

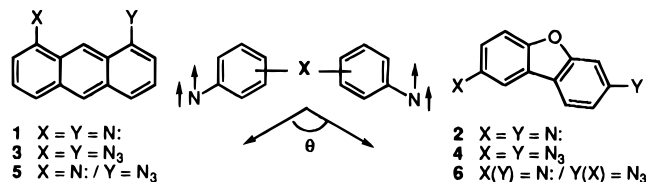
Rigid Geometry Bis(arylnitrenes) as Definitive Tests for Angular Dependence of Zero-Field Splitting in High Spin Molecules

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As part of model studies aimed at the development of new magnetic materials, we¹ and others^{2,3} have carried out a number of cryogenic electron spin resonance (ESR) spectroscopic and ground state spin multiplicity studies of dinitrenes with varying structural features. The complexity of rigid, randomly oriented ESR spectra for quintet species with large zero field splitting (zfs) has previously rendered difficult the assignment of specific features in the spectra to specific conformations in cases where bond rotation is possible.⁴ Recent advances allow the simulation of quintet ESR spectral lineshapes in randomly oriented media, rendering spectral assignments rather easier. It is thus possible in principle to make *a priori* predictions about ESR spectral appearance as a function of molecular structure in a quintet molecule that is composed of interacting triplet sites, by using the classic paper of Itoh⁵ which models ground state multiplicity and zfs as a function of the tensor interaction between the triplet sites. To date, most high-spin ground state, non-disjoint quintet species to which Itoh's model may be applied been conformationally flexible, leading to uncertain application of the model. Also, all non-disjoint dinitrenes studied to date have had triplet interaction angles of ca. 120°,⁶ hence by Itoh's model it is perhaps not surprising all have shown ESR spectra of great similarity. In this paper, we describe what we believe to be the first rigorous tests of the Itoh model that use geometrically inflexible conjugated quintet molecules.



Dinitrenes **1** and **2** have well-determined vector interaction angles between their C–N bond angles of ca. 0° and 153° ± 3° based upon computational geometries optimized by force field methods.⁷ These angles are considerably different from the 120° angles in previously studied^{1–3} non-disjoint dinitrenes that are based completely on *m*-phenylene, ethylenic, and acetylenic units. Both **1** and **2** are non-disjoint by the Borden–Davidson criterion⁸ and expected^{1,2,6} to have high spin quintet ground states. Semiempirical AM1-CI computations^{9,10} confirm this qualitative prediction, finding the quintet to triplet energy gaps ΔE_(Q–T) to be 3.6 and 2.3 kcal/mol for **1** and **2**, respectively.

(1) Minato, M.; Lahti, P. M. *J. Phys. Org. Chem.* **1991**, 4, 459. Ling, C.; Minato, M.; Lahti, P. M.; van Willigen, H. *J. Am. Chem. Soc.* **1992**, 114, 9959. Minato, M.; Lahti, P. M. *J. Am. Chem. Soc.* **1993**, 115, 4532. Ling, C.; Lahti, P. M. *Chem. Lett.* **1993**, 769–772. Ichimura, A. S.; Lahti, P. M. *Mol. Cryst. Liq. Cryst.* **1993**, 233, 33. Minato, M.; Lahti, P. M. *J. Phys. Org. Chem.* **1993**, 6, 483. Ling, C.; Lahti, P. M. *J. Am. Chem. Soc.* **1994**, 116, 8784. Minato, M.; Lahti, P. M. *J. Phys. Org. Chem.* **1994**, 5, 495. Ling, C.; Lahti, P. M. *Chem. Lett.* **1994**, 1357, 2447. Lahti, P. M.; Minato, M.; Ling, C. *Mol. Cryst. Liq. Cryst.* **1995**, 271, 147. Ichimura, A. S.; Sato, K.; Kinoshita, T.; Takui, T.; Itoh, K.; Lahti, P. M. *Mol. Cryst. Liq. Cryst.* **1995**, 272, 57.

(2) Iwamura, H.; Murata, S. *Mol. Cryst. Liq. Cryst.* **1989**, 176, 33. Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, 113, 5547. Tukada, H.; Mutai, K.; Iwamura, H. *Chem. Comm.* **1987**, 1159. Sasaki, S.; Iwamura, H. *Chem. Lett.* **1992**, 1759. Matsumoto, T.; Ishida, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, 114, 9952. Iwamura, H. *Pure Appl. Chem.* **1993**, 65, 57. Doi, T.; Ichimura, A. S.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, 115, 8928.

Diazide precursors **3** and **4** were synthesized¹¹ by adaptation of standard methodologies and were photolyzed for 5 min each through Pyrex at ≤ 77 K in 2-methyltetrahydrofuran (MTHF) frozen solutions. The 77 K ESR spectra obtained at 9.3 GHz under these conditions are shown in Figure 1. The spectra are different from one another, and both are quite different from typical spectra previously observed for non-disjoint dinitrenes.

Quintet dinitrene zfs values have previously often been assigned by methods similar to that first used by Wasserman *et al.*,¹² since high-spin randomly oriented spectral simulation methods were unavailable for systems with large zfs. Recently, this method has been shown to be inadequate to explain all observed lines. Indeed, quintet spectral lineshapes for non-disjoint dinitrenes observed previously to the present study may be well simulated using the eigenfield method¹³ and found to correspond to |D_q/hc| ≈ 0.23 cm⁻¹. Using Itoh's model,⁵ one may predict quintet zfs parameters for **1** and **2** as a comparison. The zfs parameters for triplet arylmononitrene **5** are estimated to be |D_t/hc| = 0.664 cm⁻¹ and |E_t/hc| ≤ 0.002 cm⁻¹; azide **4** gives rise to two mononitrenes **6**, with |D_t/hc| = 0.908 and 1.004 cm⁻¹.¹⁴ For a quintet state made up of weakly interacting triplet mononitrene spin sites a and b, the quintet zfs tensor $\hat{D}_{S=2}$ can be approximately expressed by eq 1

$$\hat{D}_{S=2} \approx \frac{1}{6}(\hat{D}_{S=1}^a + \hat{D}_{S=1}^b) \quad (1)$$

$$\hat{D}_{S=2} = \begin{bmatrix} \frac{1}{3}(-\frac{D_t}{3} + E_t) & & \\ & \frac{1}{3}(-(D_t + E_t)\sin^2 \theta + \frac{2}{3}D_t) & \\ & & \frac{1}{3}((D_t + E_t)\sin^2 \theta - (\frac{D_t}{3} + E_t)) \end{bmatrix} \quad (2)$$

$$\text{OR}$$

$$\hat{D}_{S=2} = \begin{bmatrix} D_x^{S=2} & & \\ & D_y^{S=2} & \\ & & D_z^{S=2} \end{bmatrix}$$

where $\hat{D}_{S=1}^a$ and $\hat{D}_{S=1}^b$ are the zfs tensors for the triplet spin sites. If one assigns directional vectors to the triplet spin sites with an intervector angle θ between them, and the spin sites are the same, one may rewrite eq 1 in terms of the triplet zfs parameters $D_t = |D_t/hc|$ and $E_t = |E_t/hc|$ to obtain the quintet zfs tensor elements in eq 2. One may then use the standard relationships $D = 1.5D_z$ and $E = 0.5(D_x - D_y)$ to obtain the quintet zfs parameters |D_q/hc| and |E_q/hc| as functions of the

(3) Ohana, T.; Kaise, M.; Yabe, A. *Chem. Lett.* **1992**, 1397. Ohana, T.; Kaise, M.; Nimura, S.; Kikuchi, O.; Yabe, A. *Chem. Lett.* **1993**, 765. Nimura, S.; Kikuchi, O.; Ohana, T.; Yabe, A.; Maise, M. *Chem. Lett.* **1993**, 837.

(4) Ling, C.; Lahti, P. M. *J. Am. Chem. Soc.* **1994**, 116, 8784.

(5) Itoh, K. *Pure Appl. Chem.* **1978**, 50, 1251.

(6) Lahti, P. M.; Minato, M.; Ling, C. *Mol. Cryst. Liq. Cryst.* **1995**, 271, 147.

(7) Optimizations were carried out using the MOPAC93 program (Fujitsu Corporation) based upon the program of Stewart, J. J. P. *QCPE, Program 455* **1989**.

(8) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, 99, 4587.

(9) The AM1 methodology is described in the following: Dewar, M. J. S.; Zoebisch, E. G.; Healey, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1987**, 107, 3902.

(10) Details of the semiempirical molecular orbital computation of state energy gaps are given in the following: Lahti, P. M.; Ichimura, A. S. *Mol. Cryst. Liq. Cryst.* **1989**, 176, 125. Lahti, P. M.; Ichimura, A. S. *J. Org. Chem.* **1991**, 56, 3030.

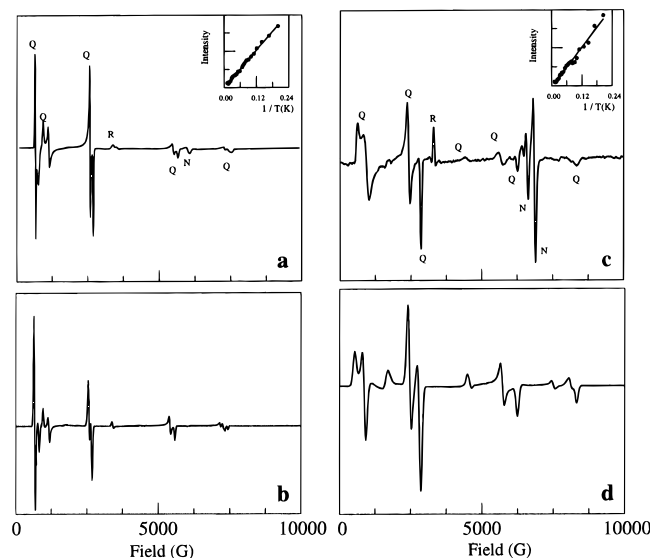


Figure 1. Spectra from 77 K photolysis of **3** and **4** in MTHF for 5 min, curves a and c, respectively. Spectrometer frequencies for curves a and c were 9618.9 and 9342.4 MHz, respectively. Spectral range is 100–9900 G. Q = quintet, R = radical, N = mononitrene. Spectral simulations over the same range by the method of ref 15 are given in curves b and d, using parameters given in the text. The insets are plots of the intensities of the spectral lines in the 2000 G region versus reciprocal absolute temperature for curves a and c, respectively.

relative angle (θ) of orientation between the C–N bonds of the interacting triplet sites. Application of eq 2 to dinitrenes **1** and **2** leads to predictions of $|D_q/hc| = 0.221 \text{ cm}^{-1}$ ($|E_q/hc| \leq 0.002 \text{ cm}^{-1}$) and $|D_q/hc| = 0.281\text{--}0.311 \text{ cm}^{-1}$ ($|E_q/hc| = 0.008 \text{ cm}^{-1}$), assuming that $\theta = 0^\circ$ and 155° , respectively. The range for dinitrene **2** is based on use of either of the mononitrene zfs values for the prediction.

Using the starting estimate for $|D_q/hc|$ provided by Itoh's model, it was possible to carry out spectral lineshape simulation using a computer program that estimates randomly oriented ESR spectral lineshapes¹⁵ based on the eigenfield method. Good fits to the quintet portions of the experimental spectra are obtained using the following parameters: for **1**, $S = 2$, $g_{\text{iso}} = 2.0023$, $|D_q/hc| = 0.243 \text{ cm}^{-1}$, $|E_q/hc| = 0.003 \text{ cm}^{-1}$; for **2**, $S = 2$, $g_{\text{iso}} = 2.0023$, $|D_q/hc| = 0.292 \text{ cm}^{-1}$, $|E_q/hc| = 0.009 \text{ cm}^{-1}$. The simulated spectra are shown with the experimental spectra in Figure 1 for comparison. Although we are not able at this time to carry out nonlinear least squares fitting to the experimental spectra by simultaneous optimization of all parameters, we can estimate the precision of our simulations, since the spectral line positions are quite sensitive to zfs parameters. We estimate our simulated parameters to fit the experimental spectra to within $\pm 0.002 \text{ cm}^{-1}$ and find an average variance between the fitted

(11) For diazide **3**: mp 163–166 °C (d). ¹H-NMR (200 MHz, CDCl₃): δ 7.25 (d, $J = 6.6$ Hz), 7.48 (t, $J = 6.6, 8.7$ Hz), 7.79 (d, $J = 8.7$ Hz), 8.38 (s), 8.94 (s). IR (KBr, cm^{-1}): 2100 (s, -N₃). UV-vis (λ_{max} , ϵ ; nm, L mol⁻¹ cm⁻¹): 209 (39 800), 261 (188 400), 350 (7900), 366 (11 200), 386 (15 200), 408 (13 100). High resolution MS (EI): Calc. for C₁₄H₈N₆ 260.080 99. Found 260.081 00. For diazide **4**: mp 235–238 °C. ¹H-NMR (200 MHz, CDCl₃): δ 7.04 (dd, $J = 1.8, 8.3$ Hz), 7.09 (dd, $J = 1.8, 8.3$ Hz), 7.21 (d, $J = 1.8$ Hz), 7.50 (d, $J = 8.3$ Hz), 7.52 (d, $J \sim 2$ Hz), 7.86 (d, $J = 8.3$ Hz). IR (KBr, cm^{-1}): 2120 (s, -N₃). UV-vis (λ_{max} , ϵ ; nm, L mol⁻¹ cm⁻¹): 206 (25 000), 228 (21 000), 259 (34 000), 312 (30 600). Chemical Anal. Calcd for C₁₂H₆N₆O: C, 57.60; H, 2.40; N, 33.60. Found: C, 56.71; H, 2.54; N, 32.00. We thank the Nebraska Center for Mass Spectroscopy and the University of Massachusetts Microanalytical Laboratory for the HRMS and microanalysis information on **3** and **4**, respectively.

(12) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

(13) Cf. an example in the following: Fukuzawa, T. A.; Sato, K.; Ichimura, A. S.; Kinoshita, T.; Takui, T.; Itoh, K.; Lahti, P. M. *Mol. Cryst. Liq. Cryst.* **1996**, *278*, 253.

(14) For calculation of the triplet mononitrene zfs values, the method used was that described in the following: Wasserman, E. *Prog. Phys. Org. Chem.* **1971**, *8*, 319.

and experimental spectra of about ± 35 G for both spectra. Given the considerable line width of the spectral peaks and the nearly 10 000 G total spectral width, the results reflect a good level of precision in the simulation by comparison to the many experimental peak positions and intensities which must be fit. The eigenfield¹⁵ theory method for obtaining the zfs parameters for these quintet species is quite effective, despite the nontrivial nature of interpreting spectra for high spin systems with large zfs. Additional confidence is lent by the good agreement between the zfs parameters obtained by fitting to the experimental spectra and the parameters predicted by the dipolar interaction model. For example, the system that has the least cylindrical symmetry, dinitrene **2**, is the one with a fairly large $|E_q/hc|$ -value in good accord with predictions, while the more symmetrical dinitrene **1** has the expected small $|E_q/hc|$ -value. Having shown that we can extract the zfs parameters of interest for both dinitrenes to a good degree of precision, we note that the observed difference in $|D_q/hc|$ between **1** and **2** is not only significant, but quite large.

Curie analyses were carried out for the ESR spectral intensities of major dinitrene peaks in each spectrum as functions of reciprocal temperature (5–60 K), the results of which are shown as insets in Figure 1. Saturation effects were minimized by use of low microwave powers ($\leq 200 \mu\text{W}$ at 100 kHz modulation frequency). For both **1** and **2**, linear plots were obtained, strongly supporting quintet ground states. A linear Curie plot does not prove absolutely that the spectrum observed belongs to a high spin ground state,¹⁶ but this result in conjunction with the computational predictions strongly indicates that both **1** and **2** are high spin, in accord with parity rule expectations.

Overall, it proved possible to predict not only the qualitative ground state spin multiplicities for **1** and **2** but also the electronic zfs parameters for the ESR spectra. The predicted zfs parameters are in very good quantitative accord with the observed zfs. This demonstrates the efficacy of theoretical models in predicting intramolecular exchange properties for open-shell molecules, even to the extent of *a priori* prediction—rather than *a posteriori* simulation—of ESR spectroscopic parameters. More widespread use of these predictive tools should go far toward aiding the interpretation of ESR spectroscopy for quintet species composed of interacting triplet sites, even when conformational flexibility is present to complicate the spectra.¹⁷ The investigation of other model dinitrenes with rigid geometries is ongoing, in order to obtain ESR spectra at various known C–N/C–N vector interaction angles for use as calibration spectra to allow more readily the interpretation of ESR spectra for flexible molecules with the same multiplicities.

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Supporting Information Available: Experimental details and a schematic description of the syntheses of diazides **3** and **4** (4 pages). See any current masthead page for ordering and Internet access instructions.

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(15) Teki, Y.; Fujita, I.; Takui, T.; Kinoshita, T.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 11499. Cf. also: Sato, K. Ph. D. Thesis, Osaka City University, 1992.

(16) See the discussion of Curie analysis by ESR spectroscopy: Berson, J. A. In *The Chemistry of Quinoid Compounds*; Patai, S., Rappaport, Z., Eds.; John Wiley and Sons: 1988; Vol. 2, pp 462–469.

(17) For examples of complex ESR behavior in conformationally mobile dinitrenes, see the following: Nimura, S.; Kikuchi, O.; Ohana, T.; Yabe, A.; Maise, M. *Chem. Lett.* **1993**, 837. Ling, C.; Lahti, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 8784.