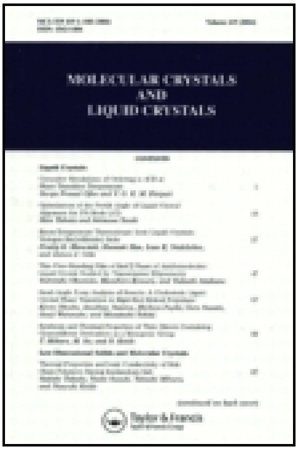

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Electronic and Molecular Structures of Quintet Bisnitrenes as Studied by Fine-Structure ESR Spectra from Random Orientation: All the Documented ZFS Constants Correct?

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ELECTRONIC AND MOLECULAR STRUCTURES OF QUINTET BISNITRENES AS STUDIED BY FINE-STRUCTURE ESR SPECTRA FROM RANDOM ORIENTATION:
ALL THE DOCUMENTED ZFS CONSTANTS CORRECT?

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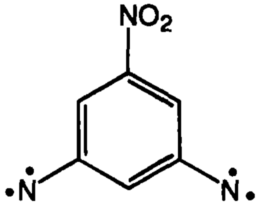
Abstract A quintet ground-state bisnitrene, 1,3-dinitreno-5-nitrobenzene, was studied by randomly oriented ESR spectroscopy as part of our project to study purely organic magnetism and supramolecular functionality expected for high spin systems. An observed ESR spectrum of the bisnitrene was interpreted using $S=2$, $g=2.003$, $|D| = 0.224$ cm^{-1}, and $|E| = 0.038$ cm^{-1}. The determined fine-structure parameter D and E values are in accord with our semiempirical treatment for the quintet state in terms of the fine-structure tensor of the triplet state of *p*-nitrophenylnitrene. In this work, we emphasize that all the documented fine-structure parameters D and E for quintet bisnitrenes do not reproduce the corresponding observed fine-structure ESR spectra from random orientation.

INTRODUCTION

In the rapidly developing research field of organic molecule-based magnetism and spin chemistry, the quest for stable high-spin building blocks with robust π-spin polarization has been an important issue. The robust spin polarization is of essential importance for the underlying mechanism in both inter- and intra-molecular spin alignment of organic systems. The robust spin polarization features in high-spin nitrene and carbene, which are suitable as models for building spin blocks or sites in intriguing organic magnetic materials: nitrene and carbene are of the isoelectronic structure. Nevertheless, in general both are regarded as highly reactive intermediates. While room-temperature stable triplet carbene has emerged very recently,[1,2] it has been known that phenyl mononitrene and its substituted mononitrenes in the triplet ground state are stable in solids. Recently we have found stable quintet bisnitrenes at room temperature in crystals. In the course of the fine-structure ESR analyses we have noticed that neither the documented fine-structure parameters D and E values for quintet bisnitrenes reproduce the documented fine-structure ESR spectra from random orientation nor the reasonable spectral assignment of fine-structure transitions has been described in the documents. In addition, all the documented D and E values have not been able to expound electronic structures of the reported quintet bisnitrenes in reference to their molecular structures. As part of our project for purely organic magnetism and supramolecular functionality expected for high spin systems, we have synthesized a typical nitro-substituted bisnitrene **1**, 1,3-dinitreno-5-nitrobenzene (see below), in its quintet ground state and attempted to derive the fine-structure parameters from the observed ESR spectra from random orientation, serving for the purposes of the establishment of ESR analyses for quintet states with relatively large D values featuring in a variety of high spin nitrenes and nitrene clusters.



1,3-dinitreno-5-nitrobenzene **1**

EXPERIMENTAL

The randomly oriented samples were prepared by quickly evaporating the solution containing the corresponding azide precursor of the bisnitrene and the *p*-dinitrobenzene which was used as a diamagnetic matrix and by grinding the obtained crystalline. The bisnitrene **1** was generated at 77K by the irradiation of the azide precursor with a SAN-EI UVF-351S 300W high-pressure mercury lamp. The ESR measurements were carried out on an X-band Bruker ESP 300 spectrometer equipped with an Oxford helium gas flow temperature controller ESR 910.

RESULTS AND DISCUSSION

ESR spectrum of the bisnitrene

Figure 1(a) shows an observed fine-structure ESR spectrum of the bisnitrene **1** from random orientation. A strong ESR signal was observed at nearby 300mT which is characteristic of the documented quintet bisnitrenes' ESR spectra.[3,4,5,6,7] In addition, several ESR signals were observed in a wide range from 80mT to 800mT.

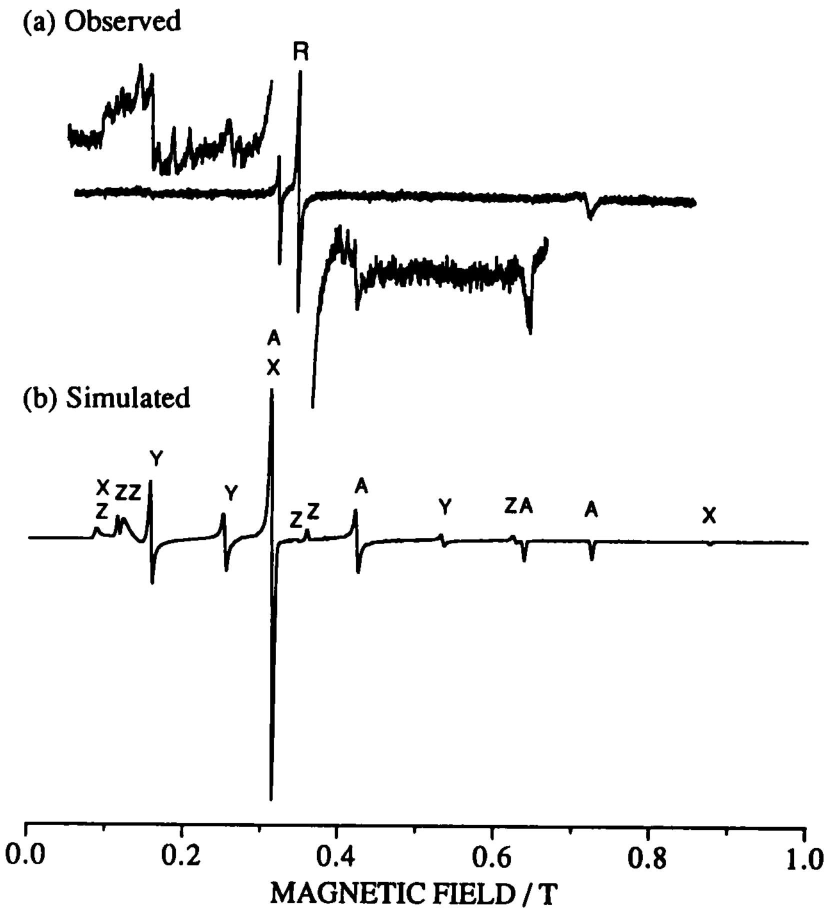


FIGURE 1 ESR spectrum of **1** from random orientation. R in (a) denotes a signal from a doublet by-product.

Temperature dependence of the ESR transition measured at 314mT was examined up to 180K. A resonance field of the monitored ESR transition was observed to be shifted to lower magnetic field (310mT) just before a decomposition of the bisnitrene. The signal intensity increased while cooling. This temperature behavior of the intensity is the same as that of a radical impurity (an internal reference) observed at 339mT, indicating that the detected high-spin state lie in the ground state. Up to the decomposition temperature of the bisnitrene, any ESR signals from other spin states except for the radical impurity were not observed. Excited spin states may be fairly far from the ground state larger than 300 cm^{-1}.

In order to determine fine-structure parameters of the bisnitrene, D and E values, we performed a spectral simulation. The simulation was carried out by numerically diagonalizing the following spin Hamiltonian consisting of electron Zeeman and fine-structure terms:

$$H = \beta_e \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}.$$

The resonance field was calculated by a numerical diagonalization based on the eigenfield method[8,9,10,11] instead of diagonalizing the energy spin Hamiltonian. The eigenfield equation was solved by the QZ algorithm of Moler and Stewart.[12] This subprogram was supplied from Netlib of Oak Ridge National Laboratory. The transition probability was calculated using eigenvectors obtained by the numerical diagonalization of the energy spin Hamiltonian with the resonance field calculated by the eigenfield method. The simulated ESR spectrum using the spin Hamiltonian parameters in Table I is shown in Figure 1(b), being in accord with the observed spectrum in Figure 1(a). Figure 1(b) includes the signal assignments (X, Y, Z, and A) to canonical orientations. 'A' stands for an extra peak arising from an off- axis stationary angle in the principal axis frame of the fine structure tensor. A few ESR signals in Figure 1 were not assigned in the present spectral simulation. This implies the existence of the conformers with fine-structure parameters that are slightly

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

	1
S	2
ν_{MW}	9.502 GHz
g	2.003
$\lvert D \rvert$	0.224 cm^{-1}
$\lvert E \rvert$	0.038 cm^{-1}
$\Delta B_{1/2}$	4 mT

different from those given in Table I. It should be noted that a small difference in fine-structure parameters affects the resonance fields because of the large fine-structure parameter.

Fine-structure parameter of the bisnitrene

The fine-structure parameters were semiempirically discussed based on those of the triplet state of a mononitrene. Assuming that one-center spin-spin interactions between π-spins in π orbitals and n-spins in nonbonding orbitals on the monovalent nitrene sites are predominant, one can construct a desired fine-structure tensor of the bisnitrene from two local fine-structure tensors of both the nitrene sites. The resultant fine-structure tensor for the quintet state is, therefore, given by

$$D_{total} = 1/S(2S-1) \sum U_i D_i U_i^{-1},$$

where D_i is the fine-structure tensor of the local mononitrene site i, and U_i a unitary matrix which transforms the fine-structure frame of the local nitrene site to the molecular frame.[13] We semiempirically calculated the fine-structure tensor of the bisnitrene 1 using the fine-structure tensor of triplet state of *p*-nitrophenylnitrene

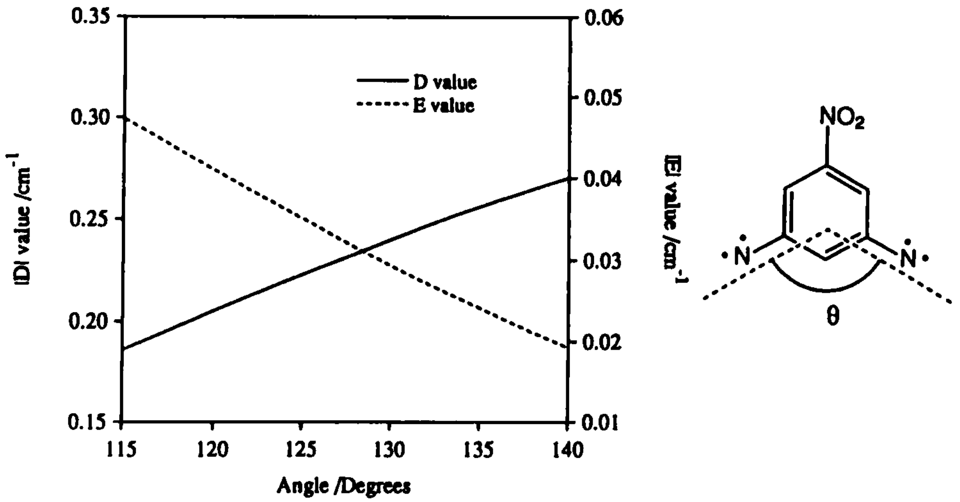


FIGURE 2 Semiempirically obtained fine-structure parameter D and E values versus the angle θ between two C-N bonds.

documented by Hebden and McDowell,[14] and obtained the D and E values for the bisnitrene 1 from the calculated fine-structure tensor. The obtained D and E values are shown as a function of the angle θ between carbon-nitrogen bonds in Figure 2. When the angle is about 124 degrees, the calculated fine-structure parameters are close to the experimentally determined ones, $|D| = 0.224\ cm^{-1}$ and $|E| = 0.038 cm^{-1}$. The determined fine-structure parameters are consistent with an expected molecular structure for **1** in the ground state that the benzene ring is slightly distorted by asymmetric substitution, indicating that such a simple assumption that the one-center spin-spin interaction at the nitrene sites is predominant in the quintet ground state is workable for the understanding of the electronic spin structure of high spin nitrenes.

All the reported fine-structure parameters not well-documented

The previously documented fine-structure parameters, D values, for various bisnitrenes are about $0.16 cm^{-1}$. The determined D value for the present bisnitrene **1** is quite different from the documented D values. Nevertheless, the documented ESR spectra of the bisnitrenes are similar with the our present spectrum. In the previous documentation's without a spectral simulation, all the analyses of the ESR spectra were based on a perturbation approach under the assumption that the ESR transition at nearby 800 mT was the highest Z transition. The present spectral simulation, however, indicated that the transition at nearby 800 mT should be assigned to an X transition. The highest Z transition should appear at about 1.1T. The misunderstanding of the assignments in the ESR analyses causes the fine-structure parameters to be underestimated to a large extent. In addition, the strongest ESR transition at nearby 300 mT is not be reproduced when the D value is about $0.16\ cm^{-1}$. All the D values reported so far are not well-documented. Such underestimated D values never provide reasonable interpretations of electronic and molecular structures of bisnitrenes in the quintet ground state.

CONCLUSION

The quintet state of 1,3-dinitreneo-5-nitrobenzene was studied using random orientation ESR spectroscopy. The random orientation ESR spectrum indicates that the fine-structure parameter D and E values are 0.224 cm^{-1} and 0.038 cm^{-1}, respectively. The present fine-structure parameters are consistent with those calculated from the semiempirical treatment of fine-structure tensors. In addition, we emphasize that all the documented fine-structure parameters D and E for quintet bisnitrenes do not reproduce the corresponding observed fine-structure ESR spectra from random orientation. All the reported parameter D values are underestimated. It is pointed out that this misunderstanding in all the previous reports arises from the misassignments of fine-structure transitions.

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