J. Am. Chem. Soc. 1993, 115, 4532–4539

Models for Intramolecular Exchange in Organic π-Conjugated Open-Shell Systems: A Comparison of Three Non-Kekulé Biphenyldinitrenes

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Received December 28, 1992

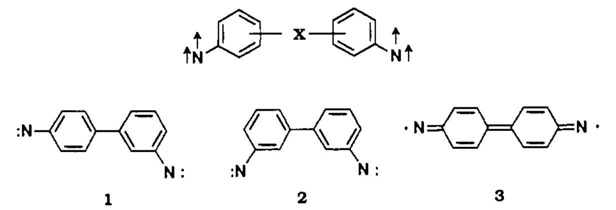
Abstract: The important effect of connectivity upon the nature of intramolecular exchange coupling of unpaired electrons by the biphenyl group was investigated by cryogenic matrix photolysis of diazide precursors expected to yield biphenyl-3,4′-dinitrene (**1**), biphenyl-3,3′-dinitrene (**2**), and biphenyl-4,4′-dinitrene (**3**). System **1** was predicted by parity-based qualitative models to exhibit a high-spin ground state. By Curie law analysis of its electron spin resonance (ESR) spectrum at cryogenic temperatures in frozen 2-methyltetrahydrofuran solution, **1** was found to be a quintet ground-state dinitrene with zero field splitting (zfs) parameters of $|D/hc| = 0.153$ cm^{-1}, $|E/hc| = 0.003$ cm^{-1}. System **2** was predicted to be disjoint with nearly-degenerate high-spin and low-spin states. Cryogenic frozen solution ESR spectroscopy showed no ESR-active dinitrene **2** upon extended photolysis of its appropriate diazide precursor, although the related mononitrene with zfs of $|D/hc| = 0.996$ cm^{-1} was clearly visible. We presume that system **2** was produced in this experiment, but that it acts either as a singlet ground-state dinitrene or as a pair of isolated mononitrenes. A biradical ESR spectrum was found for photolysis of the diazide precursor to **3**, with zfs of $|D/hc| = 0.189$ cm^{-1} and $|E/hc| < 0.003$ cm^{-1}. The thermal dependence of this biradical spectrum shows it to be an excited state, consistent with quinonoidal dinitrene **3** having a singlet ground state and a triplet excited state ca. 0.6 kcal/mol higher in energy. The results for dinitrenes **1–3** were compared to related work on dicarbene molecules described by others, and it was found that the dinitrenes and dicarbenes exhibit similar electron exchange coupling behavior.

Introduction

The relationship between molecular connectivity and ground-state spin multiplicity in non-Kekulé molecules has been of great interest to theoretical and experimental chemists since the turn of the twentieth century.[1] To allow study and understanding of non-Kekulé molecules, a variety of qualitative models and quantitative models and quantitative calculations have been presented by theoreticians, while experimentalists have attained impressive advances in trapping reactive intermediates and spectroscopically examining solvent-transient species under rigid cryogenic conditions. In addition to advancing basic understanding of the electronic structure of molecules, study of non-Kekulé molecules has recently attracted much attention with an eye to allowing the rational design of molecular-based magnetic materials. As a result, much work at present is directed toward understanding both intramolecular and intermolecular exchange coupling between electrons in open-shell organic molecules.

One approach to studying intramolecular exchange of π-conjugated systems in a systematic manner involves variation of connectivity and molecular linker group -X- in a model compound wherein two unpaired electrons are coupled in the general structure shown in Chart I. The phenylnitrene moiety is a particularly convenient spin-bearing moiety in experimental studies of intramolecular exchange coupling. We described in earlier work[2] our AM1-CI semiempirical molecular orbital based computational modeling of polyradical and dinitrene models of exchange coupling. Based on our computational studies, we embarked on the experimental study of intramolecular exchange as a function of connectivity and linker group -X- for a variety of dinitrene model systems.

Chart I



1 2 3

In other work, we described a study of intramolecular exchange by cross-conjugating linker groups -X- = $\rangle C{=}CH_2$ and $\rangle C{=}O$.[3,4] In this contribution, we describe exchange interactions in three isomeric biphenyldinitrenes **1–3**, where -X- is a C–C bond linking two spin-bearing phenylnitrene units. The biphenyldinitrenes are of substantial interest, because their simple structural nature allows close proximity of the nitrene groups (both in terms of nitrene proximity and π-system conjugation length) but also allows phenyl ring torsion that can potentially complicate ground-state multiplicity expectations based upon qualitative models.

Synthesis

All dinitrenes were generated by photolysis of the corresponding diazides, the syntheses of which are shown schematically in Figure 1. In all cases, catalytic reduction of a dinitrobiphenyl compound, followed by diazonium salt formation and treatment with sodium azide, readily yielded the desired diazide. The diazides were very stable in the absence of light and could be kept for many months at −20 °C in the dark without apparent degradation of melting point, appearance, or ability to generate ESR spectra in a reproducible fashion.

[†] Amherst, MA.

[‡] Boston, MA.

(1) Berson, J. A. In *The Chemistry of Quinoid Compounds*; Patai, S., Rappaport, Z., Eds.; John Wiley, and Sons: New York, 1988; Vol. 2, pp 462–469.

(2) Lahti, P. M.; Ichimura, A. S. *J. Org. Chem.* **1991**, *56*, 3030.

(3) Ling, C.; Minato, M.; Lahti, P. M., van Willigen, H. *J. Am. Chem. Soc.* **1992**, *114*, 9959.

(4) Cf. also: Matsumoto, T.; Ishida, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 9952.

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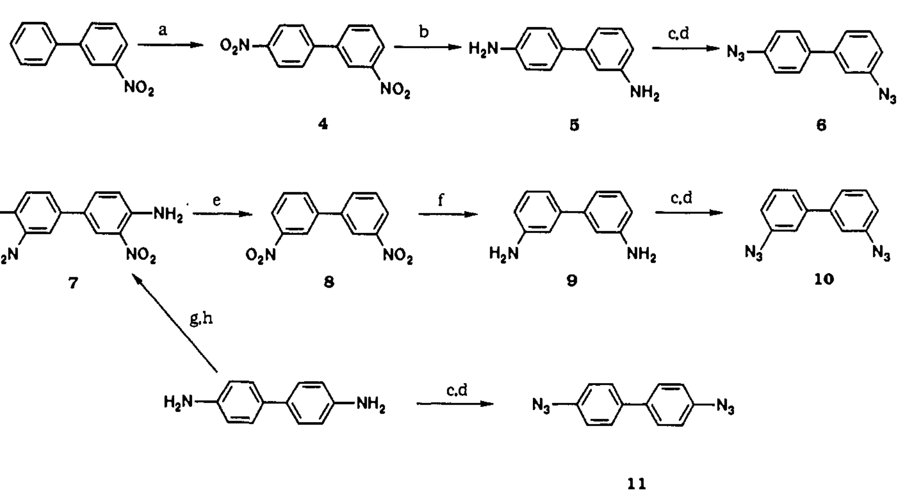

Figure 1. Synthesis of biphenyl diazide precursors to biphenyldinitrenes: (a) HNO_3/H_2SO_4; (b) 60 psi H_2, PtO_2, ethanol; (c) $NaBF_4$/aqueous $HCl/NaNO_2$ at −10 °C; (d) NaN_3/H_2O; (e) $NaNO_2$/aqueous H_2SO_4, then HOAc/EtOH/CuO; (f) $SnCl_2{\cdot}2H_2O$/EtOH; (g) $Ac_2O/HOAc/HNO_3$; (h) H_2SO_4/H_2O/reflux.

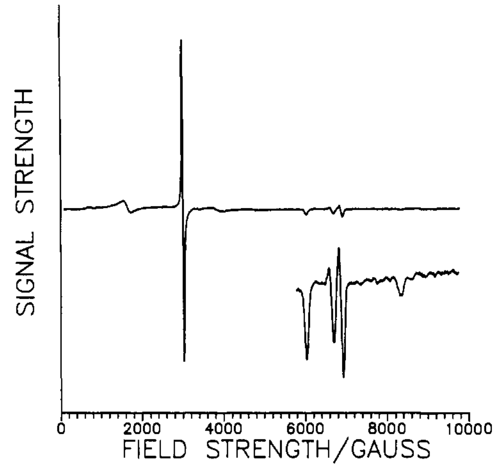

Figure 2. Electron spin resonance spectrum from photolysis of diazide **6** in 2-methyltetrahydrofuran at 77 K. Abscissa is in gauss; ordinate is in arbitrary units from the spectrometer digitizer. Spectrometer frequency ν_0 = 9.57 GHz. Peak assignments are described in the text.

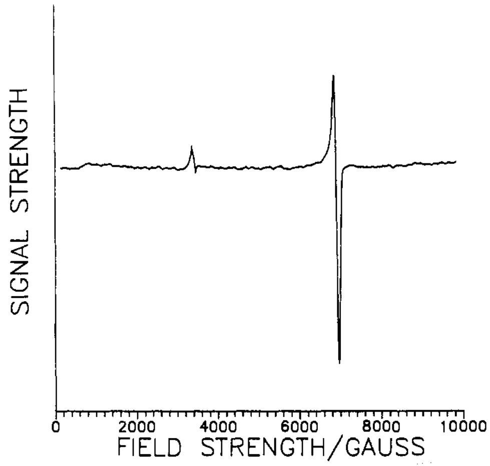

Figure 3. Electron spin resonance spectrum from photolysis of diazide **10** in 2-methyltetrahydrofuran at 77 K. Abscissa is in gauss; ordinate is in arbitrary units from the spectrometer digitizer. Spectrometer frequency ν_0 = 9.57 GHz. Peak assignments are described in the text.

Results

Photolysis of the various diazide precursors was carried out in degassed, frozen solutions at 77 K or below, using an Oriel 1000-W xenon arc lamp with Pyrex or 300–400-nm band-pass filters, or with a Lambda Physik XeCl excimer laser (308 nm). In photolyses of diazide **11**, the wavelength of irradiation did make some difference in the degree of production of one ESR peak; for the other diazides, no wavelength-dependent effect was noted for the types of conditions noted above.

Photolysis of diazide **6** at 77 K in Fluorolube, frozen 2-methyltetrahydrofuran, or poly(methyl methacrylate) matrices gave rise to the same ESR spectrum (except for variations in the $g = 2$ region due to radical impurities) described in a preliminary communication[5] and shown in Figure 2. Photolysis of diazide **10** at 77 K in 2-methyltetrahydrofuran gave rise to the ESR spectrum shown in Figure 3. Photolysis of diazide **11** at 77 K in 2-methyltetrahydrofuran gave rise to an ESR spectrum dominated by a very strong peak at about $g = 2$ in the ESR spectrum (Figure 4). This presumed radical impurity peak was present in a number of variants of the photolysis scheme used by us, regardless of the methods used to purify **11**. An ordinate-expanded version of the ESR spectrum from photolysis of **11** is also shown in Figure 4.

We also studied the behavior of the ESR peak intensities derived from **6**, **10**, and **11** as functions of temperature. Figure 5 shows a Curie–Weis plot of ESR signal intensity vs reciprocal absolute temperature for the 3010-G peak of the quintet spectrum of **1**. The diazide sample was photolyzed at temperatures of 60–70 K and maintained at this temperature for 15 min before analysis of the ESR spectral behavior. Previous work[6,7] had shown that diazide photolysis at very low (ca. 10 K) temperatures must be followed by annealing at 65 K to achieve usefully reproducible Curie law data. We found similar behavior in our experiments. However, our procedure of photolyzing at higher temperatures gave reproducible thermal behavior without the need for an extra annealing step.

Although as substantial number of photolyzed samples of disjoint diazide precursor **10** were analyzed, in no case was any reproducible spectral feature seen other than the major peaks in the regions of 3300–3400 and 6900 G shown in Figure 3. Even with gradual lowering of the temperature of a sample from 70 to 10 K at high spectral gain, no new peaks could be detected in the region of 1000–3500 G. In additional experiments, the 308-nm line of an excimer laser was used to photolyze a sample of **10** at 65 K until the intensity of the mononitrene peak at 6940 G no longer increased, followed by substantial further photolysis under the same conditions. Again, no change in the ESR spectral region of 1000–3500 G was detected under these "exhaustive

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[5] Minato, M.; Lahti, P. M. *J. Phys. Org. Chem.* **1991**, *5*, 459.

[6] Iwamura, H.; Murata, S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 33.

[7] Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 5547.

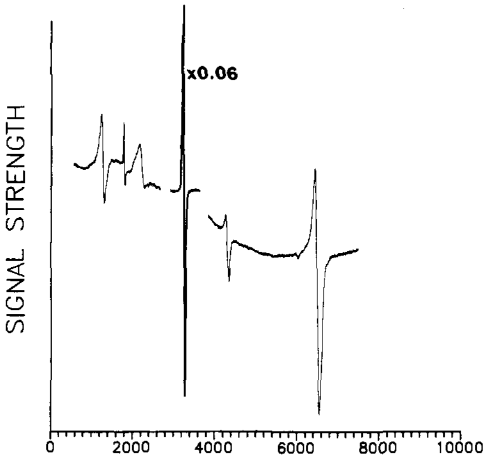

Figure 4. Electron spin resonance spectrum from photolysis of diazide **11** in 2-methyltetrahydrofuran at 77 K. Abscissa is in gauss; ordinate is in arbitrary units from the spectrometer digitizer. Spectrometer frequency ν_0 = 9.57 GHz. Peak assignments are described in the text.

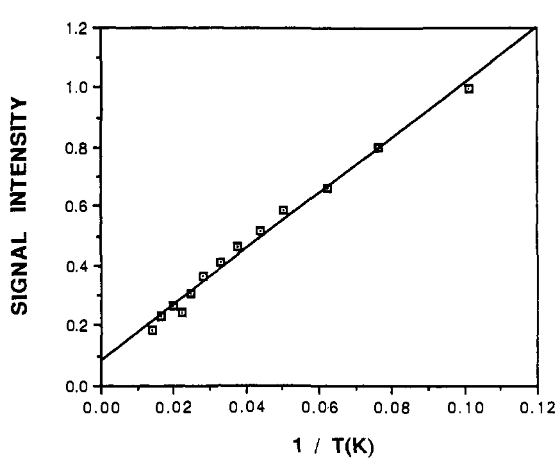

Figure 5. Curie–Weis plot of signal intensity for the peak at 3010 G in Figure 2 of dinitrene **1**. Abscissa is in reciprocal absolute temperature (K^{-1}); ordinate is in double-integrated signal intensity.

photolysis" conditions, nor were any peaks detected upon gradual cooling of this sample to 10 K.

Photolysis of **11** at 35 K with the 308-nm line of an excimer laser produced a spectrum that showed only the 1790-G (small, sharp), 3300-G, and 6500-G features shown in Figure 4. However, warming of the sample to 70 K also yielded the peaks attributable to triplet **3** (cf. Discussion section below). Upon cycling the sample temperature between 40 and 70 K, it was found that the thermal behavior of all peaks was quite reproducible, in that the 1790-, 3300-, and 6500-G peaks all increased with decreasing temperature, while the biradical triplet peaks were not observable at <50 K but grew as the temperature increased. A comparative plot of signal intensities for the peaks at 1790 and 1270 G is shown in Figure 6, the significance of which will be further discussed below.

Discussion

I. **Biphenyl-3,4′-dinitrene.** The spectrum from photolysis of **6** in Figure 2 shows a strong peak at 3010 G, a weak H_1 transition at 8350 G, and the presence of other several weak peaks that are consistent with the spectrum expected for quintet state dinitrene **1**. By methods described elsewhere,[8] the zero field splitting (zfs) parameters for **1** may be estimated as $|D/hc|$ = 0.153 cm^{-1} and $|E/hc|$ = 0.003 cm^{-1}, if we assume the peaks at 6030 and 8350 G to be the two highest field peaks for the quintet.[9] Two fairly small mononitrene peaks at 6680 and 6920 G correspond to single photocleavage of the 4- and 3-azide moieties, respectively. These peak positions compare well to the positions of the mononitrene $H_{x,y}$ peaks produced by us in photolyses of 4- and 3-azidobiphenyl and correspond to zfs parameters[10] of $|D/hc|$ = 0.925 and 1.018 cm^{-1}, respectively, with $|E/hc|$ being essentially zero as in most aromatic mononitrenes. Wasserman[8] previously described the 4- and 3-biphenylnitrene systems as having zfs $|D/hc|$ values of 0.9367 and 1.008 cm^{-1}, in reasonable agreement with the zfs values found in our work.

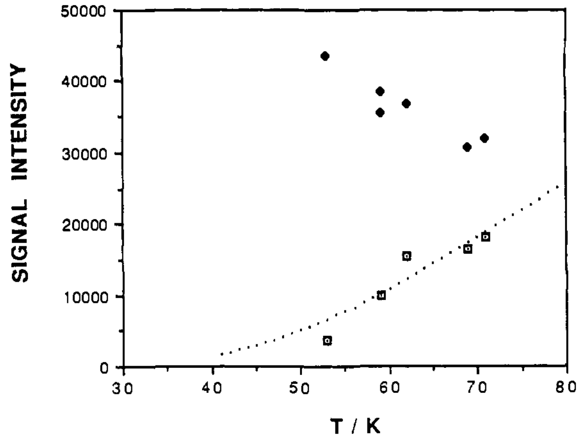

Figure 6. Thermal dependence of signal intensity for the peaks at 1270 and 1790 G in Figure 4. Abscissa is in absolute temperature (K); ordinate is in ESR signal intensity directly from the signal digitizer. □ are 1270-G points; ◆ are 1790-G points; dotted line is fit to eq 1 in the text with ΔE = −583 cal/mol.

As described in our preliminary report,[5] the ESR spectral pattern and temperature-dependent intensity behavior for the quintet **1** established this in all likelihood to be the ground-state spin multiplicity. While Berson pointed out the dangers of using Curie law ESR spectral behavior as the determinant of ground-state multiplicity,[1] the only alternative explanations to a quintet ground state for **1** would be (1) a near-exact energetic equivalence of the quintet state with another state (to within a few cal/mol) and (2) a substantial kinetic barrier to intersystem crossing that prevents relaxation of an ESR-active, excited quintet state to a state of different multiplicity. While the first alternative explanation cannot be disproved by our experimental data, our previous computational results appear to rule out ground-state degeneracy in **1**, regardless of its geometry. Berson and co-workers noted the formal possibility of the second alternative explanation in work upon the non-Kekulé hydrocarbon 1,2,4,5-tetramethylenebenzene,[11] but this also seems unlikely for quintet **1**, given the presence of a modest spin-orbit coupling effect due to the nitrogen atoms of the nitrene centers, which should promote intersystem crossing to the state of lowest multiplicity.

If we accept the Curie study of **1** as being consistent with a quintet ground state, we come to the conclusion that despite heteroatom substitution in **1**, the parity-based models are successful in predicting a high-spin ground state. In addition, it is possible that the biphenyl moiety in **1** is twisted, restricting conjugation. The energy barrier to biphenyl torsion is known to be low and the biphenyl system itself to have rings twisted 35° relative to one another.[12] AM1-CI computation indicates that

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[8] Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

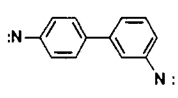
[9] In our earlier communication, we estimated the zfs parameters for **1** as $|D/hc|$ = 0.153 cm^{-1} and $|E/hc|$ = 0.019 cm^{-1}, in a manner analogous to Wasserman[8] that the second-highest field peak underlays the mononitrene peaks.

[10] Wasserman, E. *Prog. Phys. Org. Chem.* **1971**, *8*, 319.

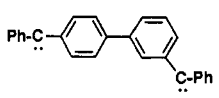
[11] Reynolds, J. H.; Berson, J. A.; Kumashiro, K.; Duchamp, J. C.; Zilm, K. W.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1992**, *114*, 763.

[12] Field, L. D.; Sternhell, S.; Tracey, A. S. *J. Am. Chem. Soc.* **1977**, *99*, 5249. Aroney, M.; Calerbank, K. E.; Pierens, R. K.; Chia, L. H. L. *J. Mol. Struct.* **1985**, *127*, 175.

Chart II



1



12

1 will remain a ground-state quintet even if substantially twisted, though by a reduced amount.[5] Unfortunately, we were unable to obtain the quintet–triplet energy gap for **1** from our experiments or from other experimental techniques available at present.

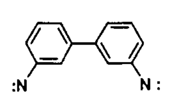
Itoh and co-workers reported the finding of a quintet ground state for the dicarbene **12** (Chart II), from the corresponding diazoalkane precursor) that is analogous to our dinitrene **1**. Quintet **12** has zfs parameters of $D/hc = 0.1256$ cm^{-1}, and $E/hc = -0.0058$ cm^{-1},[13] which are reasonably comparable to values observed by us for **1**. Despite the presence of heteroatoms in dinitrene **1**, and the possibility of extra delocalization onto the terminal phenyl rings in **12** by comparison to **1**, the parity rules predicting a high-spin ground state for the 3,4′-biphenyl linking group appear to hold for both of these. The topology of these systems, which favors high-spin ferromagnetic exchange, appears to dominate over factors that might tend to diminish or reverse the preference for a high-spin ground state in these systems.

II. Biphenyl-3,3′-dinitrene. The result obtained in the photolysis of the disjoint precursor **10** is extremely different from that in the photolysis of **6**. The ESR spectrum in Figure 4 from photolysis of diazide **10** is dominated by an intense mononitrene spectrum at 6940 G, corresponding to a zfs value of $|D/hc| = 0.996$ cm^{-1}. This resonance is very similar to the position expected by comparison to our own observations for photolysis of 3-azidobiphenyl, as well as to Wasserman's[10] analogous result. No other peaks besides those attributable to the mononitrene and to radical impurities (in the 3300–3400-G region) were observed under any conditions. Attempts at exhaustive laser photolysis of **10** at 308 nm and 65 K led to eventual maximization of the mononitrene ESR peak intensity but yielded no peaks attributable to a dinitrene over a temperature range of 20–70 K. Since no major difference was expected in photoefficiency for double photolysis of the two diazide precursors **6** and **10**, the spectral difference is consistent with a lack of quintet-producing exchange interactions in **2**. It seems highly unlikely that **10** alone of all the diazides studied by us and others yielded only mononitrene photolysis.

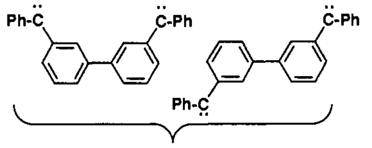
In an effort to discern whether the mononitrene intermediate formed in a presumably[14] sequential photolysis of diazide **10** might be diminished by further photolysis to an ESR-inactive singlet-state dinitrene **2**, we carried out a study of the mononitrene signal intensity as a function of photolysis time at 300–400 nm for both **10** and 3-azidobiphenyl. The purpose of irradiating the monoazide was to check for possible photobleaching of nitrene centers under these conditions upon extended photolysis. Both species gave monotonic increases in mononitrene ESR peak intensity, with eventual leveling out to a maximum intensity that did not downturn in over 20 additional min of irradiation. This negative result does not give any indication of ESR-inactive **2** but also does not rule out the presence of **2** as a pair of noninteracting nitrenes, or as a singlet formed by very rapid sequential double photolysis or by single-photon double photolysis.

Overall, our findings are in qualitative accord with the disjointness criterion of Borden and Davidson.[15] The apparent finding of very poor exchange between nitrenes in **2** is also consistent with our most recent AM1-CI computational results[16] showing a <10 cal/mol difference between the singlet, triplet, and quintet states of planar **2** (earlier results[2] showed a small favoring of a quintet state). Any degree of torsion about the 1–1′ central bond in **2** would serve to decrease further any exchange interactions between the nitrenes.

Chart III

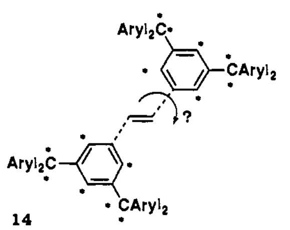


2

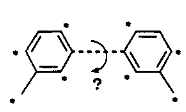


13

Chart IV



14
(perchlorinated)



2

Itoh and co-workers extensively studied by cryogenic ESR[17] and ENDOR[18] spectroscopy the disjoint 3,3′-connectivity for linkage of two phenylcarbene groups by a biphenyl linker unit. They found the system **12** (Chart III) to have an antiferromagnetically coupled singlet ground state having very low-lying, thermally accessible triplet and quintet states. Two triplet conformational isomers of **13** have zfs values of $D/hc = -0.29583$ cm^{-1} ($E/hc = 0.06032$ cm^{-1}) and $|D/hc| = 0.23895$ cm^{-1} ($|E/hc| = 0.06452$ cm^{-1}).[17] Two quintet isomers have zfs of $D/hc = 0.10349$ cm^{-1} ($E/hc = -0.01457$ cm^{-1}) and $D/hc = 0.08329$ cm^{-1} ($E/hc = 0.02114$ cm^{-1}).[17] The energetic near degeneracy of these states is consistent with the disjoint connectivity of this system and with a valence-bond picture (rather than a molecular pseudo-Hund's rule picture) of its bonding. Unfortunately, we were unable with our present results to compare the heteroanalogous system **2** to the dicarbene **13**, since we lacked direct evidence for the formation of **2**.

Assuming that dinitrene production does occur in our system, the lack of any spectrum other than the mononitrene is consistent either with a singlet–triplet and singlet–quintet gap that is too large to allow thermal population of the excited ESR active states, or with an exchange coupling so small that **2** acts as a pair of isolated mononitrenes. A recently studied stilbene-derived disjoint tetraradical system (**14**) has been described[19] as acting like a pair of isolated triplet biradicals, apparently due to the effect of disjointness and of geometric twisting (Chart IV). It is tempting to suggest that twisting in the central biphenyl 1,1′-bond could lead to nitrene isolation in disjoint **2**. If this is occurring, however, it appears that heteroatom effects in dinitrene **2** cause it to be different from dicarbene **13**, in which exchange interaction is sufficiently present that both triplet and quintet thermally populated spin states are identifiable.

III. Biphenyl-4,4′-dinitrene. Photolysis of **11** gives the spectrum in Figure 4, with a mononitrene peak at 6480 G in a position (zfs value $|D/hc| = 0.830$ cm^{-1}) analogous to the mononitrene peak

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[13] Itoh, K. In *Magnetic Molecular Materials, NATO ASI Series*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; p 67.

[14] Reiser, A.; Wagner, H. M.; Marley, R.; Bowes, G. *Trans. Faraday Soc.* **1967**, *63*, 3162.

[15] Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

[16] The method of computation was essentially that of ref 2, but with use of the active space keyword C.I. = (5,1) for quintet, triplet, and singlet dinitrene computations, using the MOPOC 6.0 program (J. J. P. Stewart, QCPE Program 455 (v6.0)). We thank Dr. Andrew Ichimura for communicating to us his improvement of the method of ref 2.

[17] Itoh, K. *Pure Appl. Chem.* **1978**, *50*, 1251.

[18] Okamoto, M.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K. *Chem. Phys. Lett.* **1990**, *173*, 265.

[19] Carilla, J.; Julia, L.; Riera, J.; Brillas, E.; Gariddo, J. A.; Labarta, A.; Alcala, R. *J. Am. Chem. Soc.* **1991**, *113*, 8281.

Figure 7. Simulation of the $\Delta M_s = 1$ and $\Delta M_s = 2$ regions of the ESR spectrum from 1000–5000 G of dinitrene **3**. Curve a is experimental; curve b is simulated using $|D/hc| = 0.189$ cm^{-1}, $|E/hc| = 0.00$ cm^{-1}, and $g_{iso} = 2.003$.

obtained from photolysis of 4-azidobiphenyl. The low-field position of the mononitrene peak is a good indication of the conjugation of the nitrene to the second phenyl ring, implying a reasonable degree of planarity. A $\Delta M_s = 2$ transition attributable to triplet biradical dinitrene **3** is visible at 1270 G. The perpendicular turning point $\Delta M_s = 1$ peaks expected of a triplet with nearly cylindrical symmetry might be seen using high spectrometer grain at 2230 (broad), and 4290 G, corresponding approximately to a biradical zfs parameter of $|D/hc| = 0.189$ cm^{-1}, with $|E/hc|$ being too small relative to the observed line width to be resolved. The biradical peaks at 1270, 2230, and 4290 G decreased in intensity with decreasing temperature, as shown for the 1270-G peak in Figure 6. Simulation of the $\Delta M_s = 1$ and $\Delta M_s = 2$ regions of the spectrum with $|D/hc| = 0.189$ cm^{-1} and $|E/hc| < 0.003$ cm^{-1} shows a good fit (Figure 7) to the observed spectrum, using a spectral simulation program upon the method described by Kottis and Lefebvre[20,21] and elaborated upon by Jain et al.[22] The peak at 1790 G in multiple experiments was produced in varying amounts relative to the other peaks, depending upon the wavelength of light used for photolysis of diazide **11**. In addition, the peak at 1790 G increased in intensity as temperature decreased from 77 K (Figure 6), while the biradical peaks decreased. As a result, while this peak might overlay the quite weak low-field z-transition of triplet biradical **3**, it is not actually part of the biradical spectrum.

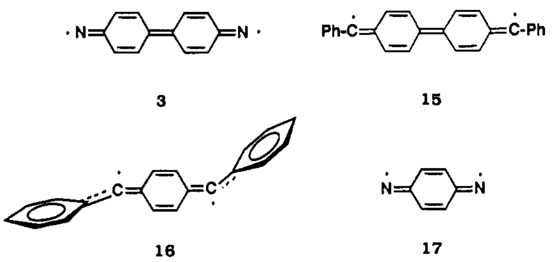
The decrease in intensity of the $\Delta M_s = 2$ peak of **3** unequivocally demonstrates this biradical to have a singlet ground state, for which we observed a thermally populated triplet state. Although the temperature range between the disappearance of signal and thawing of the 2-methyltetrahydrofuran matrix is small (50–80 K), we carried out a nonlinear least-squares fit for the intensity of the $\Delta M_s = 2$ peak as a function of temperature using eq 1, in

$$I = (C/T)[(3\exp(-\Delta E/RT))/(1 + 3\exp(-\Delta E/RT))] \qquad (1)$$

which ΔE is the singlet–triplet energy gap, R is 1.987 cal/mol·K, I is intensity, T is absolute temperature, and C is a constant chosen to scale the function to correspond to the data. The dotted line in Figure 6 shows our fit to the experimental data, where $\Delta E = -583 \pm 120$ cal/mol for a 95% confident fit to the data (the negative sign of ΔE signifies a singlet ground state).

The experimental finding of a singlet ground state for **3** is consistent with valence-bond theoretical expectations and with our recent semiempirical AM1-CI computations[16] showing **3** to be a quinonoidal biradical with a singlet–triplet (S–T) gap of 460–900 cal/mol, depending on the geometry used for the dinitrene. The planar benzenoid quintet dinitrene state of **3** lies rather higher in energy at this level of theory. The agreement of computation and experiment in this case was quite gratifying and justified ongoing efforts to correlate and further improve semiempirical computational schemes by comparison to experimental results for open-shell molecules.

Chart V



A number of other factors in the ESR spectrum derived from photolysis of diazide **11** are notable. First, in 2-methyltetrahydrofuran, all peaks save the monoradical peak at ca. 3300–3400 G are fairly modest in size, even upon extended photolysis. For photolysis through Pyrex at 77 K for 5 min, the mononitrene and biradical peaks are of similar intensity. For photolysis with an excimer laser at 308 nm, the mononitrene is substantially stronger than the biradical peaks. These two results, and the results of a previous UV–vis study of 4,4′-bis(aryl azides) by Reiser et al.,[14] suggest that a substantial amount of dinitrene **3** may be lost to secondary photolysis of the dinitrene. Reiser et al. suggested a secondary photoionization of **11** in cryogenic matrix when using light of wavelength <300 nm, as it could be monitored by production of highly colored impurities at >500 nm in the UV–vis spectrum. We found similar behavior in cryogenic UV–vis experiments with **11** in 2-methyltetrahydrofuran glasses, which gave a deep green color or brown color upon prolonged photolysis at 77 K. Brief photolysis of **11** through Pyrex or through an Oriel 300–400-nm band-pass filter gave only a reddish colored sample and a UV–vis spectrum very similar to that reported by Reiser et al. Photolysis at 308 nm with the excimer laser apparently was even more selective, giving rather more mononitrene relative to the monoradical peak than was the case for Pyrex-filtered photolysis. However, regardless of any method of purification or photolysis of **11**, the 3300–3400 G-monoradical peak was always dominant in these experiments.

We recently became aware of work by Yabe and co-workers,[23] which indicates that upon extending the duration of photolysis of diazide **11** in ether/isopentane matrix at 77 K, an ESR peak attributable to a bisected form of dinitrene **3** can be observed, as well as the quinonoidal triplet spectrum observed by us. We did not observe such behavior in our studies with **11** but observed analogous behavior in the 2,2′-dimethyl derivative of **11**, which must be bisected. Although the photochemistry of **11** was complicated by such issues, in the present study the triplet spectrum of **3** described above was readily attributable to a planar or near-planar quinonoidal form of **3**.

Both a Russian group[24] and the Itoh group[13] described a 4,4′-biphenyl linked system of phenylcarbene units (**15**, Chart V) that is the connectivity analogue to **3**. The Russian group found a triplet-state ESR spectrum upon photolysis of the corresponding bis(diazoalkane) precursor. The Itoh group also found a triplet ESR spectrum for **15** from the same reaction, with $|D/hc| =$

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[20] Kottis, P.; Lefebvre, R. *J. Chem. Phys.* **1963**, *39*, 393.

[21] Kottis, P.; Lefebvre, R. *J. Chem. Phys.* **1964**, *41*, 379.

[22] Jain, R.; Sonsler, M.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 1356. The ESR spectral simulation program described in this reference includes simulation of the $\Delta M_s = 2$ transition of the biradical spectrum. Cf. Eaton, S. S.; More, K. M.; Sawant, B. M.; Eaton, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 6560 for an example of the use of the $\Delta M_s = 2$ transition for finding $|D/hc|$ in biradical ESR spectra with large zfs.

[23] Ohana, T.; Kaise, M.; Nimura, S.; Kikuchi, O.; Yabe, A., to be submitted for publication. Cf. also: Ohana, T.; Kaise, M.; Yabe, A. *Chem. Lett.* **1992**, 1397.

[24] Derkach, V. I.; Lyalin, G. N. *Vestn. Leningr. Univ., Ser. 4: Fix. Khim.* **1979**, *4*, 48.

0.0403 cm^{-1} and $|E/hc|$ = 0.0007 cm^{-1}. This triplet was attributed to a thermally excited state lying above a singlet ground state, based upon a Curie study. We noted that the triplet $|D/hc|$ value of the dicarbene system is substantially smaller than the zfs $|D/hc|$ = 0.19 cm^{-1} value observed in our triplet dinitrene **3**. The smaller zfs for the dicarbene might be partly attributable to delocalization of the unpaired electron spin in the dicarbene onto the terminal phenyl rings, though the size of the effect seems rather large for it all to be due to delocalization. A similar trend is noticed in the comparison of zfs parameters for dicarbene **16** ($|D/hc|$ = 0.052 cm^{-1}, $|E/hc|$ < 0.002 cm^{-1}) and 1,4-phenylenedinitrene **17** ($|D/hc|$ = 0.171 cm^{-1}, $|E/hc|$ = 0.004 cm^{-1}). Chart V shows how the terminal phenyl rings of the dicarbenes could delocalize unpaired electron spin in a fashion that is not available to corresponding quinonoidal dinitrene systems. AM1 UHF triplet level computations by us show the dicarbene molecules to have phenyl rings twisted relative to one another, in a manner that could permit delocalization of both electrons on each carbene center. ENDOR spectroscopy of **16** shows substantial spin density on the terminal phenyl rings,[25] consistent with the computational picture of a twisted ring system that allows delocalization of the nominally "σ" type electrons of the carbene sites onto this ring.

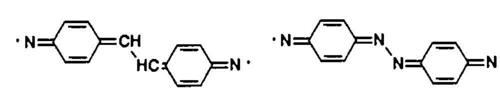
It is worth noting that the zfs of $|D/hc|$ = 0.19 cm^{-1} in our system **3** is also somewhat larger than the value of 0.171 cm^{-1} observed[26] in the smaller homologue **17**. We found this surprising, given that the isolated electrons in **17** are nominally closer together than in **3**, 5.5 Å vs 9.7 Å, if the interelectronic distance is taken to be the distance between the nitrogens in AM1 UHF triplet calculations. For a purely dipolar approximation to the zfs caused by interaction of two electrons in the triplet state, $|D/hc|$ is proportional to the inverse cube root of the interelectronic distance r_{ij} in eq 2,for which β is the Bohr magneton in appropriate units.

$$|D/hc'| = 3\beta g/r_{ij}^3 \qquad (3\beta = 1.299\ \text{cm}^{-1}\cdot\text{Å}^3) \tag{2}$$

The zfs $|D/hc|$ parameter should decrease sharply as interelectronic distance increases. Thus, one might expect a decrease in zfs for **3** relative to **17**. However, the zfs value for **17** is already substantially larger than would be expected for a purely dipolar approximation with completely localized electrons on the terminal nitrogens. Using a nitrogen–nitrogen distance of 5.5 Å for **17**, if one assumes that the two unpaired electrons are exactly at the internuclear distance, the dipolar approximation of eq 2 yields a zfs of $|D/hc|$ = 0.016 cm^{-1}, rather than the 0.171 cm^{-1} observed. Ab initio computations by us[27] at the 6-31G* SCF-SDCI level for **17** show negligible spin polarization in the σ-framework electrons of **17**, apparently arguing against a simple σ-delocalization effect[28] that could have increased the zfs value within the purely dipolar approximation.

Further study of localized quinonoid dinitrenes such as **3** and **17** is needed to clarify the relationship between their structures and zfs values. For instance, we found that $|D/hc|$ value of the triplet state of 4,4′-(*E*)-stilbenedinitrene **18** to be 0.121 cm^{-1}, substantially larger than the value of 0.059 cm^{-1} reported by Singh and Brinea[26] for the very close analogue 4,4′-azobenzenedinitrene **19** (Chart VI). We believe the zfs parameters of quinonoidal dinitrenes to be strongly influenced by small changes in spin density distribution, induced by the relative energy spacings, by electronic natures of various low-lying states of these unusual molecules, and by the relative electronegativities of the atoms bearing unpaired spins. Any factors that influence spin density distribution might therefore influence the zfs here, such as geometric and torsional changes or π-isoelectronic heteroatom-for-carbon substition. We are studying the variation in ground-state multiplicity and ESR zfs for a variety of quinonoid dinitrenes of varying chain length,[29] in hopes of being able to clarify these effects.

Chart VI



18 19

Summary and Conclusions

The study of ground-state spin multiplicity of open-shell systems consisting of two phenylnitrene moieties linked together to make different connectivity isomers has been studied. Biphenyl-3,4′-dinitrene is a ground-state quintet molecule, despite the possibility that it is twisted and somewhat deconjugated about its central 1,1′-bond. This result is in agreement with AM1-CI semiempirical molecular orbital computations showing biphenyl-3,4′-dinitrene (**10** to be a ground-state quintet. Attempts to produce biphenyl-3,3′-dinitrene (**2**) gave no ESR or UV–vis spectral evidence directly attributable to this species, despite observation of radical impurities and a mononitrene resonance; **2** is therefore believed to be a ground-state singlet or isolated bis(arylnitrene) system. Biphenyl-4,4′-dinitrene (**3**) is a quinonoidal ground-state singlet biradical in 2-methyltetrahydrofuran glass with a thermally accessible triplet state, in agreement with qualitative and AM1-CI computational considerations.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work (PRF #25968-AC4). This work was also partly supported by the National Science Foundation (CHE 9204695). We are grateful to Dr. Akira Yabe and his co-workers for communicating to us in advance of publication their results on extended photolysis of biphenyl-4,4′-diazide in ethanol/pentane matrices. We thank Prof. Dennis Dougherty for providing us with his group's computer program for simulation of randomly oriented triplet ESR spectra and Prof. Takeji Takui for stimulating conversations concerning the ESR spectroscopy of dinitrenes and dicarbenes.

Experimental Section

General. Unless otherwise described below, all reagent chemicals were used as received from Aldrich Chemical Company. 2-Methyltetrahydrofuran was distilled from calcium hydride and tetrahydrofuran from potassium/benzophenone, both under argon. All reactions were run under dry nitrogen atmosphere unless otherwise indicated.

UV–vis spectra were obtained on a Shimadzu UV-260 double beam spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1420 spectrophotometer and were referenced against polystyrene at 1601 cm^{-1}. ^{1}H NMR spectra were obtained on an IBM Instruments NR-80A Fourier transform spectrometer and were referenced against internal tetramethylsilane on the δ scale in parts per million. Chemical analysis were performed by the University of Massachusetts Microanalytic Laboratory.

Electron spin resonance (ESR) spectra by ESR method A were obtained on a Bruker ESP-300 X-band spectrometer interfaced to a standard Bruker data system allowing multiscan spectral digitization and analysis. ESR peak positions are reported in units of glass (10 G = 1 mT); peak intensities were obtained by computer-aided double integration using standard Bruker software routines. ESR method B spectra were obtained on a Varian E-9 X-band spectrometer interfaced to an IBM-AT personal computer with ASYST software for ESR data acquisition and manipulation.

3,4′-Dinitrobiphenyl (4). This compound was synthesized in satisfactory yield and purity by the method of Blakey and Scarborough.[30]

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(25) Teki, T.; Sato, K.; Okamota, M.; Yamashita, A.; Yamaguchi, Y.; Takui, T.; Kinoshita, T.; Itoh, K. *Bull. Magn. Reson.*, in press. We thank Prof. Takeji Takui and Prof. Koichi Itoh for a preprint describing this work.

(26) Singh, B.; Brinen, J. S. *J. Am. Chem. Soc.* **1971**, *93*, 540.

(27) Ichimura, A. S. Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1992. Ichimura, A. S.; Lahti, P. M., to be published.

(28) Trozzolo, A. M.; Murray, R. W.; Smolinsky, G.; Yager, W. A.; Wasserman, E. *J. Am. Chem. Soc.* **1963**, *85*, 2526.

(29) Minato, M.; Lahti, P. M., to be published.

(30) Blakey, W.; Scarborough, H. A. *J. Chem. Soc.* **1927**, 3000.

3,4′-Diaminobiphenyl (5). A mixture of 1.0 g (41 mmol) of **4** and 0.2 g (0.88 mmol) of platinum oxide in 20 mL of ethanol was stirred under 60 psi of hydrogen overnight and filtered, and the solvent was removed. The crude solid product was redissolved in diethyl ether, dried over magnesium sulfate, filtered, and recovered by solvent evaporation to give 0.7 g (88%) of yellow solid **5** with mp 73–75 °C. This material was sufficiently pure for use in the subsequent diazotization step.

3,4′-Diazidobiphenyl (6). A suspension of 0.68 g (37 mmol) of **5** in 3.6 mL of water and 2.1 mL of concentrated HCl was heated to 80–90 °C with stirring to effect dissolution, cooled to 0 °C in an ice bath, and treated dropwise with a solution of 1.1 g (15.9 mmol) of sodium nitrite in 2.3 mL of water. After being stirred for 1 h at 0 °C, the solution was filtered, recooled to 0 °C, treated with a solution of 1.0 g (15.4 mmol) of sodium azide in 2.3 mL of water, and then stirred for 15 min. The resultant precipitate was collected by filtration, dissolved in diethyl ether, dried over magnesium sulfate, and recovered by removal of solvent under vacuum. The product was 0.81 g (92%) of **6** as an off-white solid with mp 45–46 °C. Anal. Calcd: C, 61.0; H, 3.4; N, 35.5. Found: C, 61.1; H, 3.4; N, 34.3. IR (KBr, cm^{-1}): 2120 (s) and 2090 (s, $N{=}N{=}N$ str). UV–vis (λ_{max} [ϵ], nm [$M^{-1}\,cm^{-1}$]): 265 [16 000].

4,4′-Amino-3,3′-dinitrobiphenyl (7). To a mixture of 7.5 mL of acetic anhyride and 10.5 mL of acetic acid was added 1.5 g (8.14 mmol) of benzidine (CAUTION: cancer suspect substance!). The mixture was heated on a steam bath for 15 min with agitation to yield a dark brown suspension of the benzidine diacetamide. The crude diacetamide was then heated in an oil bath to 100 °C and 2.9 mL of concentrated nitric acid carefully added dropwise with stirring. As the mixture began to boil, the flask was removed from the oil bath and cooled in ice water. Filtration of the resultant reaction mixture gave a solid that was thoroughly washed with water and recrystallized from nitrobenzene to give 1.1 g (37%) of 3,3′-dinitrobenzidine diacetamide as a light yellow powder that was sufficiently pure to use in the following deacylation step.

To a flask containing 4.3 mL of concentrated sulfuric acid and 1.1 mL of water was added 1.1 g (3.07 mmol) of 3,3′-dinitrobenzidine diacetamide. The flask was heated to 100 °C with an oil bath for 1 h under reflux and poured into water. The resultant reaction mixture was filtered and the solid washed with water, dilute aqueous ammonia, and water. The solid was then recrystallized from aniline to give 0.83 g (31% from benzidine) of **7**, a bright orange powder with mp 285–285.5 °C (lit.[31] mp 275 °C).

3,3′-Dinitrobiphenyl (8). In a 125-mL Erlenmeyer flask were mixed 0.48 g (6.96 mmol) of sodium nitrite and 4.8 mL of concentrated sulfuric acid. The flask was then carefully warmed to 70 °C with stirring to dissolve the solids. This solution was then cooled to 10 °C, and 0.8 g (2.9 mmol) of **7** was added portionwise, followed by stirring for 1 h at 10 °C, addition of 4.8 mL of glacial acetic acid, and stirring for 15 min at 10 °C. Next, 32 mL of ethanol was added cautiously to the reaction, followed by 0.24 g of cupric oxide (bubbling). The mixture was stirred for 30 min, diluted with 30 mL of water, and filtered. The solid crude product was dissolved in chloroform and again filtered. The chloroform solution was dried over a anhydrous magnesium sulfate and evaporated to give 0.6 g (74%) of light yellow **8**, mp 170–175 °C (lit.[31] mp 200 °C).

3,3′-Diaminobiphenyl (9). In a 35-mL round bottom flask were placed 1.2 g (4.91 mmol) of **8** and 1.8 g of stannous chloride dihydrate in 3.3 mL of absolute ethanol. The flask was purged with nitrogen and heated with an oil bath to 70 °C for 1 h. After cooling to room temperature, the reaction mixture was poured onto cracked ice, neutralized to pH 7–8 with 5% aqueous sodium bicarbonate, and extracted with ethyl acetate. The organic phase was washed with brine, treated and charcoal, and dried over anhydrous sodium sulfate. The solvent was then removed to give 0.5 g (59%) of **9** as a light tan solid with mp 106–110 °C (lit.[31] mp 92–94 °C).

3,3′-Diazidobiphenyl (10). A solution of 0.86 g (7.8 mmol) of sodium tetrafluoroborate in 3.5 mL of water and 3.6 mL of concentrated hydrochloric acid was cooled with a dry ice/chloroform bath to −10 °C. In a separate flask, 0.54 g of **9** (2.9 mmol) was added portionwise to 0.43 g (6.2 mmol) of sodium nitrite in 6 mL of water to give a solution of bis(diazonium) salt. The diazonium salt containing solution was then added to the sodium tetrafluoroborate solution, maintaining the reaction temperature below −10 °C. After this addition, the mixture was left to stir in the cold bath for 20 min and then suction filtered. The collected solid was washed with water and then ether and air-dried to give 0.4 g (36%) of 3,3′-biphenylbis(diazonium) ditetrafluoroborate as a grey powder.

The bis(diazonium) salt was then added in small portions with stirring to a solution of 0.17 g (2.6 mmol) of sodium azide in 13.2 mL of water, which was in a flask that was cooled at 0 °C with an ice bath and protected from light by being covered with aluminum foil. After addition, the reaction was stirred at 0 °C for 30 min. The resultant mixture was filtered and the collected solid dissolved in diethyl ether. The ether solution was dried over anhydrous magnesium sulfate, treated with charcoal, filtered, and evaporated to give a white solid. The crude compound was redissolved in ether, filtered through a plug of silica gel, and collected by evaporation to give 0.15 g (22% from **9**) of diazide **10**, mp 58–59 °C. Anal. Calcd: C, 61.0; H, 3.4; N, 35.5. Found: C, 60.8; H, 3.5; N, 33.5. IR (KBr, cm^{-1}): 2140 (w) and 2110 (s, $N{=}N{=}N$). UV–vis (λ_{max} [ϵ], nm [$M^{-1}\,cm^{-1}$]): 245 [49 600], 295 [shoulder, 6500].

4,4′-Diazidobiphenyl (11). To a flask containing 6.7 mL of water and 6.7 mL of concentrated hydrochloric acid was added 1.6 g (14.6 mmol) of sodium tetrafluoroborate. The resultant solution was cooled in a limited dry ice/chloroform bath to −10 °C. In a separate flask, 1.0 g (5.43 mmol) of benzidine (CAUTION: cancer suspect agent!) was added portionwise to 0.80 g (11.6 mmol) of sodium nitrite in 11 mL of water to give a solution of bis(diazonium) salt. The diazonium salt containing solution was then added to the sodium tetrafluoroborate solution, maintaining the reaction temperature below −10 °C. After this addition, the mixture was left to stir in the cold bath for 20 min and then suction filtered. The collected solid was washed with water and then ether and air-dried to give 1.1 g (53%) of grey, powdery 4,4′-biphenylbis(diazonium) ditetrafluoroborate.

The bis(diazonium) salt was then added in small portions with stirring to a solution of 0.47 g of sodium azide in 36 mL of water, which was in a flask that was cooled at 0 °C with an ice bath and protected from light by being covered with aluminum foil. After addition, the reaction was stirred at 0 °C for 30 min. The resultant mixture was filtered and the collected solid dissolved in diethyl ether. The ether solution was dried over anhydrous magnesium sulfate, treated with charcoal, filtered, and evaporated to give 0.25 g (20% from benzidine) of diazide **11**, mp 116–118 °C (lit.[14] mp 127–128 °C). Anal. Calcd: C, 61.0; H, 3.4; N, 35.5. Found: C, 61.1; H, 3.8; N, 33.4. IR (KBr, cm^{-1}): 2110 (s, $N{=}N{=}N$). UV–vis (λ_{max} [ϵ], nm [$M^{-1}\,cm^{-1}$]): 297 [36 700].

Cryogenic Temperature Photolyses of Diazides. Cryogeniic ESR spectra were obtained in three manners: (1) in a Suprasil liquid nitrogen dewar (Wilmad Glass) for 77 K fixed temperature measurements; (2) with an APD Cryogenics CS-202 Displex closed cycle circulating helium cryostat; (3) with an Oxford Instruments DCT2 liquid helium ESR cryostat.

All 77 K fixed temperature measurements were obtained using method 1. The appropriate diazide precursor was quickly weighed out into a aluminu foil-wrapped vial and dissolved in purified, degassed 2-methyltetrahydrofuran, avoiding as much as possible any exposure to room light, which tends to turn the diazide reddish. About 500 μL of solution was placed in a quartz 4-mm o.d. ESR tube, frozen and evacuated to less than 0.05 Torr, and subjected to a 3-fold freeze–thaw purging. The tube was then placed in a transparent Suprasil ESR dewar, frozen with liquid nitrogen, and irradiated through a Pyrex cylindrical filter or 300-400-nm band-pass filter with a 1000-W xenon arc lamp at a distance of about 10 cm for 1–5 min. The resulting frozen, glassy solution (typically yellow or reddish) was placed in the ESR spectrometer cavity with the dewar and the spectrum recorded at about 9.6 GHz.

For method 2, the APD Cryogenics CS-202 Displex cooling head was attached to a mobile cart holding a vacuum line capable of attaining 5 μTorr. A particular diazide sample was prepared as a mull in fluorolube/dichloromethane, the dichloromethane removed under vacuum, the mull smeared on the sample spindle, the sample chamber evacuated to less than 0.01 mTorr inside a standard APD Cryogenics DMX-15 ESR Suprasil shroud, and the sample cooled to 60–70 K for photolysis of the diazide. ESR spectral sample holders included an APD Cryogenics commercially available copper spindle for solid samples and a Suprasil optically transparent vacuum tube shroud. The temperature of the samples in method 2 could be monitored at the base of the Displex cooling stage, using an iron-doped gold–chromel thermocouple (Scientific Instruments, Inc. Model CG07FC-4). A correction to this nominal temperature could then be applied, based upon calibration experiments in which an additional thermocouple was attached to the portion of the sample tube that was to be situated within the ESR sample cavity. This method is best for samples that give strong ESR signals, such as diazide **1**.

For method 3, temperatures were monitored using a Au(0.3% Fe doped)–chromel thermocouple placed just below the sample position in the Oxford Instruments DCT2 cryostat, which was emplaced in a Varian

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(31) Barker, C. C.; Casson, F. D. *J. Chem. Soc.* **1953**, 4184.

E-9 ESR spectrometer X-band cavity. The temperature readings with sample tubes in place were calibrated prior to each sample use, by measuring the temperature at the actual position of the sample in the ESR cavity, using a Lake Shore Cryotronics Ga-Al-As calibrated diode sensor (Model XTG-100FP-4D-3).

Curie Analyses of Dinitrenes. Using sample preparation method 2 above, the sample was cooled to 77 K and irradiated for 1–5 min through a Pyrex tube at a distance of 10 cm using a 1000-W Kratos xenon arc lamp. The sample was then cooled to 10 K and maneuvered into the spectral cavity of a Bruker ESP-300 X-band spectrometer and ESR spectral collection commenced. We used a microwave power setting of ≤500 μW to avoid signal saturation effects. All spectra for a Curie law analysis was obtained with an identical number of scans and with identical microwave power settings. Reproducibility of signal intensities was checked by raising and lowering the temperature in the region of 10–70 K, once the sample was produced.

For method 3, the Curie law procedure was identical to that just described for method 2, save that the samples were frozen and degassed under vacuum in 3-mm o.d. quartz tubes, placed in the cavity of a Varian E-9 ESR spectrometer, cooled to 60–65 K by the cryostat, photolyzed by ca. 1800 pulses from a XeCl excimer laser (Lambda Physik EMG 103 MSC, λ = 308 nm, pulse power at sample ca. 50 mJ), and then examined spectroscopically as described in the previous paragraph.

After spectra were obtained, double integration was carried out using standard Bruker software. Plots of double integration intensity vs corrected temperature were analyzed by nonlinear least-squares methods.