bromo-2-methoxy- and 1-methoxy-2-bromoalkanes in a ratio of 1/1. The same experiment was also carried out in the presence of 0.10 M NaBr and yielded 36% dibromide. Anal. Calcd for $C_7H_{15}BrO$: C, 43.09; H, 7.75; Br, 40.96. Found: C, 43.01; H, 7.78; Br, 40.98. ^{13}C NMR: CH_3O $\delta = 58.65$, OCH_2 $\delta = 76.72$, CHBr $\delta = 53.27$, CH_3 $\delta = 13.69$, CH_3O $\delta = 57.06$, CH_2Br $\delta = 34.34$, OCH $\delta = 80.02$, CH_3 $\delta = 13.81$. Anal. Calcd for $C_8H_{17}BrO$: C, 45.95; H, 8.19; Br, 28.21. Found: C, 45.90; H, 8.20; Br, 28.12. ^{13}C NMR: CH_3O $\delta = 58.79$; OCH_2 $\delta = 76.82$; CHBr $\delta = 53.00$; CH_3 $\delta = 13.94$; CH_3O $\delta = 57.19$; CH_2Br $\delta = 34.49$; OCH $\delta = 80.12$; CH_3 $\delta = 13.90$. Anal. Calcd for $C_9H_{19}BrO$: C, 48.44; H, 8.58; Br, 35.81. Found: C, 48.40; H, 8.49; Br, 35.78. ^{13}C NMR: CH_3O $\delta = 58.44$, OCH_2 $\delta = 76.62$, CHBr $\delta = 52.97$, CH_3 $\delta = 13.69$; CH_3O $\delta = 56.87$, CH_2Br $\delta = 34.03$, OCH $\delta = 79.95$, CH_3 $\delta = 13.71$. Anal. Calcd for $C_{11}H_{23}BrO$: C, 52.59; H, 9.23; Br, 31.81. Found: C, 52.37; H, 9.30; Br, 31.60. ^{13}C NMR: CH_3O $\delta = 58.78$; OCH_2 $\delta = 76.86$; CHBr $\delta = 52.99$; CH_3 $\delta = 14.01$; CH_3O $\delta = 57.19$; CH_2Br $\delta = 34.43$; OCH $\delta = 80.15$; CH_3 $\delta = 14.01$. Anal. Calcd for $C_{13}H_{27}BrO$: C, 55.91; H, 9.74; Br, 28.61. Found: C, 55.86; H, 9.71; Br, 28.59. ^{13}C NMR: CH_3O $\delta = 58.65$, OCH_2 $\delta = 76.77$, CHBr δ 53.20, CH_3 $\delta = 13.95$; CH_3O $\delta = 57.07$, CH_2Br $\delta = 34.24$, OCH $\delta = 80.11$, CH_3 $\delta = 13.95$.

Bromination Kinetics. Solution of alkenes in CTAB were prepared by mixing stock solutions of 0.20 M alkene in MeOH (the percentage of alcohol in the final solution was <0.10 %), 0.05 M CTAB in water, and 5.00 M NaBr in water. The kinetic runs were performed on a Durrum-Gibson stopped-flow spectrophotometer at 25.0 ± 0.1 °C. Each run was performed six times, and the reproducibility was ±3% or better.

One syringe contained micellized alkene (2.00×10^{-4} M) and NaBr (when used), the other bromine and HCl (0.01 M). The acid was used in order to suppress HOBr formation and consequently the presence of another brominating agent. However, runs performed in absence of HCl agreed with those performed in its presence. Bromine concentration after mixing was 1.30×10^{-5} M, and first-order conditions were maintained.

The kinetics of the bromination reaction of 1-hexane with 2×10^{-4} M added *n*-decane were performed under the same conditions. For bromination of *cis*-4-cyclohexene-1,2-dicarboxylic acid dimethyl ester in water, one syringe contained 4.60×10^{-4} M alkene in water and the other 3.00×10^{-5} M Br_2, NaBr, and 1.00×10^{-2} M HCl. Reactions were followed by monitoring the decrease in absorbance at 270 nm. First-order rate constants were calculated by using the kinetic equation

$$\ln\left(\frac{A_\infty - A_0}{A_\infty - A_t}\right) = kt$$

The initial absorbance of Br_3^- in CTAB at 270 nm did not increase on addition of NaBr and for CTAB > cmc did not increase with added CTAB.

Competitive Kinetics. Bromine (40 mg, 0.25 mmol) was added dropwise to 25 mL of $CHCl_3$ containing 42 mg (0.50 mmol) 1-hexene and an equimolar amount of another 1-alkene (1-octene, 1-decene, or 1-dodecene). The product composition was compared with standard solutions of dibromides by GLC. The same experiment was performed in $CHCl_3$ in the presence of 5.00×10^{-3} M Bu_4NBr and in MeOH with and without NaBr. Reaction of Br_2 was quantitative and equimolar products were isolated.

Acknowledgment. We wish to thank Prof. C. A. Bunton for revising the manuscript.

Semiempirical Study of Electron Exchange Interaction in Organic High-Spin π Systems. Classifying Structural Effects in Organic Magnetic Molecules

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A semiempirical AM1 molecular orbital plus configuration interaction model is applied to π-conjugated organic open-shell molecules in order to understand qualitatively the manner and degree to which they are spin-coupled by various electronic mechanisms, either in simpler open-shell systems or, in some examples, in larger polyradicals. A "library" of spin-coupling spacer groups (X in radical–X–radical or nitrene–X–nitrene) is delineated with relative exchange interaction strengths and natures described, including alkenes and polyalkenes, alkynes, phenyl rings, heteroatoms, and nonalternant pseudoaromatic systems. Example systems in which ferromagnetic (high-spin) coupling is observed in diradical models are predicted to remain high-spin as higher oligomeric species with like connectivity. The implications of these semiquantitative computational predictions in relation to simple qualitative models of radical–radical spin coupling are discussed in several cases. Overall, the semiempirical MO–CI method is shown to be both conceptually useful and highly cost effective for semiquantitative study and classification of broad classes of electron exchange coupling effects in non-Kekulé molecules.

Introduction

Recently, there has been much interest in the synthesis of organic materials with magnetic properties for potential information storage purposes.[1,2] Different groups have aimed variously at the synthesis of charge-transfer organometallic mixed-crystal materials,[3] high-spin molecular ferromagnetic materials based upon ground-state paramagnetic crystalline materials,[4,5] nonconjugated polynitroxide radicals,[6,7] and π-conjugated polyradicals[8-10] and

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(1) Cf. the various papers in: *Proceedings of the Symposium on Ferromagnetic and High-Spin Molecular Based Materials*, 197th National Meeting of the American Chemical Society, Dallas, TX, Fall 1989; Miller, J. S., Dougherty, D. A., Eds.; American Chemical Society: Washington, DC, 1989. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 1ff. Some of these are cited variously in the following references.

(2) Cf. *Proceedings of Symposium Q*, Materials Research Society Meeting, Boston, MA, Nov 1989; Chiang, L. Y., Chaikin, P. M., Cowan, D. O., Eds.; Materials Research Society: Pittsburgh, PA, 1990. *Mater. Res. Soc. Symp. Ser.* **1990**, *173*, 1 ff.

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polycarbenes.[11] The different strategies have in many cases been based upon efforts to apply to organic substrates different theoretical models of ferromagnetic coupling. Models for ferromagnetic coupling in organic or organometallic species include superexchange,[12] high-spin charge-transfer exchange,[3,4,13] and application of different versions of parity rules to very high-spin π-conjugated polyradical systems.[14-17]

As part of our investigations of magnetism in organic diradicals and polyradicals, we have applied semiempirical computational methods to predict experimental ground-state (GS) spin multiplicities for such species. We have previously shown[18,19] the success of models based upon semiempirical molecular orbital (MO) plus configuration interaction (CI) computations in correctly predicting GS spin multiplicities for a variety of experimentally known diradicals and diradicaloids. In this paper, we extend our computational procedure to a number of systems in order to study the application of the parity rules as qualitatively applied to π-conjugated open-shell systems, not only for a number of still-unknown diradical models, but also for some polyradical oligomers that are experimentally plausible. We will show that for high-spin predictions the parity rules are generally in agreement with our semiquantitative predictions, that a variety of structural types allow fairly efficient ferromagnetic coupling of unpaired electron spin to give high-spin GS's, and that electron exchange coupling in several polyradical systems is predicted to be of sufficient magnitude to permit very high-spin GS's. This information is of use, not only as general information concerning the approximate magnitude of exchange interaction in polyradical systems hitherto treated by qualitative methods, but as guidance for specific experimental tests of theory.[20]

Background

We shall limit our background discussion of the various models for electron exchange coupling in organic magnetic materials, since the models and their justifications are described in detail in the references variously cited in the following text. We will focus upon the parity-based models of coupling, since we are particularly interested in using such models to design high-spin organic systems. A valence bond based description of spin coupling in polyradicals has been advanced by Ovchinnikov.[14] Related models have been described by Klein[15] and Mataga,[16] but the predictive results are quite similar, so we shall restrict ourselves explicitly to the Ovchinnikov model.

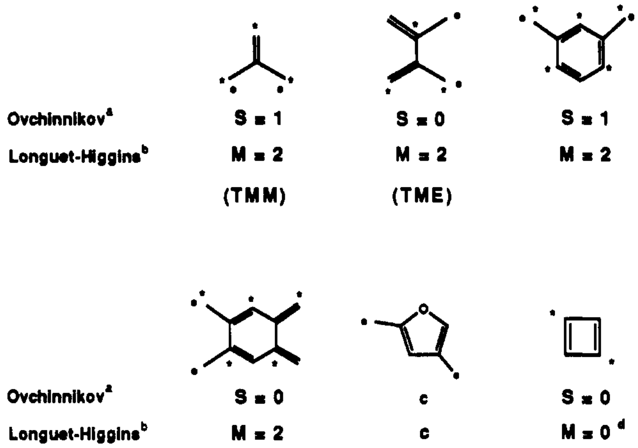

Figure 1. Qualitative ground-state spin multiplicity prediction in non-Kekulé molecules. Key: a, predictions by the Ovchinnikov model[14] (similar predictions are given by Klein's methodology[15]) S = spin quantum number; b, predictions by Longuet-Higgins model,[25] M = multiplicity (number of spin parallel electrons); c, no prediction, since the system is nonalternant. Hund's rule predicts a triplet GS; d, this prediction assumes no special effects upon orbital degeneracy of delocalized annulenoid geometry.

By Ovchinnikov's formulation, an alternant π-system with $n^* > n^0$ will have a ground-state (GS) spin quantum number S given by eq 1 (see examples in Figure 1). Thus,

$$S = (n^* - n^0)/2 \qquad (1)$$

trimethylenemethane (TMM) is predicted to possess a triplet GS, while tetramethyleneethane (TME) should possess a singlet GS. For an appropriate connectivity polymeric system of N units each with spin quantum number $S > 0$, the spin multiplicity of the polymer would be $N(2S + 1)$. Such a system would in principle possess a very high-spin GS and be a one-dimensional ferromagnet. Ovchinnikov noted in his derivation that heteroatom substitution would not greatly effect predictions,[14] but only the parity of connectivity in the π system. Simple tests of this model would thus be provided by the synthesis of high-spin diradical models with $n^* > n^0$ and low-spin diradical models with $n^* = n^0$. The Klein description[15] of polyradicals is quite similar in application to the Ovchinnikov model, whereas the Mataga model[16] is related except in being explicitly applied to polycarbenes instead of polyradicals, hence the spin quantum numbers S for a π system in Mataga's treatment are two times those for corresponding polyradicals (assuming each phenyl carbene center is a triplet). Figure 1 shows the predicted values of S for some typical model diradicals.

Experimental work has shown that the Ovchinnikov model and related parity models are not always successful in their prediction of low-spin GS multiplicities for systems in which $n^* = n^0$. Both parent tetramethyleneethane[21] (TME, 1) and conformationally constrained near-planar TME's[22,23] 2 and 3 have been generated under matrix isolation conditions, and experimental electron spin resonance (ESR) spectroscopic results[21,23] strongly support

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triplet GS multiplicities for these, despite the singlet prediction of eq 1 and related parity models.[24]


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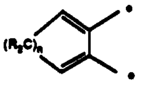
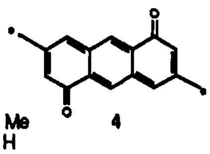

2 $n = 1$, R = Me
3 $n = 2$, R = H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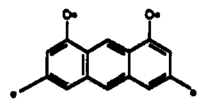
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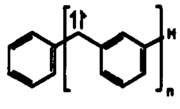
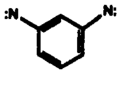

6 $n = 2$-5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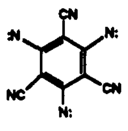
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It is worth noting at this point that a model[25] by Longuet-Higgins, on the basis of Hund's rule, predicts a *triplet* GS for the TME's, in accordance with present experimental interpretations. By this model, for a planar alternant system with N π centers and T double bonds in the structure of highest Kekulé bondedness, the spin multiplicity M is given by eq 2. Examples are shown in Figure 1, by comparison to the predictions by the Ovchinnkov model.

$$M = N - 2T + 1 \qquad (2)$$

In a case related to TME, Berson and Seeger[26] have generated organic diradical 4, which experimentally has a triplet GS at variance with the Ovchinnikov model, but in agreement with the Longuet-Higgins model. In addition, some TME related systems that are bridged by heteroatoms, instead of saturated carbon centers, have experimental singlet GS's,[27] which are nominally in accordance with the Ovchinnikov model. However, the heteroatoms in these systems may perturb them sufficiently to invalidate a strict application of the parity rules in these cases, and they should rather be considered as nonalternant π systems. Previous computational work by ourselves[19] and others[28] in treating such heteroatom-bridged systems has been in good qualitative accord with experiment.

Having noted these apparent violations of the Ovchinnikov and related models, it is important to note that presently available experimental methodology does not permit one to differentiate whether a system with an observed high-spin GS has a small or large energy gap to the lowest lying excited state of lower multiplicity. As a result, except for systems with very low-lying excited states (<0.5–1.0 kcal/mol), little is known about the quantitative energies of states with different multiplicities for non-Kekulé molecules. This is important, since a formal violation of any of the qualitative models of polyradical GS multiplicity might be observed, when in a more complete sense a fairly small energy gap to an experimentally inaccessible excited state would actually be in accord with a less strict interpretation of the models that predict less stabilization for high-spin GS's in certain connectivity classes. The background and implications of this experimental difficulty in interpreting the theoretical significance of various observed π diradicals GS spin multiplicities is described in some detail by Berson elsewhere.[29] Overall, the result is to render less important the actual GS spin multiplicity that might be computationally predicted for a polyradical, but to make quite important three classes of such systems: those with strong ferromagnetic coupling, those with strong antiferromagnetic coupling, and those with fairly weak coupling of any sort. The weakly coupled class might be of either high- or low-spin GS, which would render experimental investigation by spin state unclear unless computational investigation is also carried out to verify the weakness of coupling.

Despite the qualitative failures for systems where a low GS has been predicted, the Ovchinnikov parity rule generally has worked quite well for systems where $n^* > n^0$.[18,19,30] In one particularly interesting example by Berson and Seeger,[26] a quintet GS was found for reactive species 5, in agreement with both eqs 1 and 2. In polycarbene oligomers 6, the parity model of Mataga is obeyed, leading to some very high-spin molecules in experimental work by Iwamura, Itoh, and their respective co-workers.[31] Similarly, some dinitrene and trinitrene species (e.g., 7 and 8) are found to have high-spin GS's when $n^* > n^0$.[32] Clearly, high-spin predictions for such cases are more dependable than predictions for the systems with near degenerate high- and low-spin states with $n^* = n^0$. For $n^* > n^0$ systems, eqs 1 and 2 typically agree in their predictions of high-spin GS's, despite their different derivation procedures.

Thus, although the parity rules are not infallible in their predictions for diradicals, they generally have functioned well as qualitative predictors of experimental GS spin multiplicity where $n^* > n^0$. However, they throw no clear insight onto the magnitude by which one spin state may be favored over another in a single such system, nor do they allow comparison of exchange coupling strength between different systems of the same qualitatively predicted GS spin multiplicity. In addition, they allow little insight into the detailed electronic nature of the species in question, save perhaps through use of spin polarization arguments[30] to predict where alternating sites of positive and negative spin density will exist in a polyradical.

Fortunately, computational methods have proved effective for understanding of diradical systems. Ab initio computations have been carried out for a number of important non-Kekulé species, and their qualitative predictions for GS spin multiplicity have in general been confirmed by experiment (TME being the most notable exception). Also, semiempirical methods have been applied

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[24] Cf. also a clear description of the factors affecting the qualitative GS spin multiplicity in tetramethyleneethane in: Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* 1977, *99*, 4587. For an ab initio study of TME, see: Du, P.; Borden, W. T. *J. Am. Chem. Soc.* 1987, *109*, 930.

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to such problems and have proved to be as efficacious for qualitative GS spin-state predictions as the more time-consuming ab initio methods for most cases tested to date.[18,19] It is highly desirable to apply the knowledge gained in the study of smaller diradical systems toward effects that might occur in very high-spin polyradicals, in hopes of pointing the way toward rational design of putative organic ferromagnetic polyradical materials. For a broadly based study of spin coupling effects in large numbers of diradical models and related oligomeric polyradicals, semiempirical methods of proven efficacy such as those described in the following text offer obvious advantages of speed and economy.

Computational Methods

All computations were carried out on the University of Massachusetts (Amherst) chemistry department Celerity C1260-D UNIX superminicomputer using Version 2.10 of the program AMPAC[33] as modified and appropriately tested to run under our local computing environment. Structures obtained from these computations are readily visualized using the PCMODEL[34] or CHEMCAD[35] programs on an IBM clone AT class computer with 80287 coprocessor, allowing easy investigation of bonding parameters.

We were mainly interested in systems that may be in principle experimentally achievable, many of which are complex, large computational problems. Although some of the smaller systems of interest in this study might be capable of being treated by ab initio theory if resources were available, the larger oligomeric systems are too large to be so treated in a practical manner. We decided to do all computations at a similar, semiempirical level of theory, in order to be able to gauge consistency of our algorithm in going from smaller systems to systems[36] larger than those that may easily be investigated by both experiment or ab initio theory. Ab initio methods have been in reasonable agreement with our semiempirical model,[19] so we may assume that extension to systems beyond the present reach of ab initio theory is not inappropriate. It is important to note at the outset that, by our choice of semiempirical methods, we necessarily restrict ourselves to qualitative or (at best) semiquantitative conclusions about energetic trends in groups of molecules,[18,19,36] rather than numerically quantitative results for any given species. Since our aim is to understand trends in large groups of molecules, we do not consider this drawback a major impediment to understanding the systems of interest. In no way do we wish to imply that this procedure is "better" than more precise ab initio methods, but merely more convenient and of sufficient accuracy to be a practically useful and economical means of looking at different states in a variety of large molecules.

For the various species of interest, choice of geometry is of importance. While small changes in various geometric parameters generally do not in our experience greatly affect the qualitative energetics of molecules that lack high symmetry, larger relative changes may be important in small systems where several states are of similar energy. We have found that MNDO,[37] AM1,[38] and the recent PM3[39] parameterization schemes give acceptably good agreement with ab initio geometries of diradical and diradicaloid systems.[19] For systems that might have either triplet or singlet GS spin multiplicity, we carried out AM1 optimization using both restricted (RHF) and unrestricted (UHF) Hartree–Fock wavefunctions. In our systems, the difference between RHF and UHF geometries generally were not large enough to affect the qualitative-state energy ordering or even the approximate relative energies of final states. Typically, UHF optimizations gave somewhat more delocalized geometries at the cost of spin contamination of the wavefunctions. Since the differences were not very large, we used the standard AMPAC RHF wavefunctions for geometric optimization in molecules with possible quartet or quintet GS's. For larger oligomeric species, we in some cases used an approximate repeat unit geometry that was based upon optimized geometries for smaller oligomers—such procedures are noted where appropriate.

To be self-consistent in an ab initio sense, we would have had to optimize separately states of differing multiplicity. We found for several small test systems that such separate optimization did not produce large differences in the relative energy separation of different states, so we satisfied ourselves with using only one geometry—that of the state of highest multiplicity—for energy computations on states of all multiplicities. This procedure is justified only by computational parsimony, not by theoretical means, but we have found it effective in previous work. This procedure may cause a slight favoring of the most delocalized spin state—typically the highest multiplicity state.

In addition, since many experimental studies aim at polyradical generation in the solid state, typical gas-phase geometries as produced by our computations may not be entirely appropriate. We decided to approximate this effect crudely by performing most optimizations with a planar restriction on the π system, even when this seemed chemically unrealistic. This reflected our desire to probe mainly the effect of connectivity and π-system type on exchange coupling efficacy, rather than geometry-governed changes in conjugation that would weaken spin interaction. In addition, by this approximation we hope to some degree to mimic flattening by crystal packing in a solid-state π system. We found that torsion about single bonds by up to about 30° still allows sufficient conjugation to leave unaffected qualitative ordering[40] of states in several test systems.

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[33] Dewar, M. J. S.; Stewart, J. J. P. *QCPE* **1987**, *506*.

[34] This program was purchased from Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076.

[35] This program was purchased from C-Graph Co., Austin, TX.

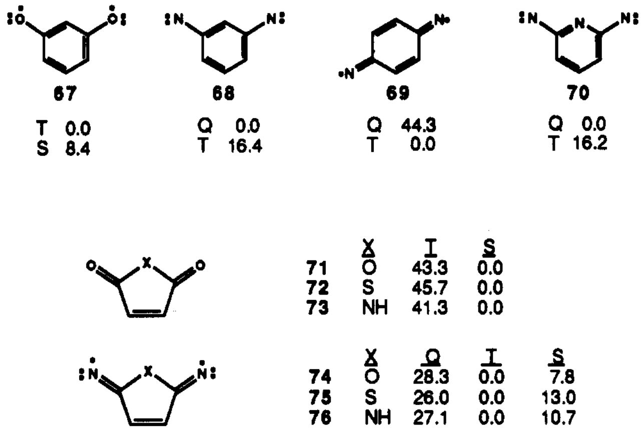
[36] Even at an ab initio level, the molecular orbital plus *truncated* configuration interaction level of theory is not size consistent, i.e., it does not necessarily follow that a computational scheme that well describes a small system will work well for a larger—though structurally related—system. References 18 and 19 have shown the calibration of an INDO semiempirical truncated CI method versus experiment and ab initio theory; similar calibrations were carried out by us for the AM1–CI scheme used in this paper. For comparison to other methodologies, the scheme whose use we describe in the text by use of AMPAC keywords yields the following number of configurations for our smallest CI = 6 active space of six orbitals: quintet = 36, quartet = 90, triplet = 225, doublet = 300, singlet = 400. The number of interacting configurations is thus quite modest for higher multiplicity states and is far from quantitatively satisfactory where numerous orbitals are energetically capable of interaction in the frontier orbital energy region. Our extrapolation of this method to large oligomers is based upon convenience and computational parsimony and remains to be verified by experiment or higher level theory in the case of larger systems such as the polymers of Figure 4. Nevertheless, we found that variation of the CI active space and excitation schemes used in our computations did not greatly affect any of our qualitative findings, so long as major configurations were seen to be included in the CI wave functions. Fortified by this finding, we proceeded with our work as described in the paper, but it is worth noting that larger CI active spaces would be desirable for some of the larger oligomers used in our system.

[37] Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

[38] Dewar, M. J. S.; Zoebisch, E. F.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3901.

[39] Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

[40] In a recent experimental example of the possibilities of highly nonplanar systems to achieve high-spin coupling of unpaired electrons, we note that the dication of perchlorobiphenyl is known to have a triplet GS. Cf. Veciana, J.; Vidal, J.; Julian, N. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 443.



67
T 0.0
S 8.4

68
Q 0.0
T 16.4

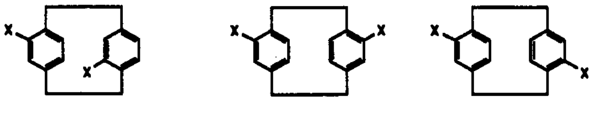
69
Q 44.3
T 0.0

70
Q 0.0
T 16.2

	X	T	S
71	O	43.3	0.0
72	S	45.7	0.0
73	NH	41.3	0.0

	X	Q	T	S
74	O	28.3	0.0	7.8
75	S	26.0	0.0	13.0
76	NH	27.1	0.0	10.7

Figure 2. AM1–CI state energy gaps for selected π-conjugated model systems. Geometries optimized by AM1 using the state wave function of highest multiplicity with a planar constraint and fixed for all state energy computations. Energy gaps are in kilocalories per mole relative to the lowest energy state; T = triplet, S = singlet, Q = quintet. For systems **69** and **74–76**, the triplet ground state is a σ,σ occupancy state; other triplet states have π,π occupancy.



87
X=O T-S^a=3.2
X=CH$_2$ 3.0

88
X=O T-S^a=0.4
X=CH$_2$ 1.5

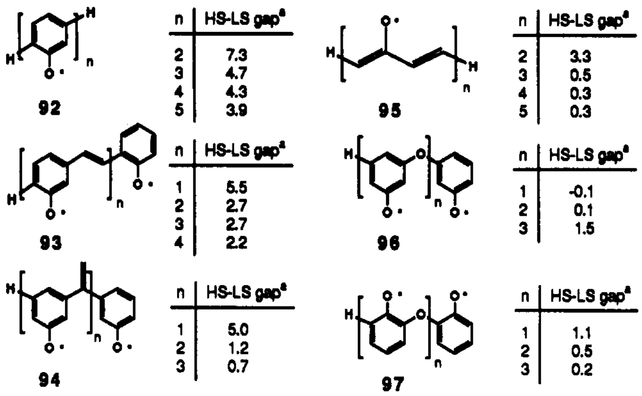
89
X=O T-S^a=1.6
X=CH$_2$ 4.8

Figure 3. AM-CI state energy gaps for some through-space coupled π systems. Key: a, geometries derived by molecular mechanics optimization of the cyclophane, then replacement of the appropriate C–H bonds with C–O bonds of 1.25-Å bond length, CH$_2$ bonds of 1.35-Å bond length. AM1-CI energy gaps in kilocalories per mole relative to the triplet state (T–S gap).

When geometries were obtained as described previously, fixed-point AM1-CI computations were carried out for states of different multiplicity by use of the appropriate algorithms in AMPAC. Molecular orbitals for the CI procedure were obtained with the open-shell RHF procedure by use of the number of open-shell MO's equal to the number of singly occupied MO's in the highest spin state of highest Kekulé bondedness.[41] For instance, the state of highest Kekulé bondedness of both TMM and TME in Figure 1 is triplet ($M = 2$). For cases that might be considered singlets due to resonance arguments, we used the OPEN(2,2) SCF computation anyway. We have found that use of at least a six molecular orbital active space gave results very similar to those from our previously used INDO/S-CI procedure for a large variety of test cases.[18,19,41]

Results

The results of the various computations are noted in Table I and Figures 2–4. Geometric parameters are not noted in this data, but may be obtained from us if desired (see Acknowledgements). Where important, specific references to the geometric data are made in the Discussion.



92

n	HS-LS gap^a
2	7.3
3	4.7
4	4.3
5	3.9

93

n	HS-LS gap^a
1	5.5
2	2.7
3	2.7
4	2.2

94

n	HS-LS gap^a
1	5.0
2	1.2
3	0.7

95

n	HS-LS gap^a
2	3.3
3	0.5
4	0.3
5	0.3

96

n	HS-LS gap^a
1	-0.1
2	0.1
3	1.5

97

n	HS-LS gap^a
1	1.1
2	0.5
3	0.2

Figure 4. AM1–CI state energy gaps for selected π-conjugated model oligomers. Key: a, geometries for **92–95** derived by AM1 optimization of trimers with planar constraints; b, systems **96** and **97** were obtained by molecular mechanics optimization of unconstrained tetramers that put OH in place of oxyradical sites, followed by removal of the phenolic hydrogens. For all computations higher oligomer geometries were generated by extension of the geometric repeat unit found. AM1–CI energy gaps in kilocalories per mole from the state of highest multiplicity to the next lowest lying excited state.

Discussion

For the sake of convenience, we divide the Discussion into sections examining various effects. In subsequent descriptions, a "spacer" refers to any structural moiety that serves to couple radicals together by through-bond effects. A through-conjugated spacer is a π system that is not cross-conjugated, including 1,2-ethenediyl, 1,4-buta-1,3-dienediyl, ethynediyl, and the phenylene moieties. Cross-conjugated spacers include any system π isoelectronic with 1,1-ethenediyl.

Our diradical models studies yield high- or low-spin GS's based upon whether the used spacers result in ferromagnetic or antiferromagnetic coupling. We may in effect consider a spacer as an operator or mechanism that couples unpaired electrons of two spin-bearing moieties in a manner dependent upon final connectivity or upon through-space interactions in different geometries. The organization of Table I is meant to reflect this approach to exchange coupling, where the spacers –X– are varied.

Diradical vs Dinitrene Models. Many of the connectivity structural types in this study were performed with both oxyradicals and nitrenes as spin carrying sites. Results for the two types of systems have been divided in Table I and may be usefully compared so long as a few general ideas are kept in mind. First, each oxyradical site contributes a single unpaired electron to the π framework (assuming for the Discussion that we are not interested in n–π-type occupancy states). A nitrene site contributes two unpaired electrons, one to the π system and one to a n- (or σ-) type orbital.[11,16] Thus, for a system with similar all-ferromagnetic spin coupling effects, a dinitrene will have twice the spin quantum number S of the corresponding diradicals (e.g., **68** vs **67**). Second, the presence of two types of unpaired electron sets in the dinitrene models—the delocalized π set and localized σ set—complicates matters in systems with antiferromagnetic coupling in the π system. The qualitative parity models generally consider *only* the effects of π-electron interactions on GS multiplicity. It is not clear from these rules whether the coupling between σ unpaired electrons will be ferromagnetic or antiferromagnetic in any given case. As a result, whereas antiferromagnetic coupling in the system **77** leads

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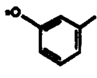
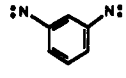
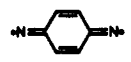
[41] For all states we used the OPEN(N,N) statement to specify the reference configuration, where N refers to the number of open-shell orbitals and unpaired electrons in the state of highest desired multiplicity. We then performed CI using the 1SCF MECI CI = M option, where M was taken as 6–8 (most commonly 6). The CI wave functions could be examined using the ROOT option. In all cases we used the keyword appropriate to multiplicity in the CI calculations (e.g., keyword QUINTET for quintet calculations, etc.).



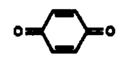
67



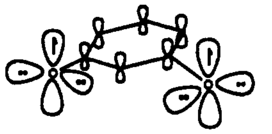
68



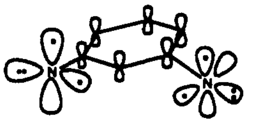
69



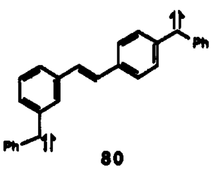
77



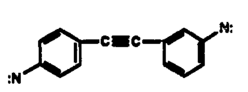
oxy radical site



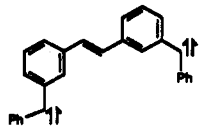
nitrene site



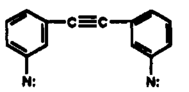
80



27



81



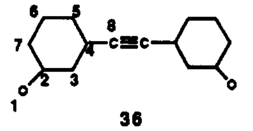
48

unequivocally to a singlet GS, in the corresponding dinitrene 69 either a singlet or a triplet might occur on the basis of the coupling between the σ electrons. In an additional comparison of related high- vs low-spin nitrene systems, the π electrons are paired parallel in 68 and paired antiparallel in 69. In looking at the dinitrene models, it is important to note in comparison to parity rule predictions that computation of a triplet σ,σ occupancy GS for a dinitrene is indicative of antiferromagnetic coupling between the π electrons, while a quintet indicates ferromagnetic coupling. Thus, singlets are not necessarily expected for antiferromagnetically coupled dinitrenes, since the parity rules as we are using them are applied only to the π electrons in a system. Experiments on matrix-isolated dinitrenes[42] confirm that a triplet may be observed in an antiferromagnetically coupled dinitrene, such as 1,4-phenylenedinitrene 69[42b] (Figure 2). In other respects, our computations indicate that dinitrenes and dioxy diradicals are quite comparable in organic π systems.

Through-Conjugated π Hydrocarbon Spacers: Olefins and Acetylenes. We find direct connection, 1,2-ethenediyl, and acetylenic spacers to be reasonably effective in coupling radical spin when eqs 1 and 2 both predict high-spin states. The *m,p'*-biphenyldioxyl system 9 is strongly coupled; even an imposed 90° twist in this system only reduces the T–S gap from 12.5 to 6.0 kcal/mol. Whether planar or somewhat twisted, the *m,p'*-stilbenedioxyl 10 and *m,p'*-diphenylacetylenedioxyl 12 are also GS triplets by modest margins, with spin distributions in all these systems showing no destabilizing "defects" that place adjacent to one another two or more centers of the same sign in net spin density.[43a] The GS triplet CI wavefunctions show the expected π–π rather than n–π electronic nature. The excited state singlets have two-configuration SCF diradical natures.[43b] These results are consistent with ferromagnetic coupling in the high-spin systems.

Supporting these results, Iwamura and co-workers have found that the *trans*-1,2-ethenediyl spacer and the ethynediyl spacer give ferromagnetically coupled high-spin GS's in dicarbene 80[44] and dinitrene 27,[32b] where eq 1 predicts high-spin coupling for these meta, para' connectivity systems.

For the meta,meta' connectivity pattern with ethenediyl and ethynediyl spacers, eq 1 predicts low-spin antiferromagnetic coupling and a singlet GS. However, in 35 and 36 we still find small preferences for a triplet GS, in qualitative accord with eq 2 (Longuet-Higgins model). The preference for the high-spin state in the meta,meta' connectivities is sufficiently small that it is probably unrealistic to attach too much significance to the order of states we compute, but is significant to note the near-degeneracy of high- and low-spin states, as expected when $n^* = n^0$. Also, the singlet CI wavefunctions for these species are essentially of open-shell nature rather than two-configurational, suggesting near-independence of the unpaired electrons in separate portions of the molecule. This may also be exemplified by examination of the triplet spin density distribution of the *m,m'*-diphenylacetylenedioxyl 36, in which a destabilizing "defect" exists in the spin pairing at the acetylenic carbons (site 8 below), where the spin density is nearly zero due to the desire of the unpaired electrons to localize in nonoverlapping regions in this system. This results in a near-degeneracy between the destabilized high spin state and the low spin state. These results are supported experimentally by Iwamura's work[32a,44] on the systems 48 and 81, which both appear not to have high-spin GS's.



36

Triplet UHF Spin Density (Calculated)

1	0.37	5	0.54
2	-0.18	6	-0.30
3	0.52	7	0.52
4	-0.37	8	-0.03

When the spacer is computationally lengthened with the meta,meta' ($n^* > n^0$) connectivity, the GS for both the 1,4-butadienediyl and 1,4-diacetylenediyl spacers (11 and 13, Table I) remains a ferromagnetically coupled triplet. Although the former result was achieved by artificially imposing a chain-extended planar geometry, ferromagnetic coupling is not lost despite lengthening of the spacer. The same result is found in the geometrically simpler diacetylenediyl-coupled systems. Overall, ferromagnetic coupling is qualitatively retained despite increasing spacer length. Iwamura[32b] has recently found that the diacetylene-linked *m,p'*-dinitrene 28 has a high-spin quintet GS just as for the previously mentioned ethynediyl-coupled system 27, in qualitative agreement with our computational result. For the meta,meta' connectivity in diacetylene system 49, a high-spin GS is not indicated by theory or experiment,[32b] as was so for the diethynediyl-coupled system. Thus, both experimentally and computationally, evidence to date indicates that increasing the length of the polyalkyne spacers does not greatly change the nature of exchange coupling in these systems.

It is unclear to what extent increasing the length of a conjugated spacer, e.g., a polyalkyne, would lead to a loss of exchange coupling between terminal spin-bearing sites. At some point the desire to localize the π electrons of the spacer in discrete double bonds should outweigh the tendency to allow delocalized electron–electron coupling, even in nominally favorable connectivity cases ($n^* > n^0$).

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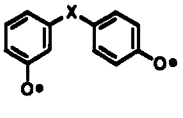
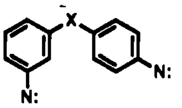
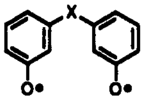
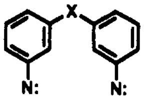
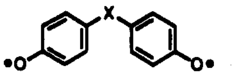
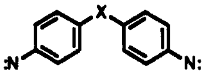
(42) (A) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076. (b) Trozzolo, A. M.; Murray, R. W.; Smolinsky, G.; Yager, W. A.; Wasserman, E. *J. Am. Chem. Soc.* **1963**, *85*, 2526.

(43) (a) In ref 19, we found a singlet GS for the *m,p'*-stilbenedioxy by use of the INDO/S-CI method. The reason for this result, which is in violation of the Ovchinnikov and the Longuet-Higgins models, is unclear, since the AM1–CI method gives a triplet GS. (b) As discussed in refs 19 and 28, a singlet state may consist of mostly one closed-shell configuration (Kekulé molecule), mostly one open-shell configuration (open-shell diradical), or a mixture of at least two, usually closed-shell configurations (two-configuration diradical).

(44) Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 1266.

Table I

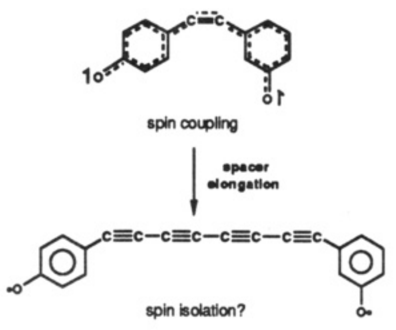
structure	X		planar high-spin to low-spin gap[a,b]	nonplanar high-spin to low-spin gap[a,b]
	(none)	**9**	12.5	11.6 (6.0[c])
	$\mathrm{CH{=}CH}$	**10**	6.5	
	$(\mathrm{CH{=}CH})_2$	**11**	6.0	
	$(\mathrm{C{\equiv}C})$	**12**	3.8	2.1
	$(\mathrm{C{\equiv}C})_2$	**13**	2.7	1.1
	$(\mathrm{C{\equiv}C})_3$	**14**	2.7	
	$(\mathrm{C{\equiv}C})_4$	**15**	1.3	
	$(\mathrm{C{\equiv}C})_5$	**16**	0.6	
	p-phenylene	**17**	1.8	
	m-phenylene	**18**	−0.2	
	$>\mathrm{C{=}CH_2}$	**19**	−1.1	
	$>\mathrm{C{=}O}$	**20**	1.9	0.1
	2,5-furandiyl	**21**	0.2	
	2,5-pyrrolediyl	**22**	0.6	
	NH	**23**	4.2	4.5[d]
	O	**24**	2.8	0.6[d]
	(none)	**25**	9.6	
	$(\mathrm{CH{=}CH})$	**26**	4.0	
	$(\mathrm{C{\equiv}C})$	**27**	2.7	
	$(\mathrm{C{\equiv}C})_2$	**28**	2.0	
	$>\mathrm{C{=}CH_2}$	**29**	2.4	
	2,5-furandiyl	**30**	1.4	
	2,5-pyrrolediyl	**31**	1.1	
	NH	**32**	3.2	1.4
	O	**33**	1.8	
	(none)	**34**	−0.6	−0.5
	$(\mathrm{CH{=}CH})$	**35**	1.4	0.9
	$(\mathrm{C{\equiv}C})$	**36**	0.5	
	$(\mathrm{C{\equiv}C})_2$	**37**	0.8	0.4
	p-phenylene	**38**	0.8	0.7
	m-phenylene	**39**	3.4	2.3
	$>\mathrm{C{=}CH_2}$	**40**	5.0	3.7
	$>\mathrm{C{=}O}$	**41**	0.7	
	2,5-furandiyl	**42**	4.2	
	2,5-pyrrolediyl	**43**	4.9	
	NH	**44**	0.3	0.3[d]
	O	**45**	−0.4	−0.1[d]
	(none)	**46**	3.0	
	$(\mathrm{CH{=}CH})$	**47**	0.8	
	$(\mathrm{C{\equiv}C})$	**48**	1.2	
	$(\mathrm{C{\equiv}C})_2$	**49**	0.5	
	$>\mathrm{C{=}CH_2}$	**50**	4.6	
	2,5-furandiyl	**51**	0.5	
	2,5-pyrrolediyl	**52**	0.3	
	NH	**53**	0.2	0.8[g]
	O	**54**	1.1	0.7[g]
	$>\mathrm{C{=}CH_2}$	**55**	5.2	2.8
	$>\mathrm{C{=}O}$	**56**	1.0	
	m-phenylene	**57**	5.4	2.4[d]
	NH	**58**	−10.3[e]	−2.8[d]
	O	**59**	−4.5[e]	−0.1
	2,5-furandiyl	**60**	−8.2	
	2,5-pyrrolediyl	**61**	−9.1	
	$>\mathrm{C{=}CH_2}$	**62**	8.5	
	NH	**63**	−1.4[f]	−7.5[g]
	O	**64**	−0.7[f]	−2.8[g]
	2,5-furandiyl	**65**	−6.4[f]	
	2,5-pyrrolediyl	**66**	−3.5[f]	

[a] Partial geometry optimization by AM1 for wavefunction of highest spin state with use of planar constraints. Gaps are given relative to the state of highest spin multiplicity in kilocalories per mole. [b] Geometries optimized by AM1 without planar constraints, except where otherwise noted. [c] AM1 optimized with imposed 90° twisted geometry. [d] Geometry obtained from molecular mechanics optimization of the diol, followed by removal of hydrogens attached to the oxygens; result is a strongly nonplanar geometry. [e] Closed-shell singlet CI wave functions were found for these ground states. [f] AM1 optimized with planar constraint. [g] AM1 optimized with imposed 90° twisted geometry.

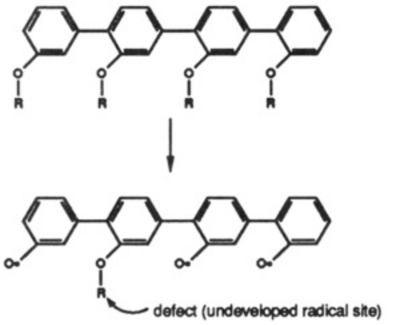
Our computations suggest that for two coplanar phenoxy systems linked by oligomeric carbon–carbon triple bonds (14–16), the coupling drops off substantially for more than four links. No doubt, similar dilution of coupling may occur in other types of systems, implying that coupling should become inefficient in systems where electrons may become localized at substantial distances apart, even where connectivity is correct for ferromagnetic coupling (Scheme I).

Through-Conjugated π Hydrocarbon Spacers: Phenyl Spacers. A synthetically attractive and experimentally likely spacer is the phenyl group (1,4- and 1,3-

Scheme I



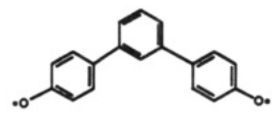
Scheme II



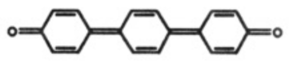
phenylene). For example, in a putative system made up of radical-generating sites on a polyphenylene oligomer, any real process used to generate the radical sites would leave some unreacted defects that did not bear the desired unpaired electron. In this situation, the defective site would be a slightly perturbed phenylene spacer. Thus, in order to allow coupling of multiple spin in a extended number of phenylene units for an experimentally realistic system of this type, effective coupling by phenylene units is desirable (Scheme II).

Our results indicate that while neither the 1,3 nor 1,4 is an extremely strong exchange-coupling spacer, both are able to couple electrons sufficiently in a ferromagnetic manner to give high-spin GS's when $n^* > n^0$ for eq 1. There appears to be a tendency of the central aromatic rings in phenylene-linked diphenoxy-based systems to maintain the integrity of the aromatic sextet, resulting in the fairly modest triplet–singlet (T–S) gaps that are observed in these systems (see Table I, **17**, **18**, **38**, and **39**). This implies that a fairly high efficiency of radical center generation will be desirable to allow experimentally practical magnetic coupling, since multiple-ring defects that are not activated to a radical-bearing form, i.e., more than one phenylene unit bridging spin bearing sites, may not effectively transmit through-bond exchange coupling.

Finally, we note that as spacers the 1,3- and 1,4-phenylene spacers have opposite parity with regard to coupling radical spins. For instance, connection of two phenoxyl radicals at their para positions to 1,3-phenylene leads computationally to high-spin triplet GS diradical **57** with $n^0 > n^*$, while the same connection to 1,4-phenylene results in strong antiferromagnetic coupling[45] and a Kekulé singlet GS molecule with quininoid structure **82**. This change in parity is also exemplified in Figure 2, for which *m*-quinone **67** and 1,3-phenylenedinitrene **68** have high-spin GS's by large margins, while 1,4-phenylenedinitrene **69** is a GS triplet of σ–σ-type occupancy—the computational findings for both dinitrenes have previously been confirmed by experiment.[42]



57



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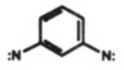

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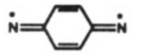
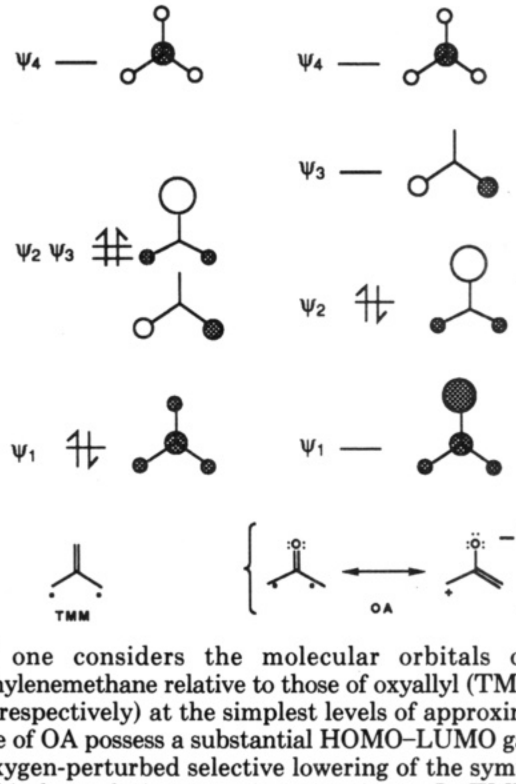
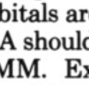


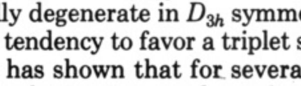
69

Effect of Using Cross-Conjugated Spacers. The cross-conjugated spacers are exemplified in our study by the 1,1-ethenediyl and carbonyl groups. Despite their similarity in a simple connectivity sense, computationally we find these two spacers to act quite differently. By the Ovchinnikov model, for instance, the two are essentially equivalent by the argument advanced in the original model description that heteroatom substitution should not greatly affect GS predictions.[14] However, MO-based considerations suggest a problem with such simplification. Because these considerations are summarized by us elsewhere[46] for the carbonyl moiety relative to 1,1-ethenediyl, we shall give only a brief description of the simple perturbation analysis for trimethylenemethane vs oxyallyl.





TMM



OA

If one considers the molecular orbitals of trimethylenemethane relative to those of oxyallyl (TMM and OA, respectively) at the simplest levels of approximation those of OA possess a substantial HOMO–LUMO gap due to oxygen-perturbed selective lowering of the symmetric π orbital ψ_2 relative to antisymmetric ψ_3. In TMM, the same orbitals are identically degenerate in D_{3h} symmetry. Thus, OA should have less tendency to favor a triplet state than TMM. Experiment has shown that for several diradical π systems, heterosubstitution need not lead to qualitative finding of a low-spin GS (see citations in refs 18 and 19). However, there has been no experimental data

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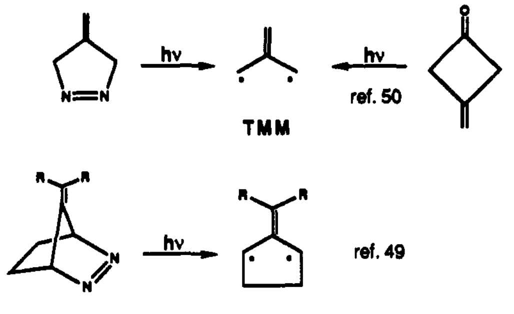
(45) Itoh, K.; Takui, T.; Teki, Y.; Kinoshita, T. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 49.

(46) Ichimura, A. S.; Matlin, A. R.; Lahti, P. M. *J. Am. Chem. Soc.* **1990**, *112*, 2868.

Scheme III



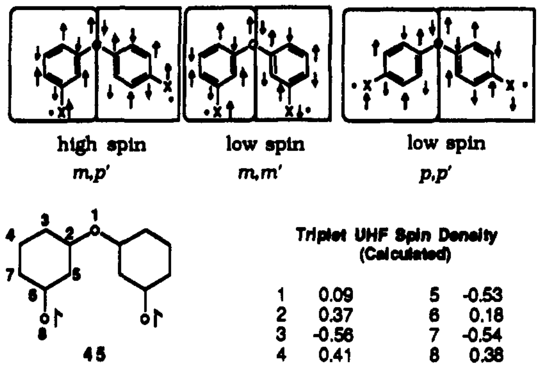
83

supporting the direct observation of an OA triplet state, to the best of our knowledge. Much of the data for OA and its derivatives have been interpreted in terms of zwitterionic or diradicaloid singlet states.[47] Recent ab initio computational results by ourselves[46] and others[48] suggest that substituted derivatives of OA do indeed possess singlet GS's, due in large part to the effect of HOMO-LUMO splitting from the extremely strong carbonyl bond in OA. The result is an electronic description of OA as two radicaloid sites weakly coupled by a central carbonyl, despite the preference for a triplet GS that might be inferred by application of the parity based models to a diradical structure of OA. Based on analysis of CI wavefunctions, the ab initio work suggests[46,48] that OA's are not "true" diradicals, but are singlet diradicaloids despite the connectivity-based prediction of a triplet by eq 1. Given the theoretical considerations and the dearth of support for triplet state OA's, it seems sufficient for us to note that the special strength of the carbonyl bond does not conduce to efficient exchange coupling.

These results for OA are quite different from the clear experimental[49,50] and computational preference for a triplet GS in TMM[51] and its simpler[52] derivatives, where the two radical sites are strongly and ferromagnetically coupled by the 1,1-ethenediyl spacer (83). In the TMM systems, triplet GS's are the rule, apparently by a strong energetic margin over the lowest singlet states.[49,50] By all previous experimental and computational evidence, the 1,1-ethenediyl group is a strongly effective exchange coupling spacer (Scheme III).

Our computations further support the notion that 1,1-ethenediyl is a far preferable exchange coupling spacer to carbonyl. No clear trend consistent with eqs 1 or 2 is found for the coupling of phenoxy or phenylnitrene systems by carbonyl. By contrast, the 1,1-ethenediyl spacer leads computationally to strong ferromagnetic coupling of spin sites where $n^* > n^0$, such as 40, 46, 55, and 62. These results suggest that 1,1-ethenediyl is worthy of experimental investigation and development. We are presently attempting to synthesize systems related to these and will report on them in due course.

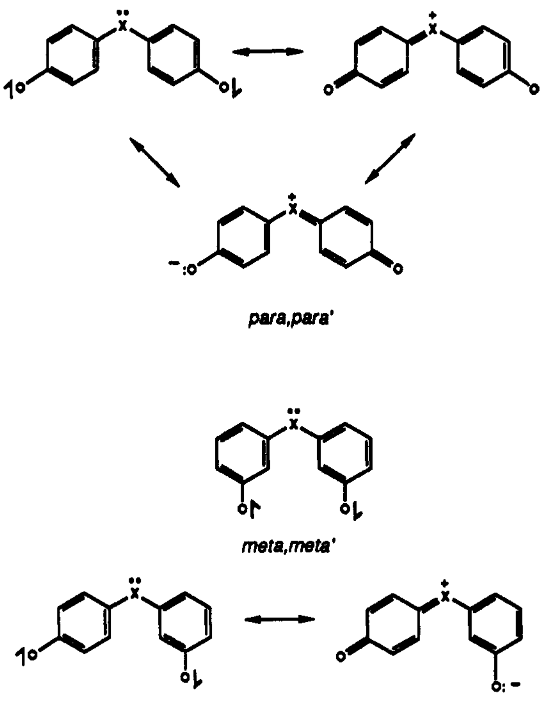
Chart I



45

Triplet UHF Spin Density (Calculated)			
1	0.09	5	-0.53
2	0.37	6	0.18
3	-0.56	7	-0.54
4	0.41	8	0.38

Scheme IV



Overall, despite the connectivity similarity highlighted by the Ovchinnikov model, the differences between carbonyl and 1,1-ethenediyl show that other effects may override connectivity in determining GS multiplicity in a π system. As a result, computational prediction is preferable to simple connectivity-based arguments in selecting experimental tests of practical "rules" governing spin coupling in organic molecules, especially where heteroatom substitution might lead to polarization of bonding.

Effect of Using Heteroatom Spacers. In this category, we primarily concerned ourselves with two-electron one-center (2e/1c) heteroatom π spacers such as oxygen and nitrogen. For these spacers, one might naively apply eq 1, since such systems are still have alternant connectivity. However, the presence of two-electron π centers alters the nature of the parity criterion. This is due to the presence of two electrons instead of one in the heteroatom π orbital. One may apply properly the parity approach to these systems by the simplified spin-pairing diagram shown (Chart I). Overall, because two electrons are contributed by the atomic p-orbital on the heteroatom, one may arrange the remaining spins in para,para' and meta,meta' systems such that two antiferromagnetically paired systems overlap at the shared p–π orbital, leading to a new low spin state. A calculation of the spin density for the triplet of the oxygen in meta,meta' coupled system

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(47) See citations in ref 46.

(48) Coolidge, M. B.; Yamashita, K.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 1751.

(49) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446. Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 4.

(50) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. Dowd, P.; Chow, M. *J. Am. Chem. Soc.* **1977**, *99*, 6498.

(51) David, J. G.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1976**, *98*, 303. Lipscomb, W. N.; Dixon, D. A. Foster, R. *J. Am. Chem. Soc.* **1978**, *100*, 1359.

(52) Schoeller, W. W. *J. Chem. Soc., Perkin Trans. 2* **1978**, 525. Dixon, D. A.; Dunning, T. H.; Jr.; Eades, R. A.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878.

45 shows a near-zero spin density defect on the central oxygen (site 1, see Chart 1) connected to larger negative spin densities on the phenoxyl moieties as shown previously. Thus, the triplet is destabilized and prefers to have spins localized on separate rings as much as possible, with resultant weak coupling.

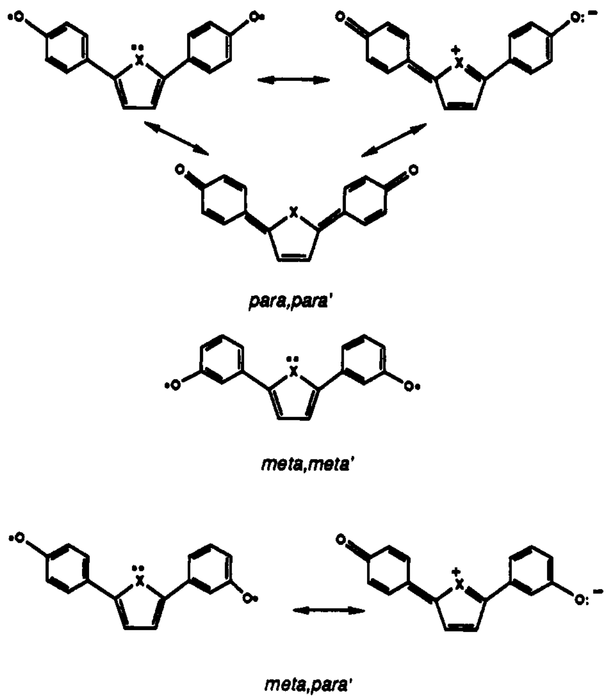
Low-spin states of the para,para′ π systems **58**, **59**, **63**, and **64** with 2e/1c spacers may be best described by a pair of equivalent zwitterionic Kekulé resonance structures, as shown in Scheme IV. The singlet CI wave functions of **58** and **59** show little multiconfigurational mixing, but consist mostly of a single, dominant closed-shell configuration. The energetic preference for the singlet state is greatest for the NH spacer, which should allow most effectively the zwitterionic resonance structure due to its electron donating ability. Given this, although we have in some places drawn these structures as diradicals for pedagogical comparison to other structures, it is clearly inappropriate to classify the singlet states of the para,para′ systems as diradicals, but rather they should be considered as zwitterionic closed-shell Kekulé molecules. The meta,meta′ systems, however, do not possess reasonable zwitterionic resonance structures, and as a result have small singlet–triplet energy separations. The singlet states in the meta,meta′ system are diradicaloid by analysis of their CI wave functions and reflect the weak coupling of the spins for this connectivity type, with the spins on the rings on either side as described earlier.

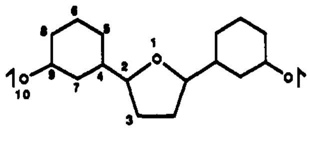
All meta,para′ connectivities in the 2e/1c coupled systems are weakly to modestly spin coupled in a ferromagnetic manner, as is easily understood by examination of the appropriate structure in the spin interaction diagram shown earlier. The coupled phenoxyl systems show diradical nature in both triplet and singlet CI wavefunctions. It appears, therefore, that the stabilization gained from the one zwitterionic resonance structure for this connectivity type is insufficient to yield a closed-shell singlet, but instead yields a diradicaloid electronic nature.

For these heteroatom coupled systems, torsion greatly reduces exchange coupling. For example, twisting of the two rings of **58** and **59** by 90° relative to the C–O–C plane essentially eliminates coupling (Table I). The strongly antiferromagnetic coupling in the para,para′ connectivity planar π systems (e.g., –10.3 kcal/mol in **58**) drops substantially in the twisted geometry. In addition, the nature of the singlet changes from predominantly closed-shell to strongly diradicaloid. This effect is readily explained by the resultant elimination of the pairwise delocalized singlet resonance forms shown for the planar geometry of the previous para,para′ system. The effects of torsion on the meta,meta′ connectivity systems are much smaller, mostly because these systems give nearly degenerate high-spin and low-spin states in any case. These findings suggest that experiments on these systems may prove difficult to interpret, since modest geometric changes such as those in frozen solution matrix vs solid crystal media could alter their electronic natures.

Itoh and co-workers[53] have recently shown that the use of oxygen as an antiferromagnetic coupling spacer for a system of appropriate connectivity was effective in producing a ferrimagnetically coupled system, with a ferromagnetic coupling spacer spanning one connection of carbene units and antiferromagnetic coupling by oxygen as the other spacer for the connectivity used in **84**. Despite the caveat noted previously, this result was in good accord with our preliminary computational results for the oxygen spacer[20] and with this work, as well as with some related computational work by other workers.[54]

Scheme V

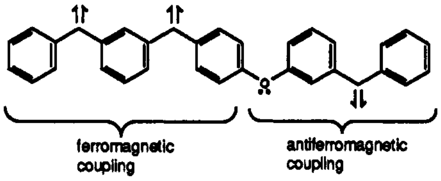




42

Triplet UHF Spin Density (Calculated)

1	0.01	6	-0.21
2	0.12	7	0.63
3	-0.19	8	0.47
4	-0.41	9	-0.42
5	0.54	10	0.47



84

Overall, although the 2e/1c-coupled systems are not directly able to be treated by the Ovchinnikov equation (1), the same types of arguments that produced eq 1 for systems containing only one-electron π centers (1e/1c) *do* apparently yield a plausible description of the 2e/1c-containing systems we studied. We are presently working on experimental tests of the predictions for 2e/1c-coupled systems and hope to report on the results of these tests in the future.

Effect of Coupling by Nonalternant Systems. Strictly speaking, the parity rule described by eq 1 (and related models) is not applicable[55] in simple fashion to nonalternant π systems. As a result, computational methods such as ours are of much importance to model

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(53) Takui, T.; Endoh, M.; Okamoto, M.; Satoh, K.; Shichiri; Teki, Y.; Kinoshita, T.; Itoh, K. *Mater. Res. Soc. Sympos. Ser.* **1990**, *173*, 63.

(54) Yamaguchi, K.; Fukui, H.; Fueno, T. *Chem. Lett.* **1986**, 1986. Yamaguchi, K.; Toyoda, Y.; Nakano, M.; Fueno, T. *Synth. Metals* **1987**, *19*, 87.

(55) A recent extension of the qualitative topological approaches to ground-state multiplicity prediction in non-Kekulé molecules is described in: Tyutyulkov, N.; Karabunarliev, S.; Ivanov, C. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 139. The model is described as applicable to "alternant and nonalternant hydrocarbons and their heteroanalogues", but few explicit examples are detailed.

and predict electronic properties for this class of molecules. We exemplify this by examining exchange coupling in systems with the nonalternant pseudoaromatic coupling spacers 2,5-furandiyl and 2,5-pyrrolediyl.

The results for these systems are quite interesting. Systems **60** and **61** and **65** and **66** with para,para′ connectivity for phenoxyl radicals and phenyl nitrenes all favor low-spin GS's—Kekulé closed-shell singlets for **60** and **61**, and σ–σ occupancy triplets for dinitrenes **65** and **66**. This is readily rationalized by reference to the appropriate resonance structures shown in Scheme V. For para,para′ systems, a connectivity path equivalent to a diene spacer may be drawn that bypasses the heteroatom in the nonalternant framework and leads to a closed-shell structure, rather than a diradical (see the discussion of structure **70** in the following text).

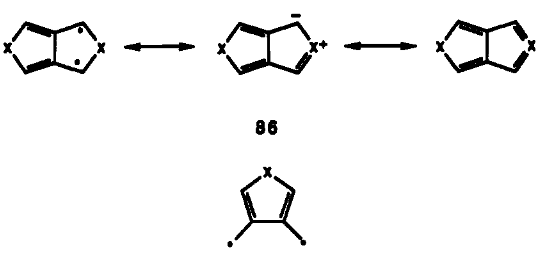
Where phenyl nitrenes or phenoxyl radicals are connected with meta,meta′ parity, no reasonable charge-separated closed-shell Kekulé structures are available. As a result, this type of system has diradicaloid singlet excited states for the dioxy systems **42** and **43** and is a triplet GS for the both the pyrrole and furan bridged cases. The dinitrenes **51** and **52** are also ferromagnetically coupled by a small margin in this connectivity. The energy gap for these is actually somewhat larger than might have been expected by the spin density analysis for **42** showing a near-zero spin density on the oxygen center (site 1) and the destabilizing presence of adjacent negative spin density in the 3 and 4 positions of the furan ring. As a result, this system somewhat resembles a meta,meta′ 1,4-butadienediyl coupled system, with the heteroatom acting as a perturbation on the carbon π centers. All the systems of this connectivity show a net modest ferromagnetic spin coupling, and so appear to be similar at this level of theory.

The meta,para′ connectivity systems **21** and **22** and **30** and **31** are weakly coupled with a slight high-spin GS preference. Thus, this connectivity pattern falls between the antiferromagnetic coupling of para,para′ and the somewhat ferromagnetic coupling of meta,meta′ coupling. Presumably, this reflects in the singlet state the desire for a single Kekulé zwitterionic resonance structure (as opposed to the two equivalent zwitterionic structure for the para,para′ systems) closely balanced by the desire to separate electrons in the diradical open-shell π electronic structure.

It is instructive to note that the para,para′ systems are related to the heterocyclic diones and dinitrenes in Figure 2. Experimentally, the pseudoquininoid diones **71–73** are well-known and are convenient calibration tests of methodology for our approach, while the dinitrene systems **74–76** are feasible experimental targets as π isoelectronic analogues. Kekulé closed-shell singlets are correctly predicted for **71–73**, whereas σ–σ occupancy triplets are found for **74–76**, showing the strong antiferromagnetic coupling in these π spin networks. The importance of the nonalternant connectivity in leading to the antiferromagnetic coupling is exemplified by the fact that a *high-spin* GS is predicted for 2,6-pyridinedinitrene **70**, which possesses a similar arrangement of heteroatoms, but which cannot achieve resonance stabilization analogous to the nonalternant systems since the ring nitrogen by connectivity can contribute only one electron to the π system. This is a clear demonstration of the desirability of devising experimental tests of systems that possess apparently similar features, but that may balance out to yield different exchange coupling effects.

The role of furan and pyrrole as spacers in diradicals has not been much explored by experiment to date.

Scheme VI



86

85 X = O, S, N-R

3,4-Dimethylenefurans, -thiophenes, and (more recently) -pyrroles (**85**, Scheme VI) have been studied by others, as have some of their bicyclic analogues (generically represented by structure **86**).[27,56] The heterocyclic systems for which data have been published to date appear to possess singlet ground states,[27,28] indicative of the effects of on these systems of heteroatom bridging by π-donor centers, relative to less substituent-perturbed, but geometrically constrained, TME's, for which triplet ground states are found as mentioned earlier in the Background. All these systems involve diradical coupling through 3,4-diyl furan and thiophene spacers rather than the 2,5-diyl coupling described previously. Computations by semiempirical MO–CI models have previously well-described the 3,4-diyl connectivity systems[19,27] by comparison to ab initio computations[28] that are also in good agreement with experiment.[27,56] Hence, we may reasonably expect a useful treatment by our procedure of the experimentally promising 2,5-diyl spacers.

Effect of Through-Space Coupling. Although the efficacy of our methods had not been demonstrated for through-space exchange interactions, we felt it could be informative to test them in this area. Although we explicitly described exchange coupling models only for through-bond linked species earlier (eqs 1 and 2 and related methods), we must now note that qualitative models of through space coupling have also been described.[3,4,57] McConnell has for instance described how certain stacking arrangements of molecules should lead to antiferromagnetic or ferromagnetic coupling through space.[57] For benzylic-connectivity systems, pseudoortho and pseudopara orientations should allow overlap through space of sites with spin density of opposite sign, leading to favorable interaction when a ferromagnetic coupling of the unpaired spin exists. Conversely, a pseudometa orientation will maximize overlap of sites with spin density of opposite sign only if an antiferromagnetic coupling exists between the radical sites. Yamaguchi and co-workers have verified this qualitative assertion by ab initio work on through-space coupled benzylic systems.[58] We have similarly[20] confirmed the applicability of the McConnell through space coupling model for ferromagnetically coupled cases by computations on dioxy-[2.2]paracyclophanes.

For simplicity, we use a standard [2.2]paracyclophane carbon skeleton that was optimized using molecular mechanics and replaced appropriate C–H bonds with C–O bonds of 1.25 Å. The usual AM1–CI computations were

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(56) (a) See the citations to several connectivity-related variations of mono- and bisheteroatom bridged TME's in the references of ref 19. (b) Work on 3,4-dimethylenepyrrole systems is underway at Yale University. Berson, J. A. Private communication.

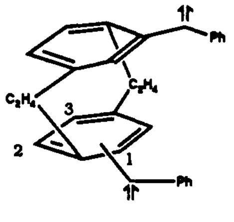
(57) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910; *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1967**, *11*, 1144.

(58) Yamaguchi, K.; Fukui, H.; Fueno, T. *Chem. Lett.* **1986**, 625. Yamaguchi, K.; Toyoda, Y.; Nakano, M.; Fueno, T. *Synth. Metals* **1987**, *19*, 87. Yamaguchi, K.; Namimoto, H.; Fueno, T. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 151.

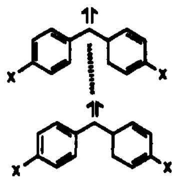
then carried out on these systems, as well as single-point UHF computations on triplets to determine spin distributions. We obtained small T–S gaps for systems **87–89**, no more than 3 kcal/mol. These T–S gaps were slightly larger for similar test systems with the C–O bond replaced by a C–CH_2 bond. We had expected that such through-space coupling would be qualitatively less effective than conjugative through-bond coupling, but the small size of the coupling obtained—even in these closely held rings—is an indication of how sensitive the design of bulk ferromagnetism will be to the geometric crystal packing or morphology in a polyradical based system.

Examination of the UHF-triplet spin densities on the [2.2]paracyclophane systems showed spin density distributions in good accord with those expected by the McConnell model. For the pseudoortho and pseudopara cases, the advantage of ferromagnetic coupling of the rings was obvious by the overlap of sites with opposite sign in spin densities. The spin density distributions in the pseudometa compound are found to be forced into unfavorable overlap between sites with the same sign in spin density, a destabilizing situation that allows the singlet to be more favorable as expected, although we do not find this sufficient to yield a singlet GS here. Our findings imply that the strength of through-space interactions between rings is quite modest in these rigid molecules as demonstrated by the small T–S gaps, appreciably smaller at our levels of theory than the through-bond interactions causing ferromagnetic coupling in most other systems of this study.

Experimentally, work by Iwamura and co-workers[59] supports the qualitative validity of the McConnell model, showing that phenylcarbene centers may through space be ferromagnetically coupled by a rigid [2.2]paracyclophane skeleton **90** when in pseudoortho or pseudopara connectivity, while near-degenerate low-spin coupling appears to be observed for the pseudometa connectivity. In addition, for carbene centers on different molecules coupled through space in a single crystal **91**, ferromagnetic coupling has been observed,[60] although this effect is greatly altered under different crystalline structural conditions obtained with different substituents on the molecules. The latter finding implies that ferromagnetic coupling between organic molecules in a through space manner is—as predicted by our computations—a closely balanced process, easily perturbed by geometry or substitution and producing only small high-spin to low-spin energy gaps. As a result, design of organic bulk ferromagnetic materials will be quite difficult if one must rely upon nature to supply geometrically appropriate crystal structures by chance.



90
(connected at sites 1, 2, or 3)



91
(intermolecular coupling)

Larger Oligomers as High-Spin Polyradicals. In order to investigate whether the strength of exchange coupling is substantially diluted in larger conjugated systems with many spins, we carried out investigation of several model oligomers of plausible organic polyradical systems. The structures of these test cases are shown in Figure 4. Geometries were artificially held planar, with optimization carried out within this constraint for lower oligomers (n = 2–3).

For the poly(1,4-phenylene)- and poly(1,4-phenylenevinylene)-based systems **92** and **93**, we found that ferromagnetic coupling was maintained up to five oligomeric units. In addition, the predicted magnitudes of the high-spin to low-spin gap (HS–LS) in these two systems is reasonably large. The connectivity in both systems leads one qualitatively to expect a high-spin state by the parity rules, but the maintainence of reasonably large HS–LS energy gaps in such large systems makes desirable the synthesis of systems connectivity-related to these.

Polymeric coupling by the cross-conjugated 1,1-ethenediyl spacer is exemplified by system **94**. Despite the fairly strong ferromagnetic coupling in the dimer (compound **40** in Figure 1), the coupling strength in higher oligomers is substantially smaller, with a quintet–triplet gap of less than 1 kcal/mol in the tetramer.

The poly(acetylene)-based system **95** is also expected by the parity rules to have high-spin GS. However, the various spin states of the higher oligomers of **95** were found to be near-degenerate, with HS–LS gaps of <1 kcal/mol for the polyoxy polyradical. By contrast, the corresponding case with simple geometric replacement of oxygen by methylene groups (no optimization) had a high-spin GS. This result is clarified by the ab initio work upon oxyallyl[46,48] discussed previously. System **95** may be formulated in terms of carbonyl-containing units, rather than oxy-substituted ethene units. Indeed, our geometry optimizations for **95** show short C=O bonds in accord with this formulation. As a result, the unusual stability of the C=O unit may effectively isolate radical-bearing sites from one another, making ferromagnetic coupling weak in this system despite connectivity. We feel that systems of this general type will not be effective high-spin molecules when oxyradicals are used, but expect that use of carbon-based radicals for the same connectivity system will have more chance to exhibit extended high-spin ferromagnetic coupling.

We also extended the results of our computations on heteroatom spacers to investigate two polyphenyl ether systems with different connectivities, **96** and **97**. Using the simple spin-pairing valence bond model we used for the diradical models earlier, we expected **96** to exhibit antiferromagnetic behavior, while **97** should have ferromagnetic coupling due to its different connectivity. These compounds have a substantial degree of conformational flexibility, and not all reasonable conformers were explored in unconstrained computation. However, in both systems we found only quite weak coupling, with HS–LS gaps of 1 kcal/mol or less for the conformers studied. Despite the qualitative prediction, it seems clear that computation predicts the oxygen spacer to insulate unpaired spin in these systems, resulting in a series of radical centers with little spin communication. Part of this effect is due to the desire of these species to be very twisted, but even artificially planarized conformers (results not shown in Figure 4) for these connectivities do not show significant increases in the HS–LS gap. Of course, some other combination of heteroatom coupled radicals may be more effectively coupled in a ferromagnetic sense, but the problem of nonplanarity in a realistic system would remain. Since the heteroatom-coupled systems are most sensitive to ring torsion of those studied by us, this suggests that some

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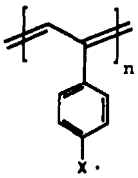
[59] Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786.

[60] Sugawara, T.; Tukada, H.; Izouoka, A.; Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1986**, *108*, 4272.

control over geometry would be particularly important in designing polyradicals based on these spacers. A recent review has noted that ring torsion about the phenyl–NH–phenyl bonds in polyanilines can strongly affect its experimental electronic properties in a manner analogous to our previous observations.[61]

Overall, it is somewhat difficult to evaluate the efficacy of our predictions for higher oligomers at present, due to a dearth of experimental comparisons. Iwamura's polycarbenes are the closest experimental analogues to our cases. We find a high-spin GS for system **6** ($n = 2$) mentioned earlier, in agreement with experiment—programming limitations prevented our evaluation of the higher oligomers of this system. System **98** has recently been synthesized,[62] with $X = O^{\bullet}$, for which formal connectivity considerations predict a high-spin GS. However, simple steric considerations as well as molecular mechanics computations by us on model oligomers show clearly that realistic conformers of this system must be highly twisted. As a result, the pendant radical-bearing phenyl rings tend not to be extensively conjugated through the backbone and the overall effect is more that of a nonconjugated pendant polyradical,[63] rather than a through-conjugated system. Very small HS–LS gaps are found by our method for model oligomers of **98**. Some of the systems suggested in Figure 4 potentially suffer from the same difficulty, namely the possibility of conformational deconjugation that would tend to isolate and decouple spins. Solid-state packing considerations may serve to flatten real polymers to some extent, but the overall effect of bond torsion may limit conjugative spin-coupling degree in a large polyradical to smaller oligomeric segments. For longer range interactions, through-space effects to couple smaller domains of ferromagnetic coupling will therefore be critical in getting bulk magnetic coupling. The simplistic models used in Figure 4 are thus at best ambiguous predictors of experimentally ferromagnetic organic materials, but are still probably useful to exemplify selection of systems with the greatest likelihood of giving experimental ferromagnetic coupling *in oligomeric segments where conformational effects allow*, thus giving longer range coupling mechanisms more of a chance to yield long range ferromagnetic coupling in the bulk system.



98

Summary

Our computational work has been aimed at correct prediction of ground-state multiplicity for open-shell π-conjugated organic molecules and at understanding the nature and mechanisms of spin coupling as a function of several variables in such systems. Our previous work has shown that use of semiempirical MO–CI methods such as AM1–CI give ground-state multiplicity predictions in good accord with experimental findings. In this paper, we compare a variety of effects in exchange coupling in π-conjugated systems. Overall, we note the following general observations: (1) The qualitative parity-based models of GS spin multiplicity in alternant π-conjugated non-Kekulé systems in most cases give predictions in accord with our computational findings when a high-spin GS is expected. The comparison of theory and computation is less clearcut for cases where a low-spin GS is expected. A number of systems for which parity considerations predict a low-spin GS are computationally found to obey the usual organic chemists' usage of Hund's rule and have a small preference for a high-spin GS. In such cases, a markedly reduced computational energy gap between high-spin and low-spin states is found. (2) the π-isoelectronic replacement of carbon-centered radical sites with heteroatoms (oxy radicals and nitrenes) does not in the large majority of cases affect the generalizations made in 1 concerning the efficacy of the parity models. In adition, π spin coupling in both nitrenes and oxyradical cases is quite similar; however, the presence of the extra σ electrons in nitrenes effects the number and order of the actual state multiplicities that may be found in polynitrenes. Systems where a carbonyl moiety may be present as a major resonance structure represent a possible exception to the extension of the parity approach to heteroatom perturbed systems, probably because the strong C=O tends to some extent to isolate attached spin-bearing sites. (3) Limited geometric torsion in some conjugated systems may be tolerated and still allow sufficient communication between spin sites to give effective spin coupling. Heteroatom-linked systems seemed to be particularly sensitive to bond torsion as a determinant of the degree and nature of coupling. (4) Use of the semiempirical MO–CI method gives results of particular interest for molecules containing nonalternant π systems and heteroatom spacers, to some of which the parity models are not applicable. Typical resonance-based arguments correlate with our predictions for these types of systems. (5) Extension of parity-based arguments beyond dimeric models of higher degree oligomers is computationally confirmed for some types of systems, at least up to 4-fold oligomers. The high-spin to low-spin energy gap in such systems decreases with increasing oligomer size to a degree that varies with the type of system. (6) Through-space effects are generally weaker than through-bond effects, even for benzenoid systems in close contact. Ferromagnetic coupling between radicals is most favored for cases where sites of opposite sign in spin-density overlap (McConnell criterion), but the difference in energy between high- and low-spin states is fairly modest, even in these cases.

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(61) Ginder, J. M.; Epstein, A. J. *Phys. Rev. B: Condens. Matter* **1990**, *41*, 674 and references therein.

(62) Nishide, H.; Yoshioka, N.; Inagaki, K.; Tsuchida, E. *Macromolecules* **1988**, *21*, 3120.

(63) Recent electron spin resonance experiments indicate hyperfine coupling of the phenoxyl moiety to each olefin segment of the backbone of **98** and argue for some degree of delocalization in the chain, despite the helical coiling of this species that one might expect on the basis of molecular mechanics of isolated chains. Cf. Yoshioka, N.; Nishide, H.; Tsuchida, E. *Mol. Cryst. Liq. Cryst.* **1990**, *190*, 45.