SHORT COMMUNICATIONS

BIPHENYL-3,4'-DINITRENE

MASAKI MINATO AND PAUL M. LAHTI*

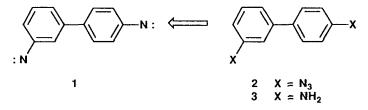
Lederle Graduate Research Tower, Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, U.S.A.

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 open-shell 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, biphenyl-3,4'-dinitrene, 1. In addition, we show that,

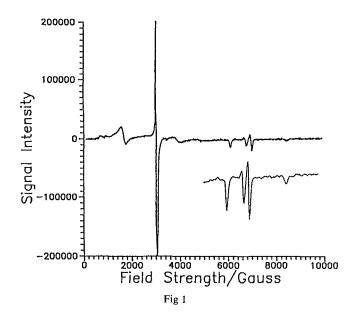
despite the likelihood of torsion in this system, electron exchange coupling remains ferromagnetic for 1, in accord with simple qualitative connectivity-based models and with semi-empirical computations by our group.

The diazide precursor 2 was synthesized by nitration of 3-nitrobiphenyl (Pfalz and Bauer), catalytic reduction (PtO₂/60 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 61·1, H 3·4, 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



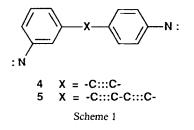
* Author for correspondence.

0894-3230/91/070459-04\$05.00 © 1991 by John Wiley & Sons, Ltd. Received 15 February 1991 Revised 25 March 1991



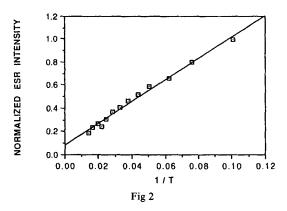
obtained by low-temperature photolysis of 2 in Fluorolube and in 1-5 wt% poly(methyl methacrylate) films cast from dichloromethane solution.

The ESR spectrum of 1 in Figure 1 shows the following resonances: ca 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 al.*⁷ 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 open-shell systems linked by a conjugated group. If we assign the quintet H-1 resonance to 8360 G, use of perturbation methods⁷ leads to an ESR zero-field splitting value of |D/hc| = 0.153 cm⁻¹. If we assume like Iwamura 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-chromel 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(methyl 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 find by use of Dewar's AM1¹⁵ method with configura-tion interaction¹⁶⁻¹⁹ that a coplanar geometry of 1 favors a quintet GS by about 9 kcal mol⁻¹, while a 90° twisted geometry still favors the quintet by about 4 kcal mol⁻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

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(phenylmethylene) 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 1, 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 barrier, ^{23,24} this may not apply to the dinitrene itself. The similarity of our |D/hc| value for 1 to that for planar 4, which has⁶ $|D/hc| = 0.1575 \text{ cm}^{-1}$ and $|E/hc| = 0.020 \text{ cm}^{-1}$, 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 |D/hc|value is altered in a manner consistent with any dramatic change in the degree of exchange interaction relative to 1.

ACKNOWLEDGEMENTS

This work was supported in part by the Office of Naval Research and the Exxon Education Foundation. Computational studies were carried out at the University of Massachusetts Department of Chemistry Celerity C-1260-D computational facility, supported in part by National Science Foundation Grant CHE-8712319. We are grateful to Professor P. Sheng for help with the synthesis of 2. ESR spectra were obtained on a Bruker ESP-300 spectrometer in the University of Massachusetts Department of Polymer Science and Engineering.

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