SHORT COMMUNICATIONS

BIPHENYL-3,4 ' -DINITRENE

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Photolysis of biphenyl-3,4'-diazide in a rigid glassy matrix at 77 K yields quintet state biphenyl-3,4'-dinitrene with **zero-field splitting parameters of** $|D/hc| = 0.153$ **cm⁻¹ and** $|E/hc| = 0.019$ **cm⁻¹ determined by electron spin resonance spectroscopic studies. Curie plot studies are consistent with assigning the quintet to be the ground state in this species. This finding confirms qualitative connectivity-based predictions for this general connectivity type of openshell system, and is in qualitative agreement with spectral INDO-CI computational predictions for both planar and twisted geometries of the dinitrene.**

Chemists have been interested for some time in the manner in which ground-state spin multiplicity is related to molecular connectivity in open-shell π conjugated organic molecules and related non-Kekulé species (e.g. see various discussions in Ref. 1). A flurry of recent interest in this area has been spurred by suggestions that the rational design of organic ferromagnetic materials and polymers might be possible, based on a variety of models.²⁻⁴ In order to test such theories, the synthesis and ground-state multiplicity determination of model fragments with desirable structural characteristics is a necessary first step. A number of studies have been carried out by different groups on various π -conjugated organic species in efforts to correlate structural effects with ground-state *(GS)* spin multiplicity, using both computational and experimental techniques. In this paper, we report the generation and electron spin resonance **(ESR)** spectral properties of a new connectivity example of such a model species, biphenyL3,4'-dinitrene, **1.** In addition, we show that,

despite the likelihood of torsion in this system, electron exchange coupling remains ferromagnetic for **1,** in accord with simple qualitative connectivity-based models and with semi-empirical computations by our group.

The diazide precursor **2** was synthesized by nitration of 3-nitrobiphenyl (Pfalz and Bauer), catalytic reduction (Pt02/60 psi hydrogen) to the diamine **3,** and diazotization via the stable bistetrafluoroborate salt followed by addition of sodium azide to give tan solid **2,** [m.p. 45-46 °C; IR (KBr, cm⁻¹) 2090, 2120 (strong, $N=N=N$ str.); chemical analysis gave C $61 \cdot 1$, H $3 \cdot 4$, N 34.3% (theoretical *C* 61-0, **H** 3-4, N 35.5%); this compound must be stored in the dark to avoid discoloration], which was stable for several months at - 20 "C in the dark. Irradiation for *5* min at **77** K with a Pyrex-filtered 1000-W xenon arc lamp of a degassed, frozen glassy solution of **2** in 2-methyltetrahydrofuran (MeTHF) gave rise to the intense 9.6 -GHz ESR X-band spectrum shown in Figure 1. Similar spectra were

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obtained by low-temperature photolysis of **2** in Fluorolube and in **1-5** wt% poly(methy1 methacrylate) films cast from dichloromethane solution.

The **ESR** spectrum of **1** in Figure **1** shows the following resonances: *cu* **750** (broad, indistinct), **1653, 3012** (strong, sharp), **3840** (broad), **6029, 6683, 6920** and **8350** G (weak). The two resonances at **6683** and **6920** G match well the positions of mononitrene peaks produced by comparison photolyses of *m-* and p-biphenylazide, respectively; these values correspond to zero-field splitting $|D/hc|$ values of 0.88 and 0.97 cm⁻¹ respectively (these mononitrenes have been described previously⁵), with | E|hc | being essentially zero. The dinitrene set of resonances resemble those of Iwamura and Murata's⁶ alkyne-linked quintet GS dinitrenes **4** and *5,* described in the single other study of

linking two phenylnitrenes in different connectivities by conjugating groups. The similarity of our spectrum to these others supports our conclusion that **1** is indeed a quintet state dinitrene. There **is** also a similarity to the monocyclic quintet dinitrene 1,3-phenylenedinitrene, whose **ESR** spectrum was checked by **us** and was first

described by Wasserman *et ul.'* Although formally a cousin of **4-5** by connectivity theory, this species is different in having two nitrenes conjugated through a single ring, rather than consituting a test of two openshell systems linked by a conjugated group. **If** we assign the quintet **H-1** resonance to **8360** G, use of perturbation methods' leads to an **ESR** zero-field splitting value of $|D/hc| = 0.153$ cm⁻¹. If we assume like I wamura and Murata⁶ and Wasserman *et al.* ⁷ that the **H-2** resonance is hidden under mononitrene resonances at *ca* **6700** and *ca* **6900 G**, we find $|E/hc| =$ 0.019 cm⁻¹. The spectrum in MeTHF is remarkably clean, and shows little radical impurity in the $g \approx 2$ region **(3300-3500** G).

We tested whether the quintet is the ground state of **1** by preparation of a Curie law plot of ESR spectral intensity **vs** reciprocal of absolute temperature, using the strong quintet peak at **3012** G for the plot. All spectra were obtained on an APD Cryogenic Displex closed-cycle circulating helium cryostat, with a copper sample spindle and Suprasil outer vacuum shroud to allow photolysis; temperatures were measured with a gold-chrome1 thermocouple attached to the sample spindle. Spectral peak intensities were measured by double integration of the standard derivative ESR spectrum, using two different methods **as** a check of results. Over the range **10-70** K, we found excellent linearity, with a correlation coefficient of 0.99 (Figure **2).** At temperatures > 80 **K,** the spectrum of **1** decays irreversibly, even in poly(methy1 methacrylate); thawing to room temperature of the sample and recooling shows no residual **ESR** peaks. Although these results do not strictly prove that **1** has a quintet GS (the difficulties of

interpreting a linear Curie plot have been well set forth by Berson⁸), the most likely interpretation of results supports this assertion.

The finding of a high-spin ground state for **1** is in accord with the qualitative expectations of various connectivity-based theories, $9-14$ which do not necessarily, however, take explicitly into account the effects upon ground-state multiplicity of possible nonplanar conformers or of heteroatom π -isoelectronic substitutions. This finding is also consistent with the computational studies by us indicating that even a twisted dinitrene **1** is expected to favor a quintet ground state. We have previously shown that semi-empirical molecular orbital plus configuration interaction computations give ground-state (GS) spin multiplicity predictions in accord with experimental findings and with more rigorous *ab initio* computational predictions. We more rigorous *ab initio* computational predictions. We find by use of Dewar's AM1¹⁵ method with configuration interaction¹⁶⁻¹⁹ that a coplanar geometry of 1 favors a quintet GS by about 9 kcalmol^{-1}, while a 90[°] twisted geometry still favors the quintet by about 4 kcalmol⁻¹. This is a remarkable demonstration of the strength of the 3,4'-biphenyl group in ferromagnetically coupling the two spin-bearing nitrene sites, despite decreased overlap in the twisted geometry.

Itoh and co-workers^{20,21} studied in some detail a 3,3 '-dicarbene connectivity isomer of our system, biphenyl-3,3 ' -bis(phenylmethylene), which was found to have a singlet ground state in agreement with valence bond⁹⁻¹² predictions. A Russian group²² has photolysed the bisdiazo precursor to biphenyl-4,4 ' bis(phenylmethy1ene) and obtained triplet ESR signals. Our study of quintet **1** now shows the ferromagnetic nature of the 3.4' -biphenyl connectivity in exchange coupling, with use of nitrene spin-bearing sites rather than carbenes. The dicarbene systems are conformationally more complex than dinitrene **l,** hence we consider the geometric simplification in this and other dinitrenes to be in some ways preferable for studies of exchange coupling.

Our experimental data do not unequivocally show

whether **1** is planar or not, since despite that fact that biphenyl itself generally has a dihedral torsional angle of 35° between rings with a low rotational energy this may not apply to the dinitrene itself. The similarity of our $|D/hc|$ value for 1 to that for planar **4,** which has $\binom{6}{1}$ *D*/hc | = 0.1575 cm⁻¹ and $|E/hc| = 0.020$ cm⁻¹, may indeed imply that **1** is planar or time-averaged planar, as **4** and **5** were believed to be despite their lack of conformational constraint. We hope to synthesize derivatives **of 1** where more torsion is mandatory, in an effort to see if the spectral 1 *D/hc* ¹ value is altered in a manner consistent with any dramatic change in the degree of exchange interaction relative to **1.**

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