

INTRAMOLECULAR EXCHANGE COUPLING OF ARYLNITRENES BY OXYGEN

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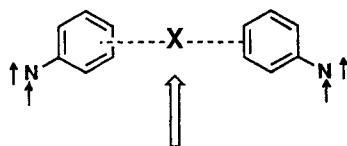
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A series of m,n' -diazidodiphenyl ethers ($m \leq n$, $m = 3, 4$; $n = 3, 4$) was photolyzed at 77 K in frozen, glassy 2-methyltetrahydrofuran matrices to generate the corresponding diphenyl ether m,n' -dinitrenes for study by electron spin resonance (ESR) spectroscopy. 3,4'-Diazidodiphenyl ether gave an ESR spectrum dominated by a mononitrene peak with $|D/hc| = 0.972 \text{ cm}^{-1}$, and also showed a weak dinitrene quintet spectrum with $|D/hc| = 0.162 \text{ cm}^{-1}$ having ESR spectral intensity vs temperature dependence (Curie law) consistent with either a high-spin ground state or a very small singlet–quintet gap. Di(3-azidophenyl) ether gave a strong mononitrene peak with $|D/hc| = 0.996 \text{ cm}^{-1}$ and a quintet dinitrene ESR spectrum ($|D/hc| = 0.162 \text{ cm}^{-1}$) which exhibited non-linear Curie law intensity behavior consistent with the quintet being a thermally populated excited state 40 cal mol^{-1} above a singlet ground state. Di(4-azidophenyl) ether gave a strong mononitrene peak with $|D/hc| = 0.961 \text{ cm}^{-1}$, but no observable spectrum related to a high-spin open-shell dinitrene. The results are consistent with oxygen being a weak exchange coupling linker in pi-conjugated open-shell molecules. The observed ground-state spin multiplicities are in accord with qualitative superexchange and connectivity models, despite any perturbations due to resonance effects between the oxygen linker and p -nitrene sites.

INTRODUCTION

The study of intramolecular exchange by using spin-carrying groups linked by various exchange coupling linker groups (Scheme 1) has been pursued by a number of groups, as part of recent efforts to understand exchange in organic molecules and to design organic and organometallic materials with novel bulk magnetic properties. We^{1–5} as well as others^{6–8,9} have pursued the study of bis(arylnitrenes), in which the spin-carrying group of Scheme 1 is an aryl mononitrene and the linker —X— is varied. As part of this study, we report here experiments aimed at generation and electron spin

resonance (ESR) spectroscopic examination of the oxygen-linked bis(arylnitrenes) 1–3 (Figure 1), via cryogenic photolysis of the appropriate diazide precursors 4–6. (As this work was being finalized, we became aware that Yabe and co-workers were independently working on the related dinitrenes linked by two-electron, one center —X— moieties, including the 3,4'- and 4,4'-dinitrenes linked by oxygen.¹⁰ Their results at 77 K described in the abstract were very similar to those obtained by us up to that time, and those described by us in this paper for 1 and 3. These workers have also investigated the diphenylsulfide dinitrenes, for which results are in some aspects interestingly different from those obtained for the diphenyl ethers.¹¹)



**EXCHANGE
LINKER**

Scheme 1

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EXPERIMENTAL

General. All chemicals were obtained from Aldrich Chemical unless stated otherwise. 2-Methyltetrahydrofuran was distilled from lithium aluminum hydride and tetrahydrofuran from potassium–benzophenone, both under argon.

Ultraviolet–visible spectra were obtained on a Shimadzu UV-260 double-beam spectrometer, and tetrahydrofuran was used as a solvent in all measurements. Infrared spectra were obtained on a Perkin-Elmer 1420 spectrophotometer, and were referenced

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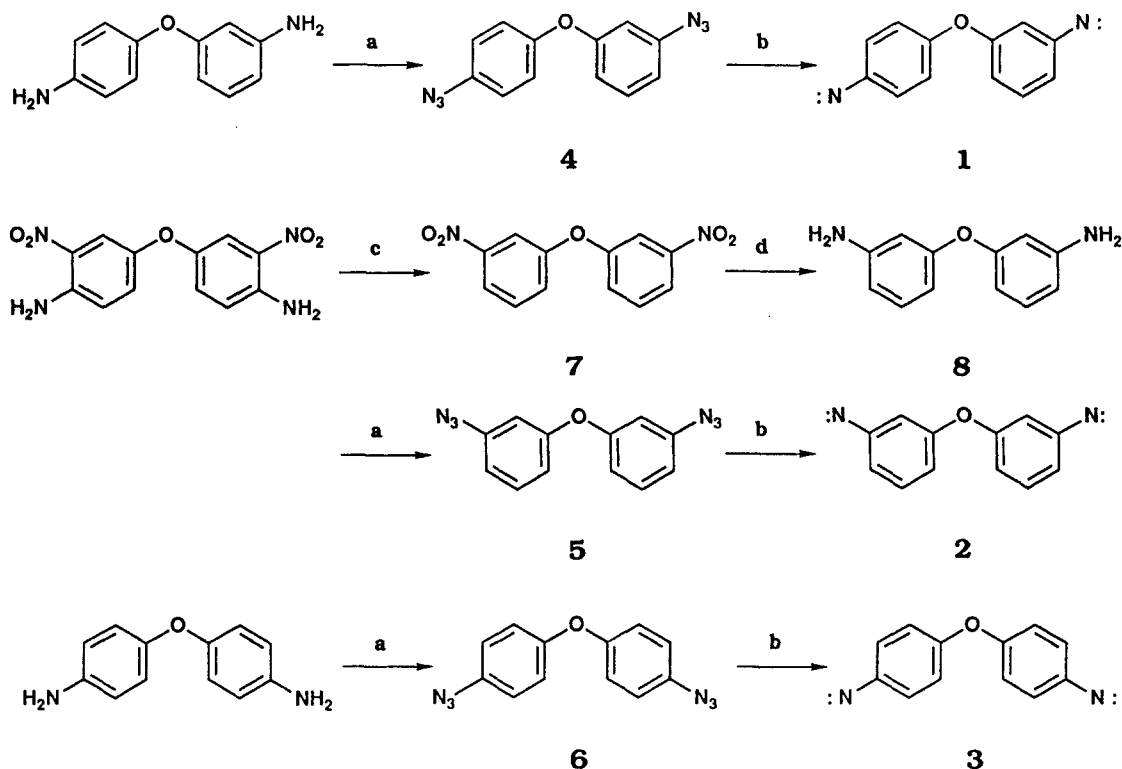


Figure 1. Synthesis of diazide precursors 4–6. a, Aq conc. HCl/NaNO₂, then NaN₃; b, 77 K photolysis at 300–400 nm in 2-MeTHF; c, conc. H₂SO₄/NaNO₂, then HOAc/abs. EtOH/CuO; d, SnCl₂·2H₂O/abs. EtOH/70 °C

against polystyrene at 1601 cm⁻¹. ¹H NMR spectra were obtained on an IBM Instruments AC-80A Fourier transform spectrometer, and were referenced against internal tetramethylsilane on the δ scale in ppm. Chemical analyses were performed by the University of Massachusetts Microanalytic Laboratory. Melting points are uncorrected.

3,4'-Diazidodiphenyl ether (4). In a 50 ml round-bottomed flask were placed 4.0 ml of distilled water, 2.3 ml of concentrated hydrochloric acid and 1.0 g (5.0 mmol) of powdered 3,4'-diaminodiphenyl ether (Chriskev). The mixture was heated to 70 °C in an oil-bath to dissolve all solids, then cooled in an ice-bath. The mixture was treated dropwise with a solution of 0.73 g (11 mmol) of sodium nitrite in 2.5 ml of distilled water while stirring, then stirred for an additional 1 h in the ice-bath. The mixture was next treated with a solution of 0.65 g (10 mmol) of sodium azide in 2.5 ml of distilled water. The mixture was then stirred for an additional 20 min. The product was extracted with diethyl ether, then the combined ether solution was treated with decolorizing charcoal and dried over mag-

nesium sulfate. The solvent was evaporated to give 0.57 g (45%) of light-brown liquid. Further purification was not carried out owing to significant instability of the material. Analysis: calculate for C₁₂H₈N₆O, C 57.15, H 3.20, N 33.31; found, C 56.29, H 3.19, N 33.50%. ¹H NMR (200 MHz, acetone-*d*₆): δ 6.68 (1 H, pseudo t, *J* = 2.1 Hz), 6.79 (1 H, ddd, *J* = 8.2 Hz, *J*' = 2.3 Hz, *J*'' = 0.9 Hz), 6.87 (1 H, ddd, *J* = 8.2 Hz, *J*' = 2.3 Hz, *J*'' = 0.9 Hz), 7.14 (br s, 4 H), 7.42 (1 H, pseudo t, *J* = 8.1 Hz). IR (neat; cm⁻¹): 2130 (s, —N=N=N), 1225 (s, C—O). UV-visible (λ_{max} [ε]; nm [l mol⁻¹ cm⁻¹]): 253 [25 200], 257 [25 000].

3,3'-Dinitrodiphenyl ether (7). In a 50-ml Erlenmeyer flask were placed 10 ml of concentrated sulfuric acid and 1.02 g (14.8 mmol) of sodium nitrite. The flask was heated to 70 °C in an oil-bath to dissolve solids, then cooled in an ice-bath. The temperature was kept at 10 °C and 2.0 g (6.9 mmol) of 4,4'-diamino-3,3'-dinitrodiphenyl ether (Polyscience) were added to the flask and stirred for 1 h. The solution was treated with 10.2 ml of acetic acid and the mixture was further

stirred for 15 min. Then 68.2 ml of absolute ethanol were added, followed by 0.52 g of copper(II) oxide (gas evolution was observed). The mixture was stirred for 1 h and 63.9 ml of distilled water were added. The resultant precipitate was collected by filtration and dried and the residue was dissolved in chloroform and dried over magnesium sulfate. The solvent was evaporated to give 1.31 g (73%) of yellow solid with m.p. 122–125°C. This material was of sufficient purity to use in the next step. ¹H NMR (200 MHz, acetone-*d*₆): δ 7.60 (2 H, ddd, *J* = 8.2 Hz, *J'* = 2.3 Hz, *J''* = 1.2 Hz), 7.77 (2 H, pseudo t, *J* = 8.2 Hz), 7.93 (2 H, pseudo t, *J* = 2.3 Hz), 8.11 (2 H, ddd, *J* = 8.2 Hz, *J'* = 2.3 Hz, *J''* = 1.2 Hz). IR (KBr; cm⁻¹): 1520 (s, NO₂), 1240 (s, C—O).

3,3'-Diaminodiphenyl ether (8). In a 50-ml round-bottomed flask were placed 20 ml of absolute ethanol and 11.2 g (49.6 mmol) of tin (II) chloride dihydrate. The flask was purged with nitrogen and 1.31 g (5.03 mmol) of **7** were added. The mixture was placed in an oil-bath set at 70°C and stirred for 30 mins, cooled to room temperature and poured over crushed ice. The pH of the mixture was adjusted to 7–8 by the addition of 5% sodium hydrogencarbonate solution, and the product was extracted with ethyl acetate. The organic solution was washed with brine, treated with decolorizing charcoal and dried over sodium sulfate. The solvent was evaporated to give 0.91 g (90%) of brown, chunky solid with m.p. 76–78°C. This material was used as soon as possible in the next step. ¹H NMR (80 MHz, DMSO-*d*₆): δ 3.2 (br s, NH₂ protons), 6.0–6.5 (m, Ar-H, 6 H), 6.95 (pseudo t, *J* = 7.1 Hz, 2 H). IR (KBr; cm⁻¹): 3410 and 3330 (s, NH₂), 1285 (s, C—O).

3,3'-Diazidodiphenyl ether (5). In a 25-ml round-bottomed flask were placed 3.7 ml of distilled water and 2.1 ml, of concentrated hydrochloric acid, followed by 0.91 g (4.5 mmol) of **8**. The mixture was placed in an ice-bath and treated dropwise with a solution of 0.66 g (9.6 mmol) of sodium nitrite in 2.4 ml of distilled water. The mixture was stirred in the ice-bath for 1 h, then treated with a solution of 0.58 g (8.9 mmol) of sodium azide in 2.4 ml of distilled water. The mixture was stirred for additional 15 min and extracted with methylene chloride. The organic layer was dried over magnesium sulfate. The solvent was evaporated to give 0.40 g (35%) of dark-brown liquid. Further purification was not carried out owing to significant instability of the material. Analysis: calculated for C₁₂H₈N₆O, C 57.15, H 3.20, N 33.31; found, C 56.05, H 3.11, N 32.88%. ¹H NMR (200 MHz, acetone-*d*₆): δ 6.74 (2 H, pseudo t, *J* = 2 Hz), 6.83 (2 H, ddd, *J* = 8 Hz, *J'* = 2 Hz, *J''* = 1 Hz), 6.91 (2 H, ddd, *J* = 8 Hz, *J'* = 2 Hz, *J''* = 1 Hz), 7.44 (2 H, pseudo t, *J* = 8 Hz). IR (neat; cm⁻¹): 2130 (s,

—N=N=N), 1270(s, C—O). UV-visible (λ_{max} [ε]; nm [l mol⁻¹ cm⁻¹]): 236 [24 500], 319 [5800], 352 [2500].

4,4'-Diazidodiphenyl ether (6). 4,4'-Diaminodiphenyl ether was purified by sublimation at 180°C (m.p. 191–193°C). In a 50-ml round-bottomed flask were placed 1.5 g (7.5 mmol) of the ether, 3.6 ml of distilled water and 2.1 ml of concentrated HCl. The mixture was heated with stirring to 80°C on an oil-bath to dissolve solids, then cooled in an ice-bath and treated dropwise while stirring with a solution of 1.1 g (16 mmol) of sodium nitrite in 2.3 ml of distilled water. The solution turned orange and was stirred for 1 h, filtered to removed undissolved material, replaced in the ice-bath and treated with a solution of 1.0 g (15 mmol) of sodium azide in 2.3 ml of distilled water. The reaction mixture was stirred for 30 min in the ice-bath. The resultant precipitate was collected by filtration, then washed with 20 ml of 10% sodium hydrogencarbonate solution and distilled water. The solid product was dissolved in diethyl ether and dried over anhydrous magnesium sulfate. Removal of the ether solvent gave 1.39 g (74%) of light-yellow solid with m.p. 71.5–73.0°C. Analysis: calculated for C₁₂H₈N₆O, C 57.15, H 3.20, N 33.31; found, C 57.00, H 3.16, N 32.78%. ¹H NMR (80 MHz, acetone-*d*₆): δ 7.09 (br s, Ar-H). IR (KBr; cm⁻¹): 2130 (s, —N=N=N). UV-visible (λ_{max} [ε]; nm [l mol⁻¹ cm⁻¹]): 263 [18 800].

Spectroscopic work. ESR studies were carried out by photolysis for 3–5 min with a 1000 W xenon arc lamp (Pyrex or Oriel 51810 filter at 300–400 nm) of a degassed 2-methyltetrahydrofuran solution of the appropriate diazide, frozen at 77 K or below in a Suprasil ESR sample Dewar vessel. Spectra were obtained on a Bruker ESP-300 X-band system at 9.58 GHz at ≤500 μW microwave power, 100 kHz field modulation frequency and 5–6 G modulation amplitude. We previously established that such conditions minimize the possibility of signal saturation in the ESR spectrum for these molecules. For variable-temperature studies, diazides were photolyzed at 77 K and quickly placed in a precooled (<60 K) ESR X-band cavity equipped with an Air Products Helitran LT-300-10 liquid helium cryostat. The temperature at the sample position was monitored using a Scientific Instruments Model CG07FC-4 iron-doped gold–chromel thermocouple. All spectra produced under these conditions remained qualitatively unchanged up to the softening temperature of the solvent matrix.

RESULTS

Figure 2 shows typical ESR spectra at 9.58 GHz for photolyses of **4–6** under the conditions described in the Experimental section. All the spectra are dominated by

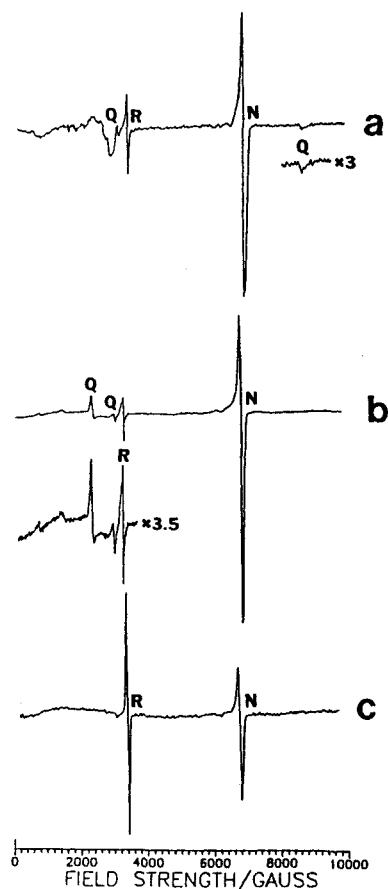


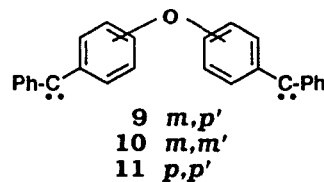
Figure 2. ESR spectra from photolyses of diazides (a) 4, (b) 5 and (c) 6. All spectra in 2-methyltetrahydrofuran at the temperatures shown ($\nu_0 = 9.58$ GHz). R = radical impurity peak; N = mononitrene triplet peak; Q = quintet dinitrene peak

aryl mononitrene resonances that are due to incomplete photolysis of the diazides. The spectra also contain varying intensity radical impurity peaks in the $g = 2$ region, which are typically produced in photolysis of bis(aryl azides). The spectrum from 4 shows a single broadened mononitrene resonance at 6850 G [corresponding to a zero field splitting (zfs) of $|D/hc| = 0.963 \text{ cm}^{-1}$] even though peaks due to both the *m*- and *p*-nitreno moieties might be expected; presumably the two expected peaks overlap to produce the observed broad resonance. The spectra from 5 and 6 show aryl mononitrene peaks at 6920 and 6840 G, corresponding to zfs of 0.989 and 0.961 cm^{-1} , respectively. The smaller zfs of the mononitrene from 6 in comparison with that of 5 shows the effect of resonance interactions between the *para*-oxygen and the nitrene moiety in 6, which is not possible in *meta*-substituted 5.

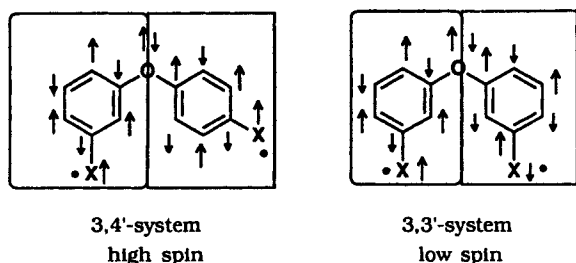
The remaining ESR resonances shown in Figure 2 are assignable to the high-spin state dinitrenes, and are discussed further below.

DISCUSSION

The ESR spectrum from diazide 4 shows a very broad resonance in the region of 2700–2800 G (containing sharper peaks at 2790 and 3080 G) and a weak peak at 8620 G that is characteristic of the quintet state.^{1–9} The latter peak corresponds to a quintet zfs of about 0.162 cm^{-1} .⁶ Owing to the weakness of this spectrum, the temperature dependence of its spectral intensity was difficult to monitor, but we found the intensity of the 2790 G peak to be nearly inversely proportional to temperature over the range 12–45 K. This implies that dinitrene 1 is either a ground-state quintet or has very nearly degenerate states. [Strictly, the observation of a linear Curie-type variation for spectral intensity as a function of reciprocal absolute temperature is dependent upon the assumption that rapid equilibrium between ground and thermally excited states of different multiplicity is maintained.^{12,13} Presumably this criterion is readily met in dinitrenes, owing to the enhancement of intersystem crossing from spin–orbit coupling moments of the heteroatoms which are present in these molecules. More pernicious is the fact that linear Curie law behavior may be observed for systems with extremely small (degenerate) gaps between ground and excited states, as well as for systems with substantial gaps. The inherent limitations of interpreting Curie experiments are well described by Berson.¹⁴] We have no clear evidence for states of other multiplicity, although it is possible that the broad resonance at 2700–2800 G contains peaks from such states. It is also possible that this broad resonance is due to a distribution of different rotational isomers of 1 with slightly different resonant peak positions. Whichever of these possibilities is true, the spectral weakness suggests that oxygen is not a very robust exchange coupling group in 1. Previous work has shown that the connectivity pattern in 1 should lead to ferromagnetic coupling (high-spin ground state) by a superexchange mechanism, based both upon experimental work on the related dicarbene 9 (Scheme 2)¹⁵ and upon computational modeling.^{16,17} (In Table I in Ref. 17, the



Scheme 2



Scheme 3

results of planar versus non-planar high-spin to low-spin energy gaps are incorrectly interchanged for the two dinitrene structures numbered **63** and **64**. Planar structures actually favor a singlet ground state, whereas non-planarity selectively lowers the quintet state energy and results in near degeneracy of states.) The computational work suggests only a modest exchange coupling strength, consistent with the desire of oxygen to avoid delocalizing its electron pairs into the π -system of **1**. A pictorial manner of representing the superexchange type coupling in **1** and **2** is shown in Scheme 3, with alternating up and down arrows representing α - and β -spin electrons in the p - π orbital system, and the two dark dots representing the remaining, localized unpaired electrons on the nitrene sites.

The ESR spectrum from the photolysis of diazide **5** has peaks at 890, 1580, 2460, 3100, 6300 and 8610 G (extremely weak), in addition to the mononitrene and radical resonances. The highest field peak corresponds to a quintet zfs of $|D/hc| = 0.162 \text{ cm}^{-1}$. This spectrum shows a markedly curved intensity dependence as a function of the inverse of absolute temperature, with an

intensity maximum at about 15 K (Figure 3). The intensity variation is reversible as the sample is warmed and then recooled at temperatures below 60 K; at temperatures significantly higher than 77 K, irreversible signal decay begin to occur, presumably owing to matrix annealing. The 3,3'-connectivity pattern for **2** is expected to lead to a low-spin ground state with low-lying excited states, based upon previously described models.^{15,17} If we assume an energetic state ordering of singlet < triplet < quintet ($S < T < Q$, Figure 3) by the usual model^{6,18} for a weakly exchange-coupled pair of aryl mononitrenes, we expect that $\Delta E(S \rightarrow T) = 2J$ and $\Delta E(S \rightarrow Q) = 6J$, where J is the exchange coupling constant from the Bleaney-Bowers¹⁹ type of model used to model the temperature dependence of ESR signal intensity in dinitrenes. The equation

$$I = (C/T) \left(\frac{[5 \exp(-6J/RT)]}{[5 \exp(-6J/RT) + 3 \exp(-2J/RT) + 1]} \right) \quad (1)$$

was used by us to fit the spectral intensity I , where J is the exchange coupling constant, R is the Boltzmann constant, T is the absolute temperature and C is an arbitrary constant chosen to fit the observed spectral intensities. A non-linear least-squares fit to our data yields $J = -6.6 \pm 1.0 \text{ cal mol}^{-1}$ (1 cal = 4.184 J) (PS-PLOT, Polysoft, Salt Lake City, UT, U.S.A.; 95% confidence), giving $\Delta E(S \rightarrow Q) \approx -40 \text{ cal mol}^{-1}$ for **2**, with the negative sign signifying a singlet ground state. This is a modest antiferromagnetic exchange, and it may be compared with the value of $\Delta E(S \rightarrow Q) \approx -20 \text{ cal mol}^{-1}$ ($2J \approx -3 \text{ cm}^{-1}$) estimated¹⁵ for the analogous, antiferromagnetically coupled dicarbene system **10**. AM1-CI computations¹⁷ predict a near degeneracy of states for **2**, as is observed here.

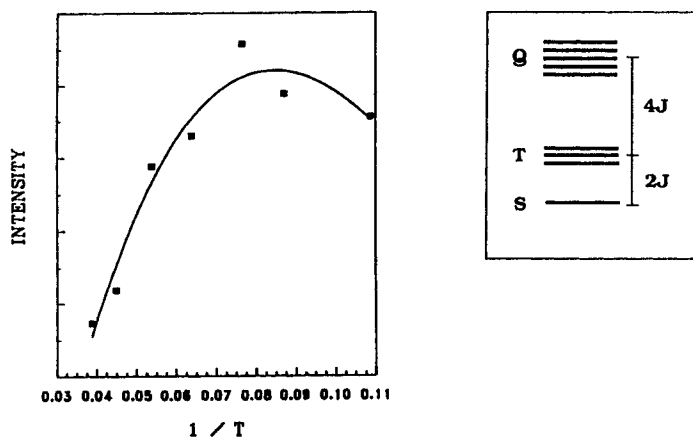


Figure 3. Curie plot for intensity of the peak at 2460 G from diazide **5** (Figure 2). The fitted curve was obtained by non-linear least squares with $J = -6.6 \text{ cal mol}^{-1}$, as described in the text. The inset shows the qualitative spacing of states for an antiferromagnetically exchange coupled pair of triplet spins

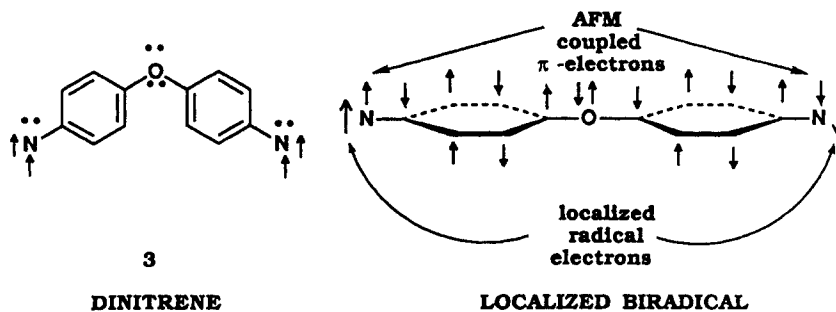
Photolysis of diazide **6** yields the usual radical impurity peak, and a strong aryl mononitrene peak with a zfs of $|D/hc| = 0.961 \text{ cm}^{-1}$. The zfs of the mononitrene shows that the oxygen linker has a modest resonance interaction with the nitrene site, by comparison to that of phenylnitrene itself²⁰ with a zfs of $|D/hc| = 0.998 \text{ cm}^{-1}$. We observed none of the ESR peaks typical of a triplet biradical species or a quintet high-spin state. The lack of other major ESR spectral features suggests that either the aryl mononitrene units of **3** are isolated by the oxygen linker, or the dinitrene **3** is an ESR-inactive singlet-state molecule whose ESR-active excited states are not thermally populated up to 77 K. In a similar fashion, 3,3'-biphenyldinitrene⁴ gives no observable quintet spectrum at 77 K in 2-methyltetrahydrofuran, despite the possibility that an excited-state quintet state should exist for this system. Semi-empirical molecular orbital computations¹⁷ have predicted a singlet ground-state preference for **3**, in accord with our not having observed a high-spin state for **3**.

Our result for **3** can be compared with that for the dicarbene analogue **11**, for which the exchange coupling constant in a benzophenone crystalline matrix was estimated by Itoh *et al.*¹⁵ as $2J = -15 \text{ cm}^{-1}$, equivalent to $\Delta E(S \rightarrow Q) \approx -130 \text{ cal mol}^{-1}$. The thermally populated exchange-coupled quintet state was observable for **11**, despite the singlet ground-state nature of this dicarbene. This is probably due in part to the fact that Itoh *et al.*'s work was carried out in a crystalline matrix which may allow for a higher stability of reactive species by comparison with results in frozen matrices.

Resonance effects in structures where the phenyl rings are both able to achieve overlap with the oxygen atom lone pair will favor a structure for **3** (Scheme 4) that has antiferromagnetically (AFM) exchange-paired nitrene pi-electrons, and nearly isolated single electrons in nitrogen lone-pair type non-bonding orbitals. The 'extra' single electrons are expected to be spin-paired in the ground state, using valence bonding arguments,^{15,18} leading to the expectation of a singlet ground state. For

highly twisted geometries of **3**, the degree of exchange interaction is computationally predicted to become much smaller¹⁷ than in planar geometries, and could lead to the isolation of the individual phenylnitrene units (a dinitrene structure). These computations suggest that geometric and conformational effects can substantially effect the exchange coupling induced by oxygen between the spin-bearing units.

Qualitative models describing the spin density distributions in **1** and **2** have been described previously. Basically, oxygen acts as a weakly interacting, superexchange 'bridge' between the two phenylnitrene units in these systems, with the ferromagnetic or antiferromagnetic nature of the final dinitrene being determined by the connectivity.^{15,17} Using PM3-optimized geometries, we carried out *ab initio* UHF 6-31G* quintet-state spin density computations on **1** and **2** using SPARTAN (Wavefunction, Irvine, CA, USA) on a Silicon Graphics Indigo R-4000 computer. (The structures of **1** and **2** were optimized without constraint using PM3 quintet wavefunctions, and the structure of **3** was optimized without constraint using a PM3 triplet wavefunction. These geometries were then fixed to obtain the UHF 6-31G* spin density diagrams shown in Figure 4, using default settings in SPARTAN for generating the surfaces.) Quantitatively, the results of such computations are arguable, since the spin density magnitudes at each atom are of unclear precision at an uncorrelated, Hartree-Fock level of theory. However, the qualitative results confirm those obtained¹⁷ at a lower, semi-empirical level of computational methodology. Spin-density maps generated by SPARTAN are shown in Figure 4. They demonstrate that the oxygen bears no substantial spin density in systems **1** and **2**. The 3,4'-system **1** has a connectivity conducive to a quintet ground state, with the oxygen bridging sites that have paired (α *para* to one nitrene, β *meta* to the other) spin densities. The 3,3'-system **2** is connected by the oxygen linker across two *meta* sites of very small, negative (β) spin density, resulting in a spin node across the aryl—O—aryl linkage that destabilizes the quintet state.



Scheme 4

Thus, computational predictions agree with theoretical concepts in describing **1** as a system with a weakly but ferromagnetically coupled, high-spin state, whereas **2** should be a very weakly coupled system with nearly degenerate states arising from exchange of the spins in the mononitrene spin-bearing units.

While we did not observe a high spin state ESR for **3**, we carried out a 6–31G* UHF triplet-state spin density computation upon the PM3 triplet optimized geometry of this system, to obtain the spin density diagram shown in Figure 4. [The geometry obtained using SPARTAN (see above) has a non-planar alignment of phenyl rings. As described in Ref. 17, the geometry of the diphenyl ether dinitrenes strongly affects the relative energies of the quintet, triplet and singlet states. Planar constrained geometries favor the singlet, but experimentally more realistic geometries where the phenyl rings are not coplanar tend to have much small energy gaps between states, and a significant decrease in the quintet state energy relative to the singlet, owing to the loss of resonance interactions that include both phenyl rings simultaneously.] The molecular geometry computed at this level of theory does not have the benzene rings coplanar with the C—O—C angle, hence direct resonance interactions between the nitrene nitrogens are reduced accordingly. At this level of theory, the system essentially is made up of isolated phenylnitrene units with alternating sites of α -spin density, consistent with experimental observation of mononitrene ESR resonances only.

CONCLUSION

Overall, oxygen is found not to be a strongly exchange coupling group in high-spin molecules. The qualitative nature of the exchange interaction in systems **1–3** is the same as is observed in the analogous dicarbenes **9–11**. Some differences are expected between connectivity-analogous dinitrenes and dicarbenes, since favorable π -zwitterionic resonance structures are available to the dinitrenes that are not available to the dicarbenes. The lack of an observable high-spin state spectrum from photolysis of **6** is possibly attributable to this resonance-based factor. However, the similarities between dinitrenes and dicarbenes are substantial, reinforcing notions that connectivity-based factors dominate the nature of exchange coupling in open-shell systems, with other factors typically being smaller perturbations. Two electron/one center pi-exchange coupling linkers such as oxygen thus experimentally seem to act in a weak exchange-coupling manner, and do not seem to be appropriate linker units for creating a ferromagnetically coupled chain of polyradicals or other open-shell spin sites.

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