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TESTING THE LIMITS OF EXCHANGE IN ORGANIC MOLECULES

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Abstract. By use of geometric/conformational constraints and extensions, it is possible to test the limits to which intramolecular exchange may be controlled in conjugated, open-shell organic models for large, extended polyradicals and magnetic domains.

INTRODUCTION

The past decade has witnessed considerable growth in research aimed at applying chemical design principles to the creation of new magnetic materials. For years, scientific research on magnetism consisted of measuring the magnetic properties of various elements and alloys as functions of temperature and composition. But, chemists and physicists now have ambitious dreams of controlling molecular properties by designing new materials with novel bulk magnetic properties.[1-4]

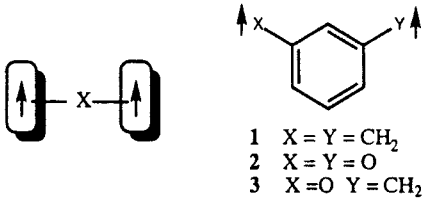
An important -- though not sufficient -- part of controlling bulk magnetic properties is to understand and control intramolecular exchange properties. For quite a long time, theoretical design principles augmented by computational modeling studies have pointed the way toward a variety of structural and geometric features that favor ferromagnetic (FM) intramolecular exchange in conjugated open-shell molecules. For example, simple connectivity based models combined with spin-polarization arguments are presently well-known to be useful paradigms for selecting a wide variety of molecules with high-spin ground states.[5-8] Although exceptions are known[9] even for molecules as simple as *meta*-phenylene linked diradicals, the exceptions observed to date seem typically to be explained by the combination of a variety of effects to overwhelm the usual connectivity-based ground state preference. It seems unlikely that such exceptions will cause chemists to abandon the usually reliable connectivity based algorithms for qualitative ground state prediction.

However, the fact that other factors can influence -- and occasionally reverse -- connectivity based ground state preferences is important. Factors such as molecular conformation, conjugation length, and even molecular geometry all can influence the overall electronic nature of a open-shell molecule. Since such molecules are the smallest units of a molecular-based magnetic material, it behooves scientists to study such effects.

In this paper, we describe recent progress and the near-future prognosis of some molecular features which influence intramolecular exchange, in an effort to probe some of the structural limits of a chemist's ability to control exchange and magnetic effects in conjugated molecules.

DO EXCHANGE LINKERS HAVE CONSTANT EXCHANGE ENERGIES?

The qualitative utility of the connectivity models for ground state prediction has been well established at present. But, it is not clear that one may measure a quantitative efficacy of exchange for any particular structural unit. In principle, one might imagine that a series of spin bearing units might be exchange coupled by a single linker unit -**X**- to give essentially the same triplet-singlet energy gap $2J = \Delta E(T\text{-}S)$ (Figure 1).[10] This simple model is complicated by variations in planarity in such a system, since the effective conjugation is decreased by any torsion that decreases coplanarity between the linker pi-system and the spin-bearing units. In addition stabilized spin-bearing sites typically have considerable variation in amounts of spin-delocalization which are on the π-site actually attached to the linker unit. Such variations make it quite difficult to establish experimentally whether an intrinsic exchange energy may be associated with a given linker unit -**X**- when it is linking different types of sites all with differing distributions of spin density.



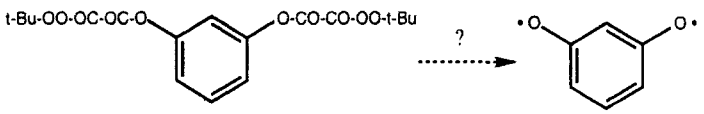
1 X = Y = CH_2
2 X = Y = O
3 X = O Y = CH_2

FIGURE 1 Generalized diradical diagram with *meta*-quinonoid examples.

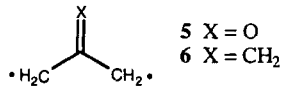
Although experimental evaluation is difficult for this problem, computational evaluation can serve as a useful means of comparisons. As with any experiment, the choice of actual molecules for comparison is of considerable importance. The exchange coupling in the series of molecules *meta*-xylylene, *meta*-quinone, and *meta*-benzoquinomethane (**1-3**, respectively) constitutes a useful set for examination of the *meta*-phenylene exchange linker unit. All three molecules are expected to be planar for their lowest lying states, and all consist

of *meta*-phenylene linkers that join a pair of single π-orbital spin sites. The only variation consists of the effects of varying oxygen-for-methylene substitution. This whole set of molecules has been of considerable interest in the general field of non-Kekulé molecules since the 19th century.[11]

At a simple π-Hückel level of approximation, the C_{2v} symmetrical molecules **1-2** have degenerate singly-occupied nonbonding molecular orbitals (SOMOs). Since all of **1-3** are connectivity nondisjoint diradicals, none have a connectivity bias against a high-spin ground state. As a result, **1-2** are qualitatively expected to favor triplet ground states, both by connectivity, and by SOMO degeneracy. At higher levels of theory, the symmetry of **1-2** is insufficient to require SOMO degeneracy, but one would still expect the energy gap between the SOMOs to be fairly small, still favoring a triplet ground state. Experimentally, fairly clear evidence has accumulated that **1** has a triplet ground state.[11] Diradical **2** has yet to be directly and unequivocally observed in any experiment known to us, although we have tried[12] generate to **2** by cryogenic matrix photolysis of **4**.

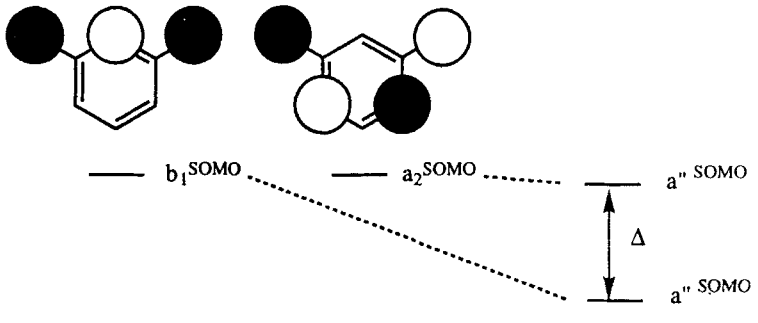


4 **2**



5 X = O
6 X = CH_2

However, diradical **3** is not C_{2v} symmetrical, and will have substantially nondegenerate SOMOs even at the π-Hückel level of theory (Figure 2). The HOMO-LUMO gap Δ in **3** would favor a singlet ground state if Δ is large enough, even though **3** is expected by connectivity arguments to have a high spin ground state, since it is nondisjoint. By this argument, a ground state



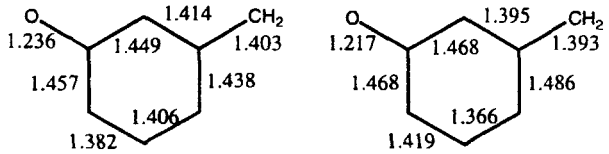
1 and 2 **3**

FIGURE 2 SOMOs for *meta*-phenylene linked diradicals.

singlet for **3** would be similar to computational[13-14] and experimental[15-16] evidence that favors a singlet ground state for the heteroatom-containing oxyallyl diradical **5**, by comparison to the clear, experimental establishment of triplet ground states for the π-analogue trimethylenemethane **6** and related[17-18] diradicals. Experimentally, however, ESR evidence strongly favors a triplet ground state for **3**,[19] despite the expected HOMO-LUMO splitting.

We carried out[20] post-Hartree Fock complete active space self consistent field (CASSCF) computations at the 6-31G* basis set level for diradical **3**, in order to compare to the results of previous[21-22] computations for **1** and **2**. The ^{3}A' and ^{1}A' states for **3** were separately optimized using a CASSCF(8,8) wavefunction, assuming that both states were planar. This assumption was justified by comparison of UHF-SCF and open-shell singlet SCF calculations showing that structures with a 90° twisted exocyclic methylene group were substantially higher in energy for both triplet and singlet.

Figure 3 shows CASSCF(8,8) 6-31G* bond lengths computed for the planar ^{3}A' and ^{1}A' states; full geometry details will be given in a later, full paper. Most notable in the geometric results is the considerable bond alternation, especially the short C-O bond lengths, 1.236 and 1.217 Å in the ^{3}A' and ^{1}A' states, respectively. The $^3B_2$ state of **2** has C-O bond lengths of 1.231 Å at the partially optimized π-SDCI level of theory. The lowest lying singlet state of **2**, the $^1B_2$ state, has quite localized C-O bonds 1.210 Å long at the same level. Both values are comparable to the C-O bond lengths for the states of corresponding multiplicity in **3**. However, the asymmetric substitution pattern in **3** gives this molecule substantial bond alternation. Neither the ^{3}A' nor ^{1}A' states of **3** have bond lengths commensurate with a purely benzenoid central ring. However, **1**-**2** also show some central ring localization, even in the triplet states, so **3** computationally is similar in bonding patterns to these other members of the benzoquinodimethane set.



^{3}A' E = -344.34438 a.u. ^{1}A' E = -344.32704 a.u.

FIGURE 3 Ab initio results for **3**. Selected bond lengths are given in angstrom units. Energies are at the MP2 CASSCF(8,8) 6-31G* level, using the CASSCF(8,8) 6-31G* geometries.

The energy gap Δ between the SOMOs in the ^{3}A' state is 0.215 a.u. at the 6-31G* ROHF level of theory. Despite this, the ^{3}A' is found to be the ground state for **3** by ΔE(T-S) = 11 kcal/mol versus the ^{1}A' state, using MP2 CASSCF(8,8) 6-31G* single point energies at the corresponding CASSCF(8,8) geometries. This

result is in qualitative accord with the experimental work for **3** to which we alluded above. Even more interesting, this ΔE(T-S) is extremely similar to the ΔE(T-S) gaps of 11 kcal/mol (6-31G* CASSCF(8,8), $^3B_2 \rightarrow {}^1A_1$ diradical singlet state)[22] and 10 kcal/mol (6-31G* ROHF(UHF)//π-SDCI, $^3B_2 \rightarrow {}^1B_2$ open shell singlet state)[21] computed for **1** and **2**, respectively. Consistent with the HOMO-LUMO gap, the $^1A'$ state in **3** is not very open-shell in nature, with natural frontier orbital coefficients at the CASSCF(8,8) 6-31G* level of 1.963 and 0.030 (a biradical would have both as nearly 1.00).

As a calibration for these computed ΔE(T-S) gaps, the only experimental estimate that is presently available puts ΔE(T-S) for **1** at9.5 kcal/mol,[23] in good agreement with the computed results. If one assumes that the quality of the computed ΔE(T-S) for **2-3** are of similar accuracy, then it appears that the exchange coupling efficacy of *meta*-phenylene is nearly of equal sign and magnitude for all the diradicals **1-3** in this series. Apparently the *meta*-phenylene linker has a constant exchange nature throughout this series, despite the considerable variation in structure.

Presumably, the use of more complex spin bearing units could confound this result. Still, we feel that this computational result speaks well to the notion that the energetic efficacy of a particular linker group -**X**- can remain constant or nearly so in a series of diradicals, so long as the series faithfully compares molecules with similar spin density distributions and conjugation strengths.

ZERO FIELD SPLITTING AS A FUNCTION OF GEOMETRY

Molecular conformation and geometry are known to affect exchange in conjugated open shell systems. The effects are most notable when extreme torsion leads to effective deconjugation of spin sites from one another in a molecule that has a nondisjoint connectivity.[9] However, subtle effects on electronic structure can in principle occur even with fairly minor changes in geometry between otherwise similar molecules.

Zero field splitting (zfs) between the substates (T_{+1},T_0,T_{-1}) of a triplet molecule reflect exchange interactions between unpaired electrons. Zfs is strongly influenced by dipolar interactions between the electrons. With sufficiently well defined electron orientations, it is possible to predict the zfs in a triplet state. In a real molecule, of course, it is not always straightforward to know the molecule geometry or conformation, so prediction is not always straightforward. However, use of the dipolar approximation can allow one to differentiate between two considerably different triplet geometries by examination of experimental zfs in the ESR spectrum.

The dipolar approximation model can be extended to $S > 1$ states. Itoh[24] has shown that, for a quintet state made up of interacting triplet spin sites a and b, the quintet zfs tensor $\hat{\mathbf{D}}_{S=2}$ can be approximately expressed by equation (1),

$$\hat{\mathbf{D}}_{S=2} \cong \frac{1}{6}(\hat{\mathbf{D}}^{a}_{S=1} + \hat{\mathbf{D}}^{b}_{S=1}) \tag{1}$$

where $\hat{\mathbf{D}}^{a}_{S=1}$ and $\hat{\mathbf{D}}^{b}_{S=1}$ are the zfs tensors for the triplet spin sites. Equation (1) is appropriate if the interaction between spin sites a and b is weak. If one assigns a specific directional vector to each of the interacting triplet spin sites with an intervector angle θ between them, and if the interacting spin sites are the same, one may rewrite equation (1) in terms of the triplet zfs parameters D_t and E_t to obtain the quintet zfs tensor elements in equation (2). One may

$$\hat{D}_{S=2} = \begin{pmatrix} \frac{1}{3}\left(-\frac{D_t}{3} + E_t\right) & & \\ & \frac{1}{3}\left(-(D_t + E_t)\sin^2\theta + \frac{2}{3}D_t\right) & \\ & & \frac{1}{3}\left((D_t + E_t)\sin^2\theta - \left(\frac{D_t}{3} + E_t\right)\right) \end{pmatrix} \tag{2}$$

or

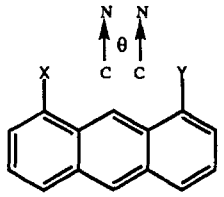
$$\hat{D}_{S=2} = \begin{pmatrix} D_x^{S=2} & & \\ & D_y^{S=2} & \\ & & D_z^{S=2} \end{pmatrix}$$

then use the standard relationships $D = 1.5D_z$ and $E = 0.5(D_x\text{-}D_y)$ to obtain the quintet zfs parameters D_q and E_q for the quintet.

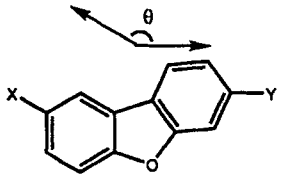
Itoh's model has already been successfully applied to the energetic spacings between quintet, triplet and singlet states of weakly interacting dicarbenes.[25] It has also been used to assign ESR peaks with specific zfs to specific dicarbene conformations.[25] However, the exact molecular geometries of dicarbenes are difficult to establish, since carbene sites are divalent and may adopt various conformations and bent geometries. We felt it would be useful to synthesize quintet molecules with well defined geometries for application of Itoh's model.

Conjugated dinitrenes are conveniently generated from diazide precursors under cryogenic conditions. Because mononitrene spin sites are monovalent, their geometries are completely determined. For these reasons, dinitrenes are well suited for study of geometric and connectivity effects upon ground state multiplicity and exchange.[26] Many dinitrenes studied to date, however, have had appreciable conformational freedom, which has led to complications in interpreting the randomly oriented ESR spectra from these molecules. We felt that, with the help of benchmark ESR spectra generated from geometrically rigid dinitrenes, we could apply Itoh's model to assign peaks to specific conformations in flexible dinitrenes with complex ESR spectra.

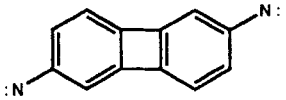
Our target molecules were dinitrenes **7-9**, all of which have fixed geometries. In these, the relative C-N/C-N bond vector angles θ are about 0°, 155°, and 180°, using AM1-UHF[27] triplet semiempirical molecular orbital computations. AM1-CI calculations by our usual methodology[28-29] predict that



7 X = N: Y = N:
13 X = N_3 Y = N_3
15 X = N_3 Y = N:



8 X = N: Y = N:
14X = N_3 Y = N_3
16 X, Y = N_3, N:



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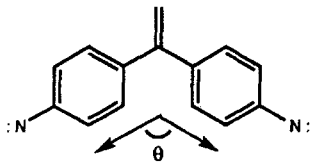

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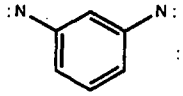

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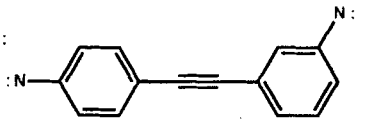

12

all of these nondisjoint systems will have quintet ground states, with $\Delta E(Q \rightarrow T)$ = 2-4 kcal/mol. With respect to expected ground state multiplicity, **7-9** are likenumerous nondisjoint conjugated dinitrenes that have been studied previously by us and others.[30] However, other nondisjoint dinitrenes made to date have all had C/N/C-N vector angles θ of 120° or nearly that; examples are structures **10-12**. Since the zfs of dinitrenes should be most influenced by the one-center exchange interactions on each nitrogen rather than by exchange between the nitrogen sites, Itoh's model should be applicable. Given this, it is less surprising that nondisjoint dinitrenes made to date -- all of which have $\theta \approx 120°$ – all have extremely similar quintet ESR spectra dominated by a single resonance at about 3000 G. Figure 4 shows such a spectrum for a typical such nondisjoint dinitrene, generated from the diazide precursor to **10**. It has recently been shown by lineshape simulation that a dinitrene made up of two triplet mononitrenes with $D_t = 0.98$ cm^{-1} and $E_t = 0.002$ cm^{-1} interacting with an angle θ of 120° has $D_q = 0.23$ cm^{-1} or thereabout.[31] With minor variation, D_q and E_q for other nondisjoint dinitrenes with $\theta \approx 120°$ appear to be the same.[32] However, **7-9** must have θ other than 120°, and so should have zfs that are appreciably different.

Figure 4 also shows the X-band ESR spectra generated from 77 K photolysis in 2-methyltetrahydrofuran (5 min, xenon arc, Pyrex filtered) of diazide precursors **13-14** to dinitrenes **7-8**. (Work on the diazide precursor to **9** is still in progress.) A number of large peaks attributable to quintet dinitrenes are generated, in addition to minor peaks from radical impurities and mononitrene from partial photolysis. Not only are the major spectral features in both very different from those in the typical nondisjoint dinitrene spectrum, but they are very different from one another, as expected if **7** and **8** have quite different zfs. Examination of the spectra from **13** and **14** shows that the

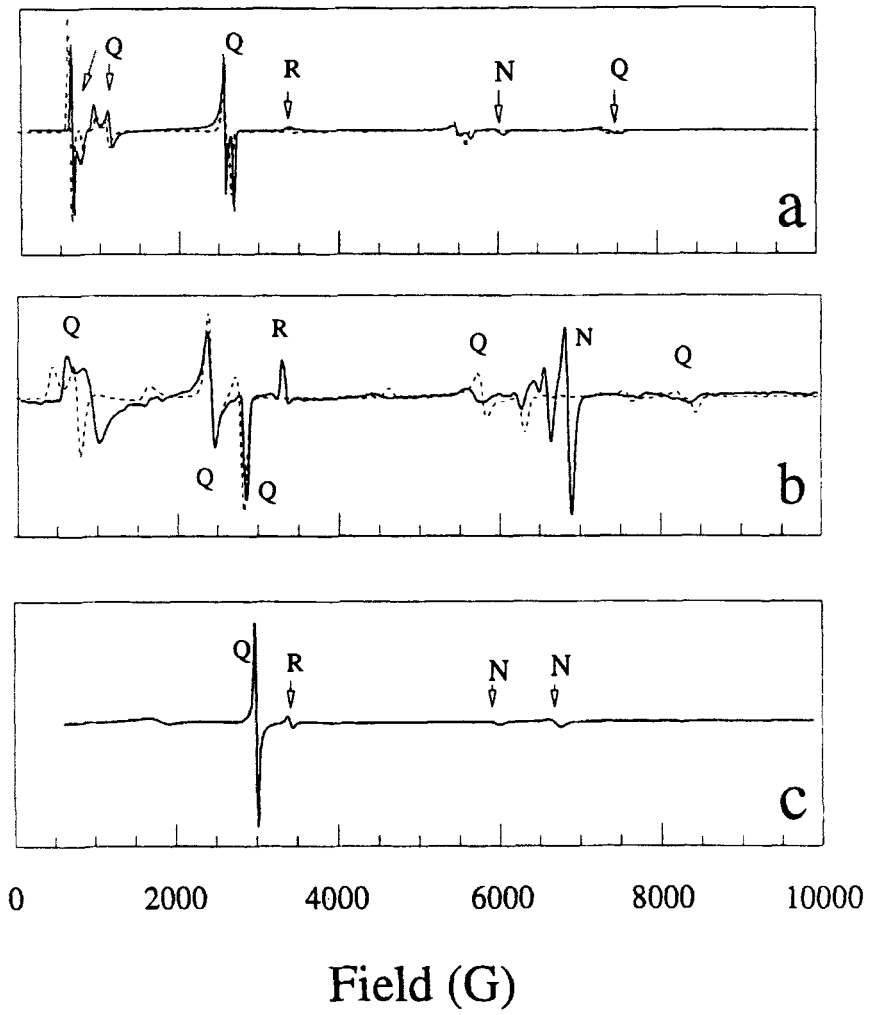

FIGURE 4 X-band ESR spectra from photolysis of **13** (a, 77 K) and **14** (b, 4 K) in frozen 2-MTHF. Also shown is spectrum for dinitrene **10** (c, 77 K). Quintet, mononitrene, and radical peaks are denoted by the letters Q, N, and R, respectively. The dotted curves are simulated[32] spectra with zfs parameters D=0.243 cm^{-1} and E=0.002 cm^{-1} for quintet **7**, D=0.297 cm^{-1} and E=0.009 cm^{-1} for quintet **8**, using g_{iso} = 2.003.

mononitrenes **15** and **16** have zfs of D_t = 0.654 and 0.908/1.004 cm^{-1}, respectively (two mononitrenes from **14**). Line-shape simulations[32] are in progress to fit the experimental spectra to zfs parameters. Preliminary results show good matches when D_q = 0.243 cm^{-1} and E_q = 0.002 cm^{-1} for quintet **7**, D_q= 0.297 cm^{-1} and E_q = 0.009 cm^{-1} for quintet **8**. If one uses the experimental mononitrene D_q values and the θ values required by the fixed molecular geometries of **13** and **14**, equation 2, predicts quintet D_q to be in reasonable agreement with these simulated values. Thus, the ESR spectroscopic results correlate well with the expectations of the Itoh model for fixed dinitrene molecular geometries. Thus, the reason that the observed spectra for **13-14** are entirely different from those of dinitrenes observed previously is their unusual, fixed geometries. Confirmation of the ground state spin multiplicities of **7-8** and attempts to generate dinitrene **9** are in progress and will be reported fully in future work.

EXCHANGE AS A FUNCTION OF CONJUGATION LENGTH

The use of conjugation to allow intramolecular exchange in organic diradicals and related open shell molecules is of extreme value. When qualitative connectivity arguments are applied to such species, conjugation is typically just assumed to operate as a kind of "exchange conduit" with complete efficiency. However, there are well known limits to the effects of conjugation. A soliton defect such as those investigated within polyacetylene has a finite conjugation length, rather than delocalizing throughout the whole of the polymer chain.[34] The longest wavelength band of the UV-visible spectrum of a conjugated polyene reaches a maximum value as the degree of conjugation increases, and remains at this value.

It seems plausible that there could be limits to the conjugation length across which interelectronic exchange can be carried out. If one only has two spins to delocalize throughout a conjugated network of increasing size, there will likely be a tendency to localize the spin density, especially if there are heteroatoms present. If the spins become sufficiently localized and separated, the triplet-singlet gap in such a system would tend toward zero; in fact, the system may act as two separate radicals rather than as a diradical. ESR spectroscopy and magnetic susceptibility can be used to probe the nature of exchange in such a system. Presumably there will be a dependence of behavior upon the type of spin sites used, since some spin bearing sites such as nitroxides are naturally more localized than others.

At present, we have only preliminary results that bear upon this problem. Our goal is to probe the systems shown in Figure 5, where conjugation length is gradually extended while keeping connectivity the same in a series of dinitrenes or diradicals.

We have generated dinitrenes **17** (n=1) and **18** (n=0) by photolysis of the appropriate diazide precursors **19-20**. The only nominal difference between these is that **17** (n=1) is a bis-styryl compound and **18** (n=0) is a bis-hydrazone,

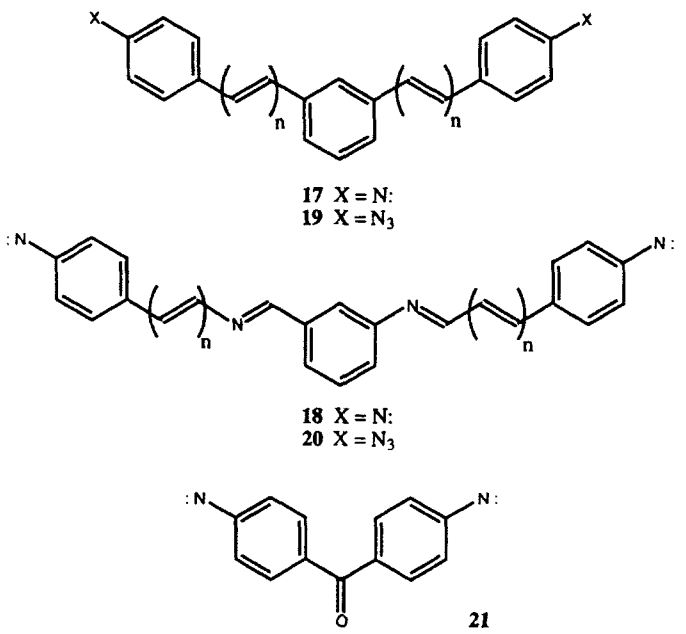

Figure 5 Dinitrenes and diazide precursors to test exchange strength as a function of exchange length.

hence heteroatom substitution could cause differences. Both diazide precursors appear to be stable indefinitely in the dark at 0 °C. Upon photolysis for 5 min (xenon arc, Pyrex filter) at 77 K in frozen 2-MTHF, the solution turns reddish. In both cases strong mononitrene and radical impurity peaks are formed. A moderate intensity peak at about 2900 G is observed in each case, consistent with the formation of a quintet dinitrene species with a 120° angle between the C-N bond vectors (see the section above). The quintet peaks do not increase in intensity as photolysis time is extended, showing that their modest intensity is not a function of slow photolysis, but apparently is due to the inherent yield of the quintet product under these conditions. The 9.6 GHz ESR spectra are shown in Figure 6.

At present have insufficient data even to speculate as to exact effects of conjugative extension upon exchange in **17-18**. It is notable that the quintet spectra in Figure 6 are weak by comparison to the corresponding mononitrene peaks that arise from partial photolysis of diazide precursors. In other nondisjoint dinitrenes that we have studied, the quintet spectral peaks have been quite strong relative to the corresponding mononitrenes, with the exception of 4,4'-benzophenone dinitrene **21**, which appears to have only a weak exchange interaction between the nitrene sites.[35-36] The weakening of the quintet peaks in Figure 6 may likewise signal a decrease in exchange strength between the nitrene sites, but we do not know this at present.

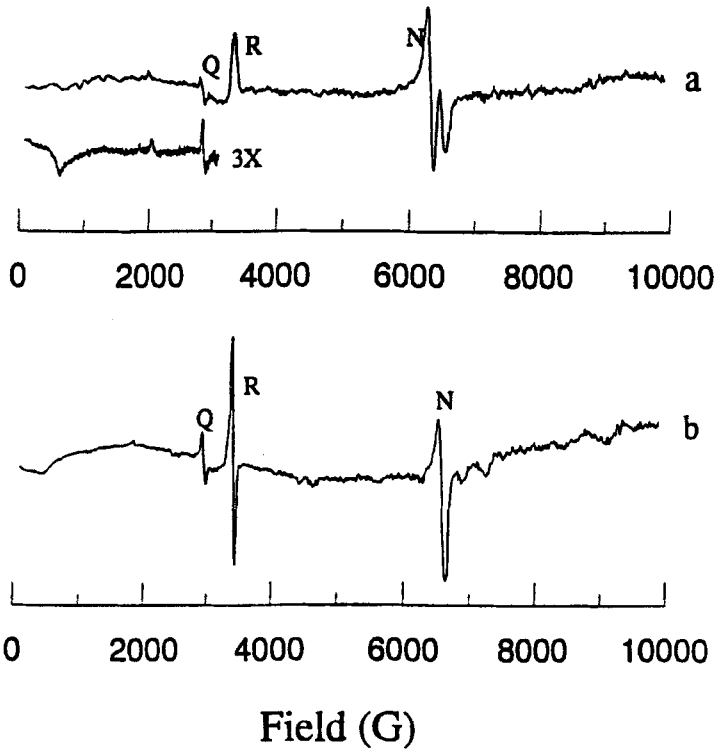

Figure 6 9.6 GHz ESR spectra from photolyses of 19 (a) and 20 (b) at 77 K in 2-MTHF. Quintet, mononitrene, and radical impurity peaks are denoted by the letters Q, N, and R, respectively.

The fact that we can see the 2900 G peak does, however, show that exchange is occurring between the nitrene sites, and also is consistent with the transoidal geometry shown in Figure 5, since a major 2900 G peak in a dinitrene ESR spectrum is consistent with the 120° C-N/C-N vector angle required by the all transoidal geometry. Additional evidence for this view is shown by the fact that, when we photolyze samples of 19 (n=1) which contain a mixture of *Z*- and*E*- C=C isomers, there is a considerable weakening of the 2900 G peak relative to samples in which the synthetic procedure produces all-*E* C=C bonds.

We have yet to observe any new peaks attributable to dinitrenes derived from precursor containing Z-geometry bonds, although we would expect these to be at rather different positions from the all-*E* precursors. It is possible that any Z-geometry precursors undergo Mallory[37] photocyclization -- as is well known for this geometry of stilbene units -- but we have not obtained evidence for this reaction up to the present time.

ACKNOWLEDGMENTS

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