{S=n}$ and $\mathbf{D}_i$ tensors are experimentally obtained by the spectral simulation. Thus, the interacting terms of the fine-structure tensor can be expressed as a function of molecular structural parameters

$$\mathbf{D}_{ij} = f(\mathbf{D}_{S=n}, \mathbf{D}_{i}, \theta, \phi, \psi).$$

In the case of dinitrene **2**, considering the projection factors of the spin component, $\mathbf{D}_{S=2}$ is calculated as

$$\mathbf{D}_{S=2} = \frac{1}{6}\mathbf{D}_{A} + \frac{1}{6}\mathbf{D}_{B} + \frac{1}{3}\mathbf{D}_{AB}$$

where $\mathbf{D}_{AB}$ is the interacting tensor between the mononitrene local fine-structure tensors. The calculation reveals that the interacting term is estimated to be less than 10% (0.02 cm^{-1}) of the principal values for the variation of $\Delta 2\theta = \pm 1°$, where 2θ stands for the angle between the Z axes of the local tensors. Therefore, the procedure of determining the molecular structure with neglecting the interacting term is still reliable for oligonitrene systems.

SUMMARY

We have synthesized polyphenylene-based oligonitrenes and analyzed their randomly oriented fine-structure ESR spectra. The dinitrene **2** and trinitrene **5** has a quintet and septet ground state, respectively. From the exact numerical spectral simulations, the spin Hamiltonian parameters were determined with high accuracy. From the semiempirical calculations for the fine-structure tensors, their molecular structures were determined and the interacting term between the mononitrene moieties was estimated less than 10% of the fine-structure parameters in the present nitrene system.

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