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Zero-field splitting of quintet conjugated dinitrenes: 2,6-biphenylenedinitrene

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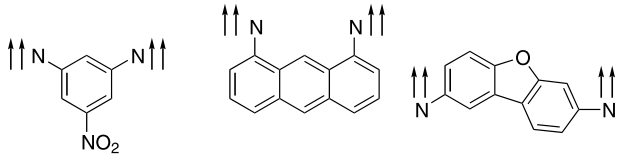
Abstract—2,6-Diazidobiphenylene was synthesized and photolyzed in frozen matrix. The resulting electron spin resonance spectrum showed the formation of 2,6-biphenylenedinitrene as a quintet species with zero field splitting (zfs) parameters $|D/hc| = 0.260 \pm 0.002$ cm^{-1}, $|E/hc| \leq 0.0005$ cm^{-1}. The zfs parameters are in excellent accord with dipolar models for a quintet state produced by interaction between triplet state nitrene sites. © 2003 Published by Elsevier Science Ltd.

Dinitrenes derived from photolysis of diazide precursors have been targets of considerable interest since the 1960s, when Wasserman and co-workers generated their electron spin resonance (ESR) spectral properties under randomly oriented, rigid matrix conditions.[1] Their ground-breaking work paved the way to study various features of π-electron delocalization and ground state preference in dinitrenes of differing structure and connectivity. Wasserman described a model[1a] for the zero-field splitting (zfs) parameters of quintet state species ($S=2$), based upon dipolar interaction between component triplet spin sites ($S=1$). Itoh used a similar model to analyze related dicarbenes.[2] But quantifying quintet zfs under randomly oriented conditions was hindered for years by uncertainty in assigning spectral peaks to the limited number of examples available.

Recently, eigenfield-based programs[3,4] have allowed simulation of rigid, randomly oriented ESR spectra for high multiplicity systems. Older assignments of zfs parameters to quintet dinitrenes require rethinking, judging by a model study of the quintet ground state system **1**.[5] Almost all quintet dinitrenes studied to date are structurally similar to **1** (nitrene units connected in a *meta* or pseudo-*meta* connectivity) and so will require similar zfs re-evaluation. We have reported[6] systems **2**–**3** as challenging tests of the dipolar model of zfs prediction for dinitrenes, since they are geometrically well defined, but are not *meta*-type systems. Since the zfs parameters of quintet dinitrenes have a sine-type angular dependence[1a,2] upon the vector angle formed by the C–N bonds, we felt it important to test the full span of C–N/C–N vector angles from 0° (**2**) through 120° (**1**) and ~155° (**3**) to 180°. We herein report the synthesis of 2,6-diazidobiphenylene, **4**, and its matrix photolysis to produce 2,6-biphenylenedinitrene, **5**, the first example of a system with a 180° angle between interacting nitrene units in a rigid, fully conjugated non-quinonoid system.



1 **2** **3**

The synthesis of **4** from biphenylene was accomplished in five steps (Scheme 1).[7] Compounds **6**–**9** were made following the procedures of Baker et al.[8] The final step of the synthesis gave poor yield as well as variable reproducibility, apparently due to ring-opening of the biphenylene ring system. The previous workers noted that diazotization of aminobiphenylenes give similar problems. But, once formed compound **4** is a bright red, stable molecule in the absence of strong light.

Dissolution of **4** in degassed 2-methyltetrahydrofuran matrix, freezing at 77 K or below, and photolysis at >300 nm (xenon arc, Pyrex filter) gave a deeply orange colored sample with the strong ESR spectrum shown in Figure 1. The spectrum was stable for hours at 77 K,

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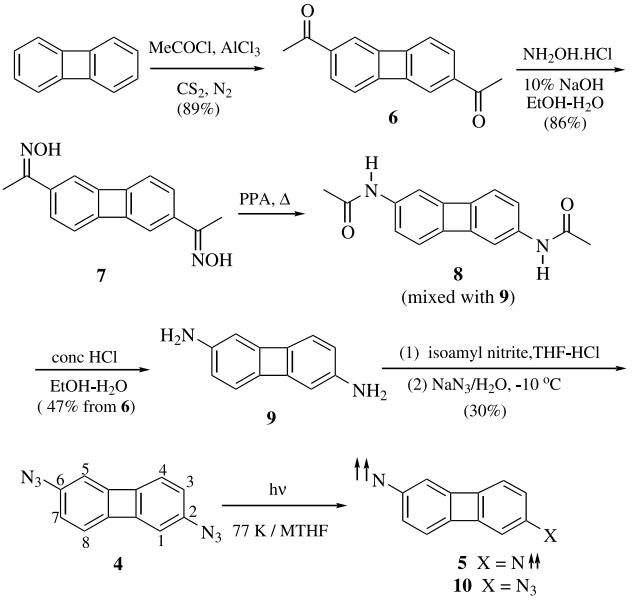
but disappeared upon thawing and refreezing. The small peak at $g \sim 2$ (3400 G, labeled 'R') is due to adventitious radical formation, at least in part from the solvent matrix. We tentatively assign a small peak at 6440 G ('N' in Fig. 1) to the x,y-transition of triplet mononitrene **10** formed by incomplete photolysis of **4**. This corresponds to a mononitrene zfs of $|D/hc| = 0.806$ cm^{-1}, with $|E/hc| \leq 0.002$ cm^{-1}.



Scheme 1. Synthesis and photolysis of **4**.

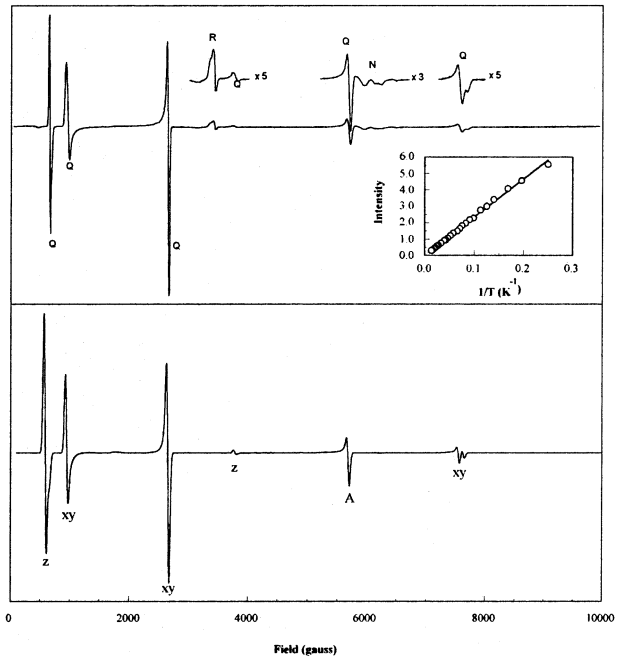


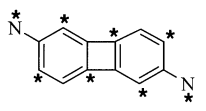
Figure 1. ESR spectrum from photolysis of **4** at 77 K in 2-methyltetrahydrofuran ($\nu_0 = 9.63793$ GHz), and simulation described in the text. R = radical, N = mononitrene, Q = quintet dinitrene; A = off-resonance peak in simulation. Inset shows intensity of 2640 G peak versus reciprocal temperature.

Other peaks observed at 650, 965, 2640, 3770 (wk), 5680, 7560, and 7685 G were assigned to quintet **5** by eigenfield simulation using parameters: $S = 2$, $g = 2.003$, $|D/hc| = 0.260$ cm^{-1}, $|E/hc| = 0.0005$ cm^{-1}. Axial assignments are given in the simulated spectrum, which gives an excellent fit to experiment. By varying the simulation, we assign the zfs for **5** to be $|D/hc| = 0.260 \pm 0.002$ cm^{-1}, $|E/hc| \leq 0.0005$ cm^{-1}. A dipolar model[1a,2–4] relates the zfs tensors for interacting triplet nitrenes (D_T,E_T) to the corresponding parameters for a quintet state formed by their interaction (D_Q,E_Q). The zfs is related to the vector angle $\theta = 2\alpha$ between the two C–N bonds in such a dinitrene. Using $\theta = 180°$ and zfs $D_T = 0.806$ cm^{-1} for **10**, the predicted $|D_Q/hc| = 0.269$ cm^{-1}, $|E_Q/hc| \leq 0.0007$ cm^{-1}. This is in excellent agreement with the experimental results, confirming that the dipolar model adequately describes the zfs of dinitrenes for the full range of C–N/C–N vector angles $0° < \theta < 180°$ that is spanned by systems **1**–**3** and **5**, even for geometrically unusual cases of this type.

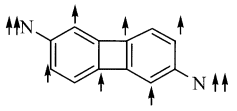
$$D_Q = \frac{3}{2}D_z^{S=2} = \frac{1}{2}\left[(D_T + E_T)\sin^2\alpha - \frac{1}{3}D_T - E_T\right]$$

$$E_Q = \frac{1}{2}(D_x^{S=2} - D_y^{S=2}) = \frac{1}{6}[-(D_T + E_T)\sin^2\alpha + D_T - E_T]$$

The intensity of the quintet spectrum of **5** was measured over 4–77 K (inset, Fig. 1). Nearly linear Curie law behavior was observed, implying[9] either virtual degeneracy of the quintet with an ESR-silent state, or a lack of thermally populated ESR-active states (robust quintet ground state). A high-spin ground state is consistent with the Borden–Davidson type nondisjoint connectivity[10] of this dinitrene, which in turn is partly due to the incorporation of a four-member ring in the π-system. The picture below shows the qualitative prediction of a high spin ground state based on Ovchinnikov's formulation[11] for a conjugated open-shell π-system. Assuming each nitrene site to be a high-spin triplet, with a delocalizable π-electron, spin polarization effects should give a high spin ground state. The pattern of spin polarization is shown. UB3LYP[12]/6-31G* computations[13] for geometry-optimized $S = 2$ and $S = 0$ states of **5** favor a high spin ground state by about 13 kcal/mol, comparing separately optimized quintet to a spin-unrestricted singlet multiplicity computation. Although there are limitations to the comparison of high spin to lower spin states in the UB3LYP formalism, this level of theory has been successful in giving reasonable qualitative predications of state ordering for dinitrenes.[14]



S = 0.5 (n* - n°) > 0



E(*S=0*) = -570.142247 (+13.1 kcal/mol)
E(*S=2*) = -570.163408 (UB3LYP,6-31G*)

Dinitrene **5** is a unique test not only of π-connectivity in ground state determination, but of the role of molecular geometry in determining zfs in high spin molecules. The experimental deployment of a cyclobutadiene ring

is unusual[15] in π-conjugated open-shell molecules, so **5** provides a test of its effect. The results show that it acts as expected based on simple connectivity (parity) considerations. In addition, thanks to the structural rigidity of **5**, an unambiguous analysis of the quintet zfs is possible that supports the dipolar model previously been proposed as the major determinant of zfs in such dinitrenes and dicarbenes.

Experimental

2,6-Diacetylbiphenylene (6). A solution containing biphenylene (0.230 g, 1.51 mmol) and acetyl chloride (0.770 g; 9.81 mmol) was prepared in anhydrous carbon disulphide (30 mL, Aldrich) by stirring at ambient temperature under nitrogen. To this solution, fresh dry aluminum chloride (approx. 1 g, 7.49 mmol, 99.99%) was added all at once under nitrogen with constant stirring. The yellow solution turned red upon stirring, as a red flocculent precipitate formed. The solution was stirred overnight at ambient temperature under nitrogen to yield a light yellow solution and a crystalline red precipitate. Cold HCl (40 mL, 2 M) was added dropwise to the light product mixture with constant stirring. The red crystalline precipitate decomposed into a yellow solid. The mixture was stirred for 20 min and filtered to yield 2,6-diacetylbiphenylene **6** as a yellow solid (0.317 g, 89%, mp 245–247°C, lit. mp 243–245°C[8a]). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.52 (s, 6H, CH_3), 6.84 (d, $J=7.2$ Hz, 2H, $H_{4,8}$), 7.34 (s, 2H, $H_{1,5}$), 7.58 (d, $J=7.2$ Hz, 2H, $H_{3,7}$). IR (KBr, $\bar{\nu}$ cm^{-1}): 1660 (s), 1390 (s).

2,6-Diacetylbiphenylene dioxime (**7**). A solution of **6** (0.476 g, 2.03 mmol), hydroxylamine hydrochloride (1.0 g, 14.0 mmol) and sodium hydroxide (0.69 g, 17.3 mmol) was prepared by dissolving the reactants in water (4–5 mL) and ethanol (25 mL, 100%) with constant stirring. The mixture was gently refluxed for 16 h with constant stirring. After 16 h of reflux the product mixture was allowed to stand overnight. The solvent was removed using a rotary evaporator and water was added to the residue. The suspension was stirred for 20 min and filtered to yield **7** as a yellow solid (0.466 g, 86%, mp 289–291°C with decomposition and gas evolution, lit mp 290–291°C[8b]). ^{1}H NMR (200 MHz, CD_3COCD_3): δ 2.14 (s, 6H, CH_3), 6.80 (d, $J=7.3$ Hz, 2H, $H_{4,8}$), 7.12 (d, $J=7.3$ Hz, 2H, $H_{3,7}$), 7.19 (s, 2H, $H_{1,5}$), 10.36 (s, broad, NOH). IR (KBr, $\bar{\nu}$ cm^{-1}): 1720 (m), 920 (s). A small portion was recrystallized from ethanol (95%) to yield **7** as a fine yellow powder (mp >340°C). ^{1}H NMR (200 MHz, CD_3COCD_3): δ 2.14 (s, 6H, CH_3), 6.80 (d, $J=7.3$ Hz, 2H, $H_{4,8}$), 7.12 (d, $J=7.3$ Hz, 2H, $H_{3,7}$), 7.19 (s, 2H, $H_{1,5}$), 10.34 (s, broad, NOH).

2,6-Diaminobiphenylene (9). Polyphosphoric acid (18 g, Aldrich) was weighed into a 25 mL Erlenmeyer flask at room temperature and heated to 100°C in an oil bath with constant stirring. To the polyphosphoric acid was added **7** (0.410 g, 1.54 mmol) as a fine powder with constant stirring. The color of the mixture turned from nearly colorless to dark brown. During the reaction, the dioxime tended to form small clumps that were broken up using a ceramic spatula. Stirring the mixture at 100°C was discontinued after all the reactant had been consumed and the mixture was completely dark brown (approx. 45 min). The polyphosphoric acid was neutralized using a 10% sodium hydroxide solution at 100°C with stirring to prevent the acid from congealing (CAUTION: highly exothermic reaction). After the neutralization was completed, the mixture was made alkaline by further addition of 10% sodium hydroxide and was cooled down in an ice bath. After standing at 10°C for 2 h, the mixture was filtered and the residue washed with water until the washings tested neutral. The residue was vacuum dried, collected as a brown powder and recrystallized from ethanol to yield a yellow powder (0.234 g, mp >200°C with decomposition). A complex ^{1}H NMR (200 MHz, $CDCl_3$) indicated that the product was a mixture of the 2,6-diacetamidobiphenylene (**8**) and the 2,6-diaminobiphenylene (**9**) that was adequate for use in the next step. IR (KBr, $\bar{\nu}$ cm^{-1}) 3400 (s), 3300 (s), 1650 (m).

The mixture of **8** and **9** from the previous step was stirred with concentrated hydrochloric acid (10 mL 12 M), absolute ethanol (10 mL) and water (10 mL) at 100°C for 1 h. The color of the solution changed from yellow–brown to purple during this period, and tiny needle shaped crystals appeared. The heating was discontinued after 1 h and the solution was allowed to stand for 90 min at ambient temperature. The solution was made alkaline by further addition of the 10% aqueous sodium hydroxide solution. The purple mixture changed into a yellow precipitate and the mixture was cooled in an ice bath for 1 h. The mixture was filtered and the yellow residue was washed with water until the washings tested neutral. The residue was dried under vacuum overnight and then stirred in about 15 mL 10% aqueous sodium hydroxide solution for 1 h. The mixture was neutralized with aqueous hydrochloric acid (2 M) and then extracted with methylene chloride (10×25 mL). The solvent was removed using a rotary evaporator to yield 2,6-diaminobiphenylene (**9**) as a yellow solid (0.134 g; mp 205–207°C, lit mp 218–220°C after decomposition at 205°C[8b]). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.54 (s, broad, 4H, NH_2), 5.89 (dd, $J=1.4$, 7.2 Hz, 2H, $H_{3,7}$), 6.04 (d, $J=1.4$ Hz, 2H, $H_{1,5}$), 6.39 (d, $J=7.2$ Hz, 2H, $H_{4,8}$). IR (KBr, $\bar{\nu}$ cm^{-1}): 3400 (br), 1690 (s), 700 (s). *Note*: Although 2,6-diaminobiphenylene darkens upon prolonged exposure to air its ^{1}H NMR spectrum remains unchanged.

2,6-Diazidobiphenylene (4). A solution of **9** (0.015 g, 82 μmol) in 4 mL of THF was treated with an aqueous solution of concentrated hydrochloric acid (0.03 mL, 0.36 mmol) with stirring at ambient temperature. A purple–gray precipitate formed almost immediately. The mixture was cooled to −12°C, and isoamyl nitrite (0.03 mL, 0.22 mmol; CAUTION: highly toxic) was added to the cold reaction mixture with constant stirring. The color of the reaction mixture darkened and a black precipitate formed almost immediately. The mixture was stirred at approximately −10°C for 15 min, then a cold solution of sodium azide (0.016 g, 0.25 mmol in

1–2 mL of a 1:1 THF:water mixture at approx. 0°C) was added to the reaction mixture with constant stirring. The reaction temperature rose to −5°C briefly after the addition, then dropped back to −10°C. No evolution of gas or color change was observed. The product mixture was allowed to warm to room temperature over the course of 45 min, then extracted with ether (5×25 mL). The combined red ethereal layers were dried over anhydrous magnesium sulfate overnight and filtered. The solvent was removed using a rotary evaporator to yield a red solid that was dried under vacuum to give 2,6-diazidobiphenylene as a bright red solid (0.005 g, 30%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.37 (dd, $J=0.7$, 1.2 Hz, 2H, $H_{1,5}$), 6.39 (dd, $J=1.2$, 7.4 Hz, 2H, $H_{3,7}$), 6.62 (dd, $J=0.7$, 7.4 Hz, 2H, $H_{4,8}$). IR ($CHCl_3$, $\bar{\nu}$ cm^{-1}): 2120 (s). HRMS (M^+): calculated for $C_{12}H_6N_6$: 234.0655. Found: 234.0655.

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