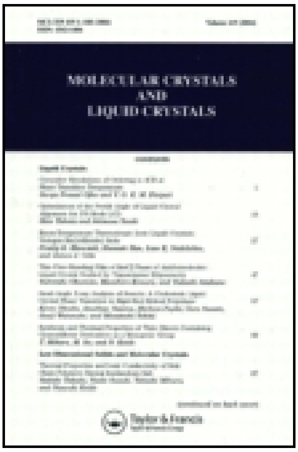

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Experimental Investigation of Exchange in Organic Open-Shell Molecular Building Blocks for Magnetic Materials

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EXPERIMENTAL INVESTIGATION OF EXCHANGE IN ORGANIC OPEN-SHELL MOLECULAR BUILDING BLOCKS FOR MAGNETIC MATERIALS

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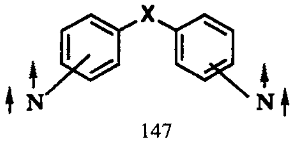
Abstract Intramolecular exchange interactions in bis(arylnitrene)s obey the Borden-Davidson disjointness criterion, although variations in the size of the interaction occur as functions of conformation and -X- in the structure :N-Aryl-X-Aryl-N:.

INTRODUCTION

As part of our efforts to identify structure-property relationships that will allow the eventual design of organic magnetic materials which incorporate organic high-spin molecules, we have studied both model open-shell molecules and larger polyradicals. As recently pointed out,[1] it is still not clear which types of molecular connectivity or spin-bearing units are best for design of large polyradicals, although the *meta*-phenylene unit is usually effective, for instance. The potential discovery of new robustly ferromagnetically (FM) coupled topologies and spin-bearing groups justifies the benefits of investigating model systems that may be eventually related to larger scale materials.

We have previously carried out semi-empirical MO-CI level computational work to identify structural features that favor FM coupling in small molecule and polymeric systems.[2-3] Both connectivity and choice of spin-bearing unit affect the type and magnitude of exchange coupling. Also, the computations have shown that conformational effects will be quite important in some systems. Short range FM coupling may be reasonable in smaller model molecules, but that extended FM coupled arrays may not be feasible in structurally related, morphologically more complex polymers. Still, knowledge of the "rule book" of exchange coupling is necessary before assembling a full-scale, complex material. In this article we summarize the results of our studies of bis(arylnitrene) model systems (:N-Ph-X-Ph-N: in Table I) and show how this approach allows detailed investigation of multiplet states in open-shell molecules.



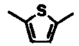
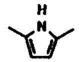
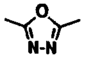
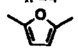
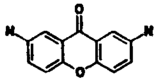
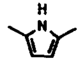
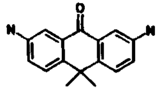
-X-		J(cal/mol)	zfs	Compound	-X-		J(cal/mol)	zfs	Compound
(bond)[a]	*m,m'*	isolated?[5]	N/A	1	-O-	*m,p'*	FM[8]	D_q=0.162	13
(bond)	*m,p'*	FM[5]	D_q=0.153	2	-O-	*p,p'*	AFM?[8]	N/A	14
(bond)	*p,p'*	-290[5]	D_t=0.169	3		*m,m'*	-16.7[7], -10.1[7]	D_q=0.16	15[b]
(bond, rings ⊥)	*p,p'*	isolated[6]	N/A	4		*m,m'*	-14.6[7]	D_q=0.16	16[b]
>C=O	*m,m'*	-8.0[4] -10,-4.7[21]	D_q=0.158	5[b]		*m,m'*	-3.0[7], -18[7]	D_q=0.16	17
>C=O	*m,p'*	AFM	D_q=0.159	6		*m,m'*		D_q=0.160	18[b]
>C=O	*p,p'*	FM[4,13]	D_q=0.156	7	CH=CH)$_n$ n =1	*p,p'*	-290	D_t=0.122	19
>C=CH$_2$	*m,m'*	-13.6[4] -12.5[13]	D_q≈0.16?	8[c]	CH=CH)$_n$ n =2	*p,p'*	-335	D_t=0.0865	20[d]
>C=CH$_2$	*p,p'*	FM[4,13]	D_q=0.151	9	CH=CH)$_n$ n =4	*p,p'*	-122	D_t=0.0442	21
-CH=CH-	*m,p'*	FM[4]	D_q=0.146	10		*p,p'*	AFM[7]	D_t=0.137 E_t=0.016	22
		AFM?	N/A	11		*p,p'*	AFM[7]	D_t=0.190 E_t=0.006	23
-O-	*m,m'*	-6.6[8]	D_q=0.162	12		*p,p'*	AFM[7]	D_t=0.183 E_t=0.012	24
							-5.3[9]	D_q=0.172	25[d]

TABLE 1. Bis(arylnitrene) summary. [a]D_q and D_t are zfs values for quintet and triplet biradical states in cm^{-1} (see E. Wasserman, *et al., J. Am. Chem. Soc.* 89, 5076 (1967) for D_q methodology). Each value of J is referenced where appropriate. AFM,FM = strongly antiferromagnetic, ferromagnetic. N/A = only triplet mononitrene observed. [b]Multiple conformations. [c]Very weak peak at >8000 G. [d]Corrected from original reference.

INTRAMOLECULAR EXCHANGE IN BIS(ARYLNITRENE) MODELS

Preparation and Characterization of Bis(arylnitrene)s

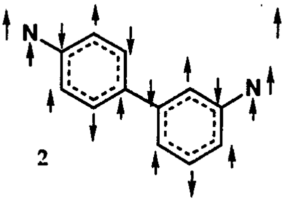
All dinitrenes (Table I, **1-25**) were generated from diazide precursors synthesized by reduction of corresponding dinitro compounds to diamines, followed by double diazotization and replacement with azide groups. Diazides were photolyzed in frozen 2-methyltetrahydrofuran matrices at ≤77 K. Exchange coupling behavior was established by investigating the Curie Law behavior of the ESR spectral intensities as a function of temperature under conditions where signals were not saturated; standard techniques were used to carry out these investigations. Experimental details of precursor synthesis and generation of all compounds listed in Table I have been published elsewhere.[4-10]

Classifying Exchange in Bis(arylnitrene)s

Conjugated bis(arylnitrenes) are convenient tests of intramolecular exchange, since: (1) electron spin resonance (ESR) spectroscopy distinguishes their quintet and triplet states, (2) aryl mononitrene impurities are readily identified in the ESR spectrum, (3) arylnitrene based systems are easily generated in rigid matrix at cryogenic temperatures, and are persistent in either frozen solution (up to ~ 80 K) or in the crystalline state.

Most of the bis(arylnitrene) systems of Table I fall into three basic exchange categories: nondisjoint, disjoint, and biradical. The first two are defined by Borden and Davidson's criteria[11], while the third occurs when strong antiferromagnetic (AFM) interaction pairs the pi-type nitrene electrons to give quinonoidal structures with biradical triplet ESR spectra[10] (*e.g.*, **3,19-24**). Finally, there are heteroatom linked dinitrenes,[8] which fit none of these categories (**11-14**). The various dinitrenes exemplify the magnitudes and types of exchange occurring in organic open-shell molecules. All the classes are exemplified in the table, but we shall restrict the present discussion to systems which show quintet state ESR spectra.

Nondisjoint diradicals are predicted both theoretically and computationally to favor FM coupled high spin ground states by an appreciable energetic margin. This is also found to be true for nondisjoint bis(arylnitrene)s **2**, **7**, **9**, and **10**. Nondisjoint di-nitrene systems studied by us[4-9] and others[12-13] all have quintet ESR spectra and linear



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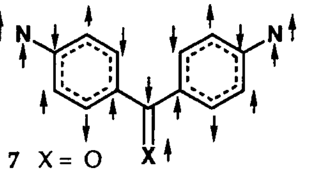
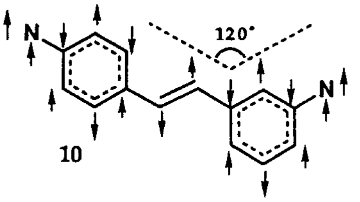


7 X = O
9 X = CH_2



10

Curie law thermal intensity behavior of these spectra, implying high spin ground states. With minor variations, all ESR spectra of nondisjoint dinitrenes examined to date have very similar ESR spectra, with a single strong resonance in the 2900-3100 G region, and a variety of less intense resonances at higher fields up to 8600 G (*cf.* Figure 1). The spectral similarity may due to the fact that all nondisjoint dinitrenes generated to date have nearly the same C-N / C-N vector angle (120°) formed by their arylnitrene units, regardless of conformation or molecular connectivity. Theory shows that this vector angle is a major determinant of the zero field splitting (zfs) in a quintet state made up of interacting triplets.[14] Although it is not clear that this angular dependence must dominate spectral appearance of *nondisjoint* dinitrenes, evidence to date suggests that it does.

Disjoint systems are predicted to have weak exchange interaction between spin sites, with a near degeneracy of states occurring. Valence bond and exchange[11] considerations suggest that disjoint systems should favor a singlet ground state by a small margin. Itoh[14] has shown that a pair of weakly interacting triplet units may interact to give a set of states with energies $E_S < E_T < E_Q$, where S, T, Q are singlet, triplet, and quintet states respectively. $E_S - E_T = -2J$, and $E_T - E_Q = -4J$, where J is an exchange constant (Table I, $J_{FM} > 0$, $J_{AFM} < 0$). Also, the zfs of disjoint systems is dominated by

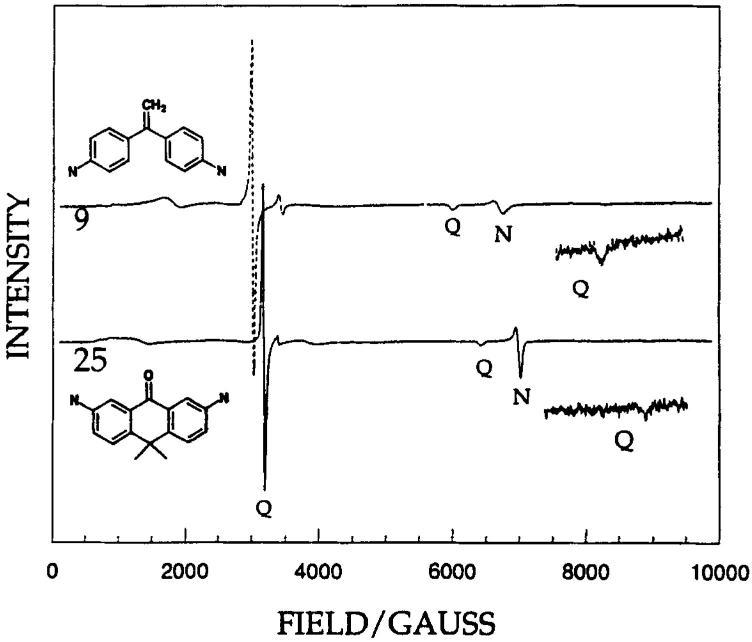
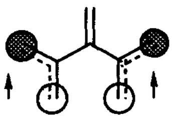


FIGURE 1 77 K ESR spectra for **9** and **25** in Table I.
(Q = quintet, N = mononitrene).

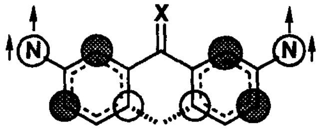
the angle formed between the interacting triplet unit zfs-tensors, so that D/hc and E/hc for disjoint quintets will vary substantially with conformation. Itoh's model has been quite successful in describing bis(carbene)[14-15] and diradical[16-17] systems.

Our group has studied disjoint dinitrenes (**1**,**5**,**6**,**8**), and also a class of pseudo-disjoint nonalternant systems (**15**-**18**). Both subtypes of connectivity are found to have singlet ground states with thermally populated states of higher multiplicity. In one case (**1**), no ESR evidence was found for a thermally populated multiplet state, leaving open the possibility that (a) the $\Delta E_{(S\text{-}T)}$ is sufficiently large to preclude an ESR-visible population of high spin state molecules, or (b) the exchange coupling $J \approx 0$, giving rise to isolated behavior of the triplet aryl mononitrene units. For all other disjoint and pseudo-disjoint cases, nonlinear Curie law behavior of ESR signal intensity was observed, showing that the spectra were due to thermally populated excited states.

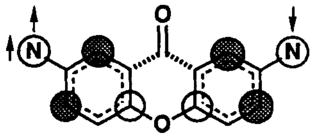
Iwamura[13] has pointed out that one may subdivide the disjoint class of connectivities into a disjoint and a doubly-disjoint class. The disjoint class has equal numbers of alpha and beta spin sites in parity based models, and should have low-spin ground states, such as **1** and **6**.[18-19] Doubly-disjoint systems may be predicted by parity based models to have high-spin ground states, but are disjoint by virtue of being made up of spin-bearing fragments exchange connected across sites of very low spin density through three[13] (rather than two) pi-orbitals, and so should have very small AFM coupling between spin sites. An example of this class of molecule is pentamethylenepropane (PMP), composed of weakly interacting allyl fragments. Despite computations indicating that planar PMPs should favor a triplet ground state by a 1-2 kcal/mol margin, no experimental evidence exists for a triplet PMP.[20] However, related doubly-disjoint carbonyl and 1,1-ethenediyl linked systems **5** and **7** have singlet ground states with thermally populated quintet states,[4,13] and so fit the disjointness model.



PMP



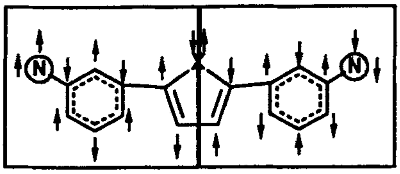
5, 7, 25



11

Pseudo-disjoint systems are made up of arylnitrene spin sites linked by nonalternant heterocyclic systems, *e.g.* **14**-**16**.[7] They may be considered as disjoint, since they have spin-bearing units linked across sites bearing minimal spin density (next page). One may also consider a spin-polarization model to explain the observed singlet ground states. If one considers pairing of spins by a valence bond type of approach, the central heteroatom need not affect a singlet spin distribution. Experimentally, heteroatom variation in the nonalternant ring in these systems seems to perturb the final electronic

PSEUDO-DISJOINT



SPIN-POLARIZATION

nature only to a small extent. By comparison, when exchange coupling is forced to proceed across a lone-pair containing heteroatom (-X- = -O-, **12-14**), the magnitude of J is quite small, and exchange apparently inefficient.[8] It is possible that this inefficiency is at least partly due to conformational mobility in the systems studied. In constrained system **11** (*vide supra*), only a mononitrene is observed, suggesting that when a choice between the >C=O and -O- exchange pathway is offered in a planar system, the -O- exchange path is dominant and a singlet ground state occurs due to resonance effects.

Several conformationally unconstrained bis(arylnitrenes) show complex quintet ESR spectra, a number of which were found to have multiple ESR-active species with different Curie law behavior (see Table I, **5**,[21] **15**,[7] **17**[7]). An example is shown in Figure 2 for **17**, demonstrating the differing thermal variations of different portions of

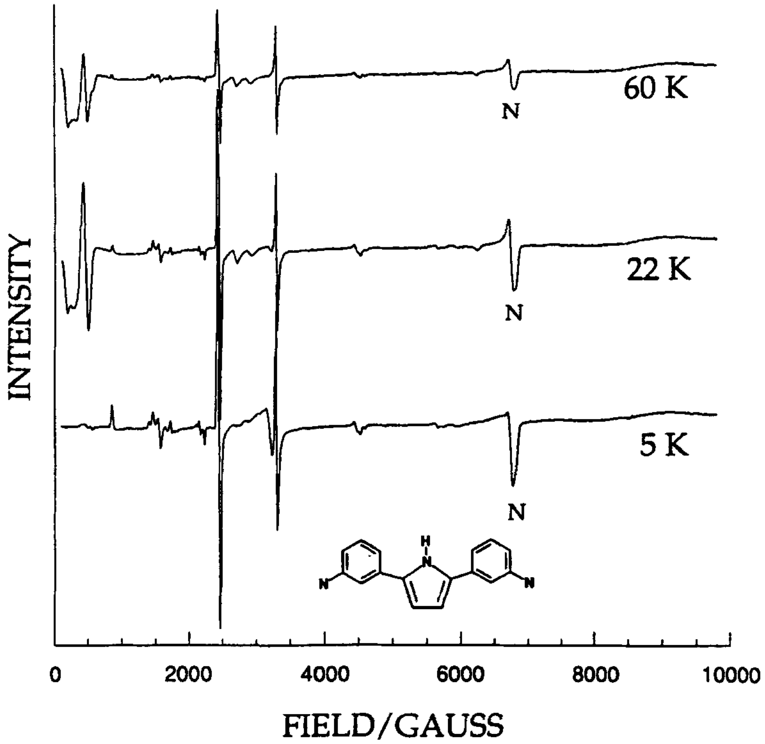


FIGURE 2 ESR spectra for **17** at 60, 22, and 5 K, with the same ordinate scale. (N = mononitrene).

the spectrum. These different species are tentatively assigned as being different conformers of the bis(arylnitrene)s, although it is also possible that some resonances are due to excited state triplet[14] species. A variety of relative C-N / C-N vector angles is possible in most of our disjoint systems which may lead to a variety of quintet zfs situations as mentioned above for Itoh's[14] model. Due to the complexity of randomly oriented quintet spectra, full analysis has been difficult, and is not yet complete. Quintet simulations of various portions of the spectra at different temperatures are in progress, and we hope eventually to relate specific spectral features to specific conformations.

Another way to relate specific bis(arylnitrene) conformations to ESR quintet spectral features is to synthesize geometrically constrained systems. An example is system **25**, which is doubly disjoint (see scheme above), but which has a C-N / C-N vector angle constrained to be ≈120°.[9] The ESR spectrum of **25** is shown in Figure 1, and is remarkably similar to the spectrum of nondisjoint system **2**. But, **25** is found to have $J = -5.3$ cal/mol and is low spin in accord with its doubly-disjoint nature. Only **25** among the disjoint systems has a spectrum resembling those of known nondisjoint systems, and only **25** is *constrained* to have a C-N / C-N angle that is the same as in known nondisjoint systems. This supports the theoretical relationship between the C-N / C-N angle and the zfs behavior described above. We are further testing this hypothesis by preparation of bis(arylnitrene)s constrained to have C-N / C-N vector angles substantially different from 120°, and hope to report the results in the near future.

Bis(arylnitrene)s -- Summary and Prospects

Table I summarizes the structures, experimental ground state spin multiplicities, zfs parameter, and exchange coupling values for bis(arylnitrene)s studied by us date. Appropriate references to these are given in the table, as well as references to related work by others. We have recently found that at least some of the bis(arylnitrene)s in Table I are stable up nearly to room temperature in a crystalline matrix of their corresponding dinitro precursors,[22] raising the possibility of further investigating their zfs tensors under oriented sample conditions. Combining the work of ourselves and others, the amount of data available for bis(arylnitrene)s is now substantially greater than it was only five years ago, and contributes considerably to the "rule book" of structure-property relationships for exchange interactions in organic conjugated molecules. The ease with which such systems are generated -- and with which various ESR spectrally active intermediates are identified -- makes them ideal model systems, despite their lack of practically useful stability. We hope that further such investigations of conformational and topological effects upon exchange will continue to advance the possibility of designing organic and organic-inorganic systems with designed magnetic properties.

ACKNOWLEDGMENTS

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