2-(4′-Nitrenophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-*1H*-imidazole-3-oxide-1-oxyl: Photogeneration of a Quartet State Organic Molecule with Both Localized and Delocalized Spins

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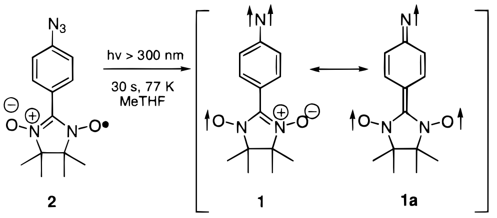
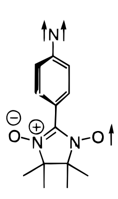
In hopes of gaining insight for the design of new molecular magnetic materials,[1] many open-shell molecules have been constructed by linking hypovalent spin carrier (SC) units with connectivities determined by parity methods.[2] Most workers have used the same types of SC units, rather than linking different types of SCs (heterospin approach). The latter approach allows the study of heteroatom substitution effects on spin multiplicity as well as expanding the number of available high-spin molecules. We have studied numerous dinitrenes in order to investigate effects of connectivity, conformation, and heteroatom substitution on their exchange behavior.[3,4] In the present study, we report the extension of this methodology to produce the novel heterospin system 2-(4′-nitrenophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-*1H*-imidazole-3-oxide-1-oxyl(**1**).



2 **1** **1a**



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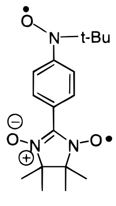

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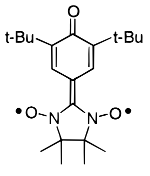

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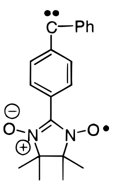

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Precursor **2** was synthesized by treatment of 4-azidobenzaldehyde with 2,3-bis(hydroxylamino)-2,3-dimethylbutane sulfate, followed by oxidation with aqueous NaIO$_4$/chloroform.[5] Radical **2** is an indigo-black solid that is stable for weeks under nitrogen at <0 °C. In degassed benzene solution, **2** displays a typical α-nitronylnitroxide (NN) electron spin resonance (ESR) spectrum with $a_N = 7.4$ G. When **2** is dissolved in 2-methyltetrahydrofuran (MTHF), degassed, frozen to 77 K, and photolyzed for 30 s at >300 nm (Pyrex filter, 1000 W xenon arc), the originally blue matrix changes color to purple.

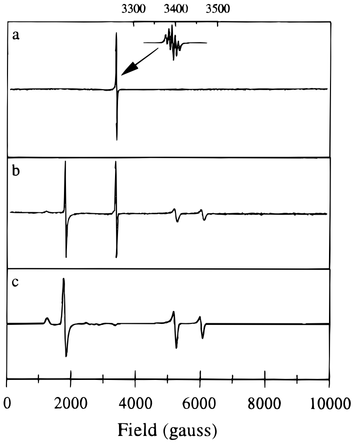

Figure 1. 9.5 GHz ESR spectra for **2** at 77 K before (a) and after (b) photolysis, compared to the $S = 3/2$ simulated spectrum with $|D/hc| = 0.277$ cm^{-1} and $|E/hc| = 0.0002$ cm^{-1} (c).

Figure 1 shows the prephotolysis and postphotolysis 9.5 GHz ESR spectra of the frozen matrix sample.[5] The initial spectrum shows only the radical peaks at $g \sim 2$ expected from the NN SC unit, while the postphotolysis spectrum also shows a series of new peaks (1230 (wk), 1830, 5225, and 6056 G) that are stable at 77 K, but which are immediately quenched by thawing of the matrix above 90 K. More extended photolysis of dilute samples of **2** lead to >80% disappearance of the $g \sim 2$ radical peaks and concurrent appearance of the new spectral peaks. The new spectrum can be fit by the eigenfield method[6] to a quartet randomly oriented spectrum with the following parameters: $S = 3/2$, $g_{iso} = 2.003$, $|D/hc| = 0.277$ cm^{-1}, $|E/hc| \leq 0.003$ cm^{-1}. Except for the $g \sim 2$ region from remaining unphotolyzed **2**, the simulated positions fit to within 25 G for all observable peaks with good agreement for line shape and intensity (Figure 1). There is no additional peak in the 6000−7000 G region attributable to an isolated triplet phenyl mononitrene unit, ruling out production of an observable conformational isomer such as **3**.[7]

Additional information about structure **1** is given by changes in the UV−vis spectrum upon photolysis[5] of a frozen MTHF sample at 77 K (Figure 2). The initial spectrum is consistent with expectations for the aryl azide chromophore plus the NN chromophore, with major absorbances at 280−300, 537, 584, 638,

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(3) (a) Lahti, P. M.; Minato, M.; Ling, C. *Mol. Cryst. Liq. Cryst., Sect. A* **1995**, *271,* 147 summarizes much of the recent aryl dinitrene work by ourselves and others. However, zfs descriptions in this reference will require revision: see: Fukuzawa, T. A.; Sato, K.; Ichimura, A. S.; Kinoshita, T.; Takui, T.; Itoh, K.; Lahti, P. M. *Mol. Cryst. Liq. Cryst., Sect. A* **1996**, *278*, 253. (b) Lahti, P. M.; Kalgutkar, R.; Walton, R. A.; Murcko, M. A. *Mol. Cryst. Liq. Cryst., Sect. A*, **1997**, *305*, 553. (c) Kalgutkar, R. S.; Lahti, P. M. *J. Am. Chem. Soc.* **1997**, *119*, 4771.

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(5) Experimental details. 4-Azidobenzaldehyde was prepared by the method of Walton, R.; Lahti, P. M. *Synth. Comm.* **1998**, *28*, 0000 (in press). For compound **2**: blue-black solid mp 120−123 °C; UV−vis (chloroform, nm (ϵ)) - - 299 (15, 400), 372 (5700), 625 (400); IR (KBr, cm^{-1}) - - 2945 (CH$_3$ str), 2115 (−N$_3$ str), 1255, 1090, 1010, 795 (*p*-phenylene), no OH band observed. HR-MS (EI) Calcd for $C_{13}H_{16}N_5O_2$ 274.1304; Found 274.1304. High-resolution mass spectrometry was performed at the Nebraska Center for Mass Spectrometry.

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S0002-7863(98)00120-6 CCC: $15.00

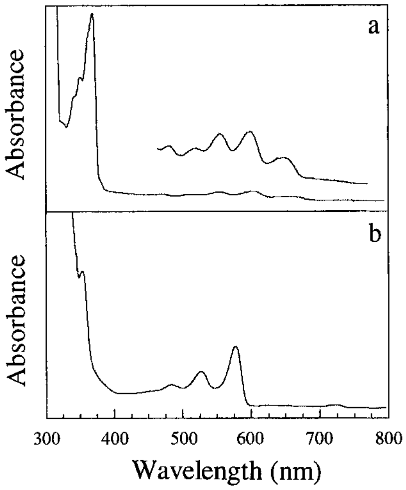

Figure 2. UV−vis spectra for **2** at 67 K before (a) and after (b) photolysis at >300 nm for 60 s. Absorbance scale is appropriate for the main curves; the expanded portions of curves (a) and (b) are displayed at approximately 14× and 4× expansion, respectively.

and 703 nm: the latter four appear to be due to vibronic spacing of about 1500 ± 60 cm^{-1}. The postphotolysis spectrum is completely changed, showing spectral features at 320 and 445 (wk) nm as well as at 486, 528, and 578 nm. The latter absorbances are responsible for the purple color of the photolyzed sample and correspond to a vibronic spacing of about 1640 ± 20 cm^{-1}. The new peaks are stable at 77 K but disappear irreversibly at >90 K. The spectra may be compared to those obtained from phenyl azide photolysis,[8a−d] which have strong absorbance at 300−380 and only weak peaks at 500 nm. The conjugation effect of the NN unit connected *para* to the nitrene in **1** may be gauged by the qualitatively similar matrix UV−vis spectra obtained from photolysis of 4-amino-4′-azido-(*E*)-stilbene.[8e]

Density functional calculations (6-31G**/B3LYP) were carried out[9] on model systems for **1** where all methyl groups were replaced by hydrogen atoms. The cylindrical computed structure for $^4A_1$ planar **1** is consistent with the near-zero zfs *E*-value of the observed ESR spectrum. The excited, low-spin $^2A_1$ state is 5.3 kcal/mol higher in energy, while bisected $^4A_1$ **3** is 18.7 kcal/mol higher. Details are given in the Supporting Information.

Quartet **1** is an unusual organic system in having a localized σ-electron interacting with a pair of delocalized triplet π-electrons. The computed singly occupied molecular orbital occupancies for $^4A_1$ **1** are $b_2(\alpha)b_1(\alpha)a_2(\alpha) = \pi^{\perp}n^1\pi^{\perp}$. "Y-conjugated" biradicals **4**[10] and **5**[11] are close structural analogues to **1**, although they are triplet rather than quartet systems. Triplet **4** has a zfs $|D/hc|$ parameter sufficiently small that it was not resolved in frozen solution spectra, but **5** has a zfs of $|D/hc| = 0.107$ cm^{-1}. The X-ray structure of **4** suggests it to have only minor quinonoidal character in terms of bond alternation, so this system is shown as a nitroxide/NN structure.

Photolysis of the azide group in **2** produces a π-electron on a nitrene site which we expected to be delocalized onto the NN group (resonance structure **1a**). The DFT calculations show 0.7 of an unpaired α-electron on *each* N−O unit of the NN in **1** (Mulliken population numbers). The exocyclic nitrene nitrogen has a spin density of 1.5. In bisected structure **3** each N−O unit has a spin density of 0.6, while the exocyclic nitrogen has a spin density of 1.6. Structure **3** is a reasonable benchmark for an enforced nitrene/NN structure. Although the trends of the numbers are in accord with greater quinonoidal character in **1** than in **3**, the magnitude of the change is surprisingly small. The DFT computed geometry of $^4A_1$ **1** has a moderate bond alternation of about 0.05 Å in the phenylene ring, very similar to that in **3**. For the important exocyclic nitrene site, rC−N = 1.31 Å for **1** versus rC−N = 1.33 Å in **3**. Similarly, the interannular bond connecting the two rings is rCC = 1.44 Å for **1** versus 1.47 Å for **3**. Again, the trends in bond lengths are consistent with those expected, but the magnitudes of change are quite small.

The electronic natures of systems with different mulitiplicities are properly compared by use of the quantity $(2S-1)|D/hc|$, where S is the spin quantum number of the state considered.[12] Arylnitrenes with conjugated substitutents in the 4-position have[8e,13] $|D/hc| \sim 0.75-0.88$ cm^{-1}. For **1** $(2S-1)|D/hc| = 0.55$, while for a typical *para*-conjugated arylnitrene $(2S-1)|D/hc| = 0.75-0.88$, where $S = 1.5$ and 1.0, respectively. By this criterion, the zfs for *quartet* **1** is appreciably smaller than that for a conjugated *triplet* arylnitrene. The balance of evidence from computation and from evaluation of ESR zfs data thus seems consistent with the planar nitrene/NN resonance structure **1**, but with significant contribution from quinonoidal structure.

The closest structural analogue to **1** is quartet carbene-nitroxide **6**.[14] This species has zfs parameters of $|D/hc| = 0.113$ cm^{-1} and $|E/hc| = 0.006$ cm^{-1}. The role of the extra phenyl group in **6** gives rise to additional electron delocalization in accord with the observed decrease of zfs relative to **1**, in addition to breaking the axial symmetry of **6** ($E \neq 0$).

Mataga has argued that networks possessing localized *and* delocalized electronic band structure should have improved prospects to exhibit molecular ferromagnetism.[15] Although **1** is an isolated molecule and not an extended material, it is a readily studied model for this genre of organic open-shell networks. Additional studies of analogous heterospin open-shell organic molecules are ongoing in efforts to generalize the application of photochemical cleavage toward producing new models for ferromagnetic materials.

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Supporting Information Available: 6-31G**/B3LYP computed coordinates and energies for the $^4A_1$ and $^2A_1$ states of **1**, the $^4A_1$ geometry for **3**, plus an edited output file for a 6-31G*/B3LYP frequency calculation on **1** (21 pages print/PDF). See any current masthead page for ordering information and Web access instructions.

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