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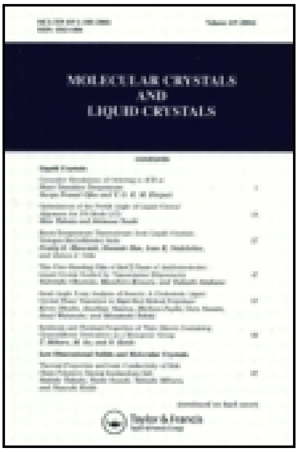

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Theory and Experiment of Investigation of Exchange Interactions in Organic Molecules and Materials

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THEORY AND EXPERIMENT OF INVESTIGATION OF EXCHANGE INTERACTIONS IN ORGANIC MOLECULES AND MATERIALS.

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Abstract Intramolecular and intermolecular exchange in molecules and polymers is investigated computationally and experimentally, in order to identify structure-property relationships.

INTRODUCTION

The design of new magnetic materials represents a difficult, long-term challenge to chemists, physicists, and engineers. While considerable improvement of existing iron-based magnetic materials is still envisioned[2] in the information-storage industry, the possibilities of creating new materials with specific, "designer" properties is not only of intellectual interest, but of potential use for future technology. Given the ever-increasing dependence of modern society upon magnetic information storage for the forseeable future, research efforts aimed at understanding and improving upon existing magnetic materials are well-justified, whatever the inherent difficulties.

Rational design strategies for magnetic materials depend critically upon understanding relationships between molecular structure and intramolecular exchange interactions, and relationships between molecular packing (or material morphology) and intermolecular exchange interactions. In effect, chemists must be able to discern the structure-property "rule book" for molecules and materials, before hoping to design useful systems by strategies other than serendipity. In previous

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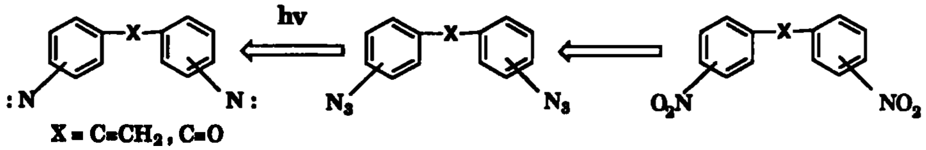
work, we have utilized computational chemistry[3] in efforts to correlate molecular structure with ferromagnetic or antiferromagnetic exchange nature and strength. In this paper, we describe some of our recent work[4] on model bis(arylnitrene)s correlating *intramolecular* exchange type and structure. In addition, we outline our ongoing strategy to study *intermolecular* exchange in molecular solids and polyradical solids, as tests of bulk systems with sufficient stability to be reasonable models for practically utilizable materials.

INTRAMOLECULAR EXCHANGE IN BIS(ARYLNITRENE) MODELS

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

General Experimental Details

Diazide Precursors: All dinitrenes were generated from diazide precursors synthesized by reduction of corresponding dinitro compounds to diamines, followed by double diazotization and replacement with azide groups (Scheme 1). All new diazides had satisfactory chemical analyses, and were characterized by infrared and nuclear magnetic resonance spectral properties. Full synthetic details for new compounds will be published elsewhere.[5]



SCHEME 1 Synthesis of diazides for dinitrene generation.

Dinitrene Generation and Study: An appropriate diazide was dissolved in degassed 2-methyltetrahydrofuran and sealed under vacuum in a 4 mm quartz tube. The tube was cooled in liquid nitrogen to 77 K in a

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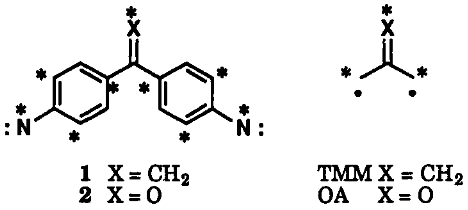
Suprasil dewar, and the resultant matrix photolyzed by one of two different means: (1) 2-5 min of irradiation with a 1000 W xenon arc having Pyrex filter or 300-400 nm band pass filter, (2) using ca. 1800 pulses from a XeCl excimer laser (Lambda Physik EMG 103 MSC, λ=308 nm, pulse power at sample ca. 50 mJ).

ESR spectra were obtained on Varian E-9 and Bruker ESP-300 X-band systems with computer data acquisition systems. Microwave power settings of 100-500 microwatts were used in all cases to minimize signal saturation effects. For Curie law analyses, double integration of ESR signals was done under with identical spectrometer settings at various temperatures from 8-70 K for a given sample. Variable temperature work was carried out using liquid helium ESR cryostats (Oxford Instruments DCT-2), and was calibrated by use of a Lake Shore Cryotronics Ga-Al-As calibrated diode sensor (Model XTG-100FP-4D-3) in the cryostat sample zones. Spectrometer frequency was calibrated using a DPPH standard ($g = 2.0037$), or a microwave counter.

Nondisjoint Bis(arylnitrene)s

Figure 1 shows 77 K ESR spectra for dinitrenes **1**-**2** (Scheme 2), generated as described above. These systems are nondisjoint by the Borden-Davidson formalism,[6] and are also expected to possess high spin ground states by parity approaches such as those of Ovchinnikov[7] and Klein.[8, 9] Both spectra are consistent with the appearance expected for quintet dinitrenes. For **1** a strong resonance is seen at 3005 G, and weak but characteristic peaks at 500-1600 G, ca. 4000 G (broad), 5990 G, and 8270 G. For **2** a strong resonance is seen at 3030 G, and weak but characteristic peaks at 500-1600 G, ca. 4000 G (broad), 6150 G, and 8445 G. In both cases mononitrene impurities are seen due to photolysis of one azide group in the diazide precursor, at 6675 G ($|D/hc| = 0.938$ cm^{-1}) in the spectrum of **1**, and 6755 G ($|D/hc| = 0.968$ cm^{-1}) in the spectrum of **2**. Photolysis of the 1,1-ethenediyl linked system **1** yields dinitrene more effectively relative to mononitrene, than is the case for carbonyl-linked system **2**. In other respects, the ESR spectral similarity of **1** and **2** shows that these systems are quite similar in electron spin distribution. Taking the highest field resonances at > 8000 G as H_1 quintet transitions, and assuming that the next highest field resonance in each case that is not a mononitrene peak is the H_2 quintet transition, these spectra may be analyzed by the method of Wasserman et al.[10] to yield zero field splittings (zfs) of $|D/hc| = 0.151$, $|E/hc| = 0.0029$ cm^{-1} for **1**, $|D/hc| = 0.156$, $|E/hc| = 0.0046$ cm^{-1} for **2**.

Curie law analyses of peak intensities at ca. 3000 G for both **1** and **2** show linear dependence with reciprocal absolute temperature, as shown in the insets to Figure 1. Thus, both systems appear to have ground state quintet multiplicities by at least 1000 cal/mol (although metastable[11] or degenerate states[12] are formally possible).



SCHEME 2 Comparison of dinitrenes **1-2** to TMM and OA.

The comparison of **1** and **2** is of considerable interest, by analogy to the relationship between trimethylenemethane (TMM) and oxyallyl (OA), Scheme 2. TMM is a well-studied system, with computational and experimental evidence supporting a triplet-singlet gap of 10-15 kcal/mol.[13] OA has not been directly observed, although computational work suggests a small triplet-singlet gap (< 2 kcal/mol) which small substitution perturbations may reverse to give a singlet ground state.[14-15] Our experimental results show that carbonyl *can* act as a ferromagnetic exchange coupling group with a quintet to excited state gap of at least 1 kcal/mol, in qualitative accord with parity arguments.

Disjoint Bis(arylnitrene)s

Figure 2 shows 77 K ESR spectra for dinitrenes **3-4** (Scheme 3). These systems are members of an unusual connectivity class that is disjoint -- and so possibly low-spin -- by the Borden-Davidson formalism, but are expected to be high-spin by the simplest application of the parity approaches. Experimental investigation of **3-4** tests this difference in qualitative prediction between the two models.

Aside from the mononitrene impurity peaks seen in the 6900 G region ($|D/hc| = 1.013$ cm^{-1} and 1.037 cm^{-1} in **3** and **4** respectively), both ESR spectra are considerably different from those of nondisjoint **1-2** in Figure 1. The substantial numbers of transitions are consistent with

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quintet species, and the spectra are qualitatively similar -- though not identical -- to those obtained by Murata and Iwamura[16] for disjoint diphenylacetylene-3,3'-dinitrene. We observed no transitions at > 8000 G for either **3** or **4**. Accordingly, it is not possible to apply in a straightforward fashion the above-referenced formula for computation of the $|D/hc|$ values of these dinitrenes. A transition at 5810 G for 1,1-ethenediyl linked system **3** may be the H_1 transition; if so, this would yield $|D/hc| = 0.077\ \mathrm{cm}^{-1}$, an unusually low value for the quintet dinitrenes observed to date. Such a low value could suggest that **3** is substantially twisted, resulting in significant decreases in spin-spin interaction between electrons on the nitrene centers -- alternatively, the actual H_1 transition may be in the usual 8000 G region, but too weak to observe. We found no quintet resonance for **4** at > 3400 G, and so can give no estimate of $|D/hc|$ for **4**.

Although the zfs of **3**-**4** is difficult to interpret at this stage, the intensities of stronger peaks at ca. 2400 G could be monitored in Curie law analyses, the results of which are shown in the insets of Figure 2. Both analyses show curvature consistent with these quintets being thermally excited states, rather than ground states. By analogy to previous work[16] for weakly interacting nitrenes (or carbenes[17, 18]) assigning an order of states Singlet < Triplet < Quintet, we carried out nonlinear least squares analysis of the quintet ESR intensity I as a function of

$$IT = C([5\exp(-6J/RT)]/[5\exp(-6J/RT)+3\exp(-2J/RT)+1] \qquad (1)$$

absolute temperature T by the equation (1), where C is a fitting constant, J is the exchange constant, and $\Delta E(S\text{-}T) = 2J$, $\Delta E(T\text{-}Q) = 6J$. We found for **3** that J = -13.6 cal/mol, for **4** that J = -8.0 cal/mol. Although we observed some ESR lineshape changes for **4** among the resonance regions at 1000-2000 G, these changes were insufficiently resolvable to prove the presence of the excited state triplet state. Since the randomly oriented triplet state ESR of disjoint **3**-**4** is expected in any case to be quite weak,[19] we simply assumed the applicability of equation 1 above, and arrived at $\Delta E(S\text{-}Q) = 84$ and 48 cal/mol for **3** and **4**, respectively. Our result for **3** is quite similar to the $\Delta E(S\text{-}Q)$ value measured independently by the Iwamura group.[20]

The finding of low spin multiplicity ground states for **3**-**4** is in qualitative accord with the Borden-Davidson disjointness formalism,

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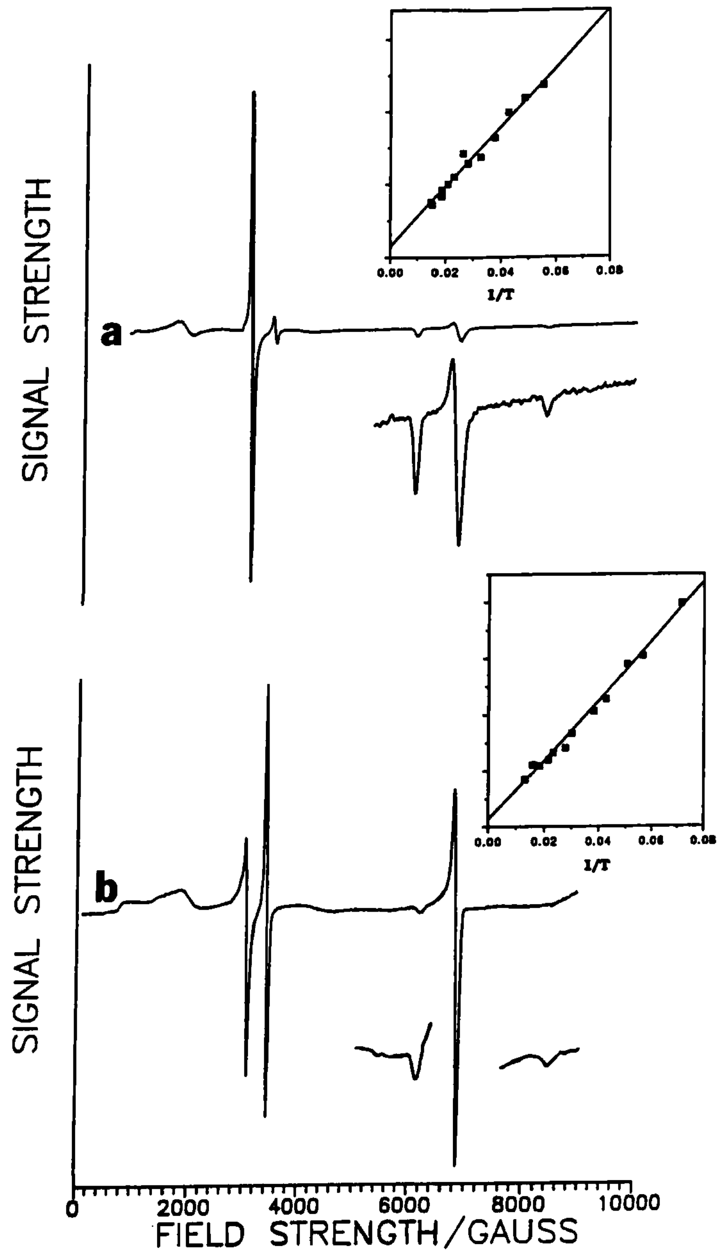

FIGURE 1 ESR spectra of dinitrenes 1(curve a) and 2 (curve b) at 77 K, 9.34 GHz. Corresponding insets show ESR intensity of major peaks (ca. 3000 G) of 1 and 2 as functions of reciprocal absolute temperature.

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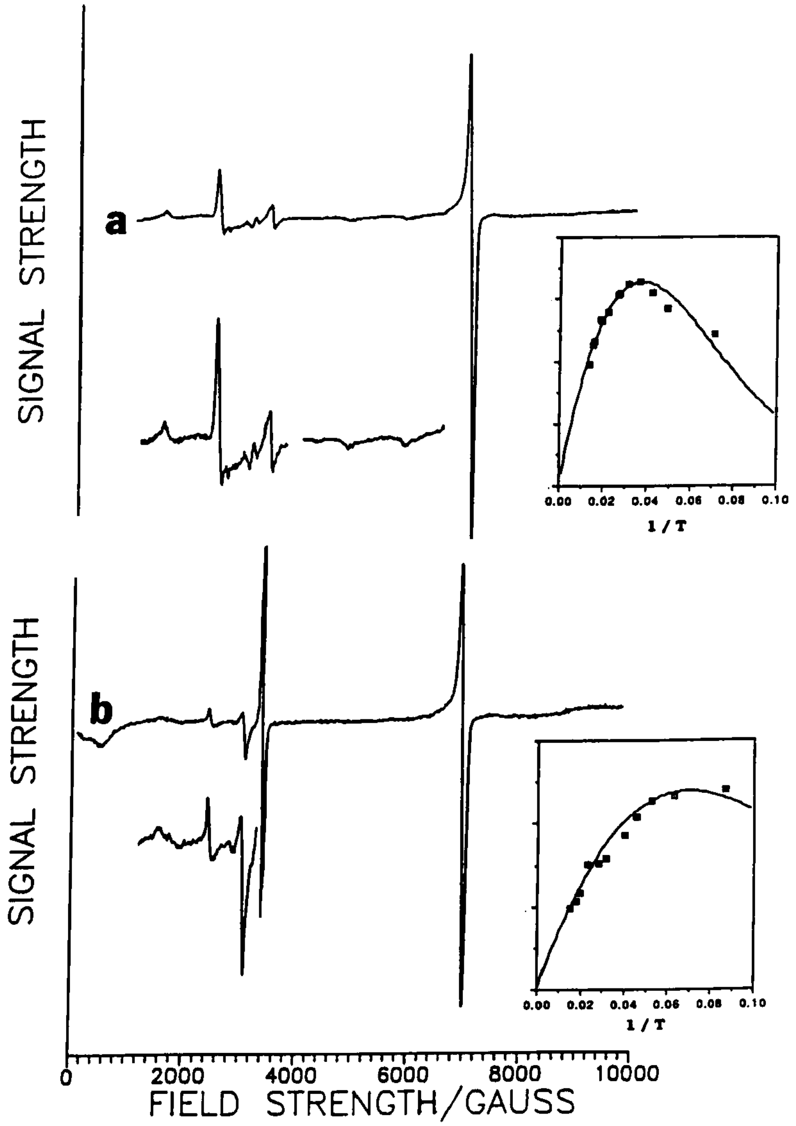

FIGURE 2 ESR spectra of dinitrenes 3 (curve a) and 4 (curve b) at 77 K, 9.34 GHz. Corresponding insets show ESR intensity of major peaks (ca. 2400 G) of 3 and 4 as functions of reciprocal absolute temperature.

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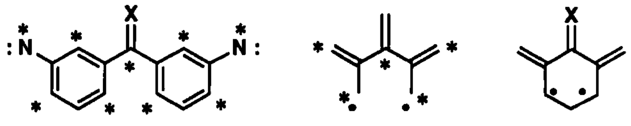
rather than the parity formalisms. In addition, these results are consistent with Iwamura's finding[16] of low spin, near-degenerate ground states for disjoint diphenylacetylene-3,3'-dinitrene and its diacetylene analogue. Also, as with the nondisjoint models, we obtained the same qualitative exchange interaction -- antiferromagnetic in this case -- for the 1,1-ethenediyl and carbonyl linker groups, consistent with the connectivity equivalence of these two groups. However, the exchange efficacy (J) of the carbonyl group is significantly less than for the hydrocarbon group. This to our knowledge is the first quantitative experimental evidence supporting computational suggestions that carbonyl is a less effective exchange conjugating unit than 1,1-ethenediyl.



3 $X = CH_2$
4 $X = O$

PMP

5 $X = CH_2$
6 $X = O$

SCHEME 3 Comparison of dinitrenes **3-4** to PMP derivatives.

Also, **3-4** are related in a connectivity sense to 1,1,2,3,3-pentamethylenepropane (PMP), which also has different predicted ground state spin multiplicities by disjointness vs. parity theoretical approaches (Scheme 3). Planar-restricted PMP derivatives **5-6** of PMP have been predicted by us[21] at a fairly high level of theory (6-31G* SDTQ-CI) to have a triplet ground state by ca. 1.5 kcal/mol. Experimental work has shown no direct evidence for a triplet state PMP **7**. It is not completely clear why this is so, when the closely related **3-4** have low spin ground states. Investigations are underway with torsionally restricted variants of **3-4**, to see whether twisting of the phenyl rings is a main contributor to ground state multiplicity in these systems, or whether connectivity alone is the main determinant.

Figure 3 shows the ESR spectrum of 3,4'-benzophenonedinitrene **8**. This system, like **3-4**, is disjoint, but by the parity rules is expected to have a low spin multiplicity ground state. Two separate mononitrene resonances may be seen with substantial intensity at 6810 and 6990 G ($|D/hc| = 0.97$ and $1.04\ cm^{-1}$), presumably corresponding to mononitrenes in the para and meta positions, respectively, from the diazide precursor.

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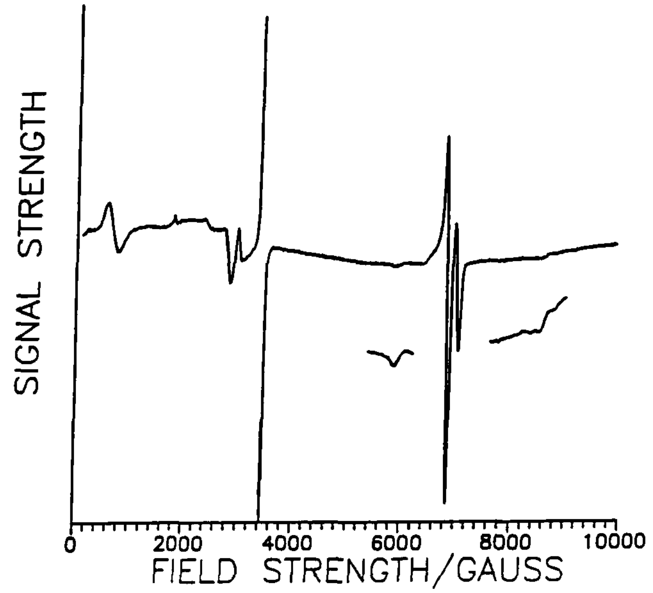

FIGURE 3 ESR spectrum of dinitrene **5** at 77 K, 9.38 GHz.

The remainder of the ESR spectrum may be assigned to quintet state **8**, and is quite similar to that found by Iwamura's group[20] for the corresponding 1,1-ethenediyl linked dinitrene, again showing that replacement of the hydrocarbon linker with the carbonyl group does not greatly affect the electronic spin distribution in these species. Assuming that the fairly weak resonances at 8480 G and 5850 G are the H_1 and H_2 quintet transitions, respectively, we estimate the zfs for **8** to be $|D/hc| = 0.159$, $|E/hc| = 0.0016$ cm^{-1}. These zfs values are similar to those found by Iwamura's group[20] for the 1,1-ethenediyl linked dinitrene.

Summary

Overall, we find bis(arylnitrene)s to be convenient in terms of synthesis, photolysis, and ease of ESR interpretation. We continue to study a variety of dinitrene systems in projects aimed at understanding the relationships of exchange coupling strength and nature to structural connectivity, the nature of linker groups **-X-** (Scheme 1), and the length of conjugating groups **-X-**.

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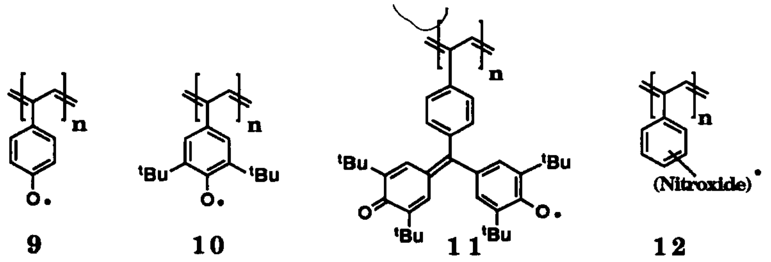
EXCHANGE IN POLYMERIC POLYRADICALS

Simultaneously to studying molecular models for intramolecular exchange, we have attempted to apply these lessons in connectivity to making polymeric polyradicals of appropriate connectivity to conduce to very high spin multiplicities. Ovchinnikov pointed out[7] that poly(4-vinylphenoxy) (**9**, Scheme 4) would be of appropriate connectivity to give a high spin ground state by the parity approach.

Variants of this connectivity type of system include systems such as **10**,[22] **11**,[23] and **12**,[24-25] synthesized with 10-95% of the expected number of unpaired spins in the isolated samples. Unfortunately, in cases of polyphenylacetylene (PPhA) based polyradicals studied to date, no ferromagnetic intrachain cooperativity has been found. We felt that some of the problems with the PPhA-based systems probably lay with incomplete spin delocalization throughout the polymer chain, which is needed for parity approaches to be applicable. We employed force field computational modeling techniques to test this hypothesis.



SCHEME 4 Polyphenylacetylene-based polyradicals.

Computational Modeling of Polyphenylacetylenes

Computational modeling of oligomers ($n \geq 8$) of PPhA was carried out using the MMX87-PI force field,[26] and used selected conformational isomers from these computations as input for the Molecular Simulations, Inc. software package QUANTA (v. 3.2.3), interfaced with the CHARMm force field on a Silicon Graphics, Inc. Iris Indigo R3000 workstation. Structures in QUANTA were optimized until no further significant changes in energy occurred (< 0.2 kcal/mol).

The two most relevant energy minimum conformers of PPhA found by both MMX87-PI and QUANTA/CHARMm are the all trans-transoid (**13**) and all cis-transoid (**14**). Ball-and-stick representations of **13** and **14**

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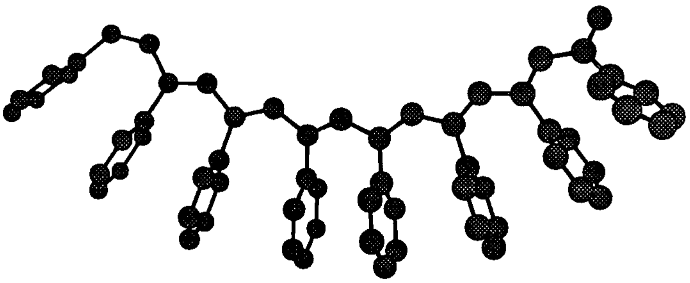
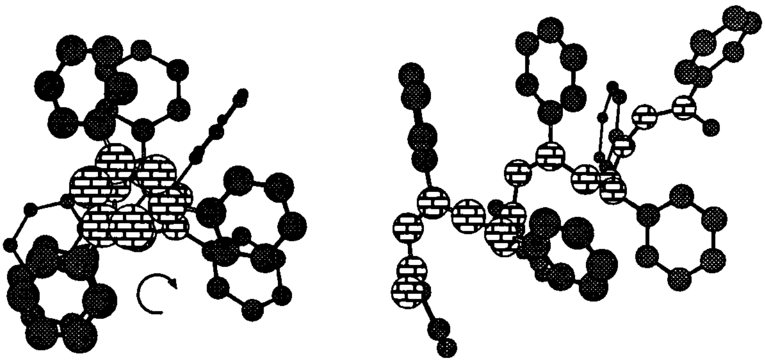
are given in Figure 4. The cis-transoid form is lower in energy than the trans-transoid by 12 kcal/mol (for the octamer) by MMX87-PI, and also lower in energy by CHARMm. For cis-transoid **14**, the typical C=C-C=C dihedral twist angle can vary between ca 30-80°, the typical Phenyl-C=C dihedral twist angle is ca. 35-55°, resulting in a helical molecule. The higher energy trans-transoid **14** has better conjugation of the poly-acetylene chain along the backbone, but has all phenyl rings twisted perpendicular to the backbone chain, with the result that complete virtual deconjugation occurs. If **13** were the proper model for PPhA based polyradicals, only weak through-space interactions between the pendant



13



14

FIGURE 4 Conformers **13** and **14** of PPhA shown without hydrogens for clarity. Spiral direction of end-on view of **14** is shown by the curved arrow.

rings (ca. 3.5 Å apart) could be expected, since conjugative intramolecular exchange would be minimal. However, some phenyl to backbone conjugation is present in cis-transoid **14**. The higher stabilty of form **14** implies that steric constraints can overcome electronic factors that would favor fully conjugated geometries in PPhA.

We also optimized by QUANTA/CHARMm the structure of the unoxidized polyphenolic precursor to polymer **10** synthesized by Nishide et al.[22] Again, a cis-transoid structure is found to be favored, similar to the result shown in Figure 4 for the unsubstituted PPhA system **14**. This geometric model for **10** is consistent with the fact that **10** shows no experimental evidence of ferromagnetic exchange coupling along the polymeric chains, but still shows ESR hyperfine interaction between the phenoxyl radical spin and the backbone -CH=C< group.[23] AM1[27] or INDO computations show that torsional angles as large as those computed by CHARMm for the Phenyl-C=C of PPhA still allow substantial electron spin delocalization from the phenoxyl oxygen to the -CH=C< backbone group, consistent with the experimentally observed[23] hyperfine interaction. The computed hyperfine interaction drops rapidly after the Phenyl-C=C torsion increases beyond 50°. Thus, a phenyl ring perpendicular to the polyacetylene chain -- as in the trans-transoid conformer **13** -- would not be expected to give significant hyperfine interaction. The other conformer **14** can allow some spin delocalization and exchange *within each monomeric unit* of the PPhA. However, large C=C-C=C torsional angles, if present in the real material, would inhibit extended conjugative exchange along the backbone. Such lack of long range exchange is just as observed by Yoshioka et al.[23] for **10**.

More generally, the computational nature of the cis-transoid structure **14** places no obvious steric constraints on a variety of radical-bearing groups being attached pendant to a PPhA chain, since the pendant phenyl groups can all face outwards from the backbone. Unfortunately, it is not clear that any such group would *necessarily* change the conformational preference of PPhA to give more extensive conjugation, hence efforts to obtain ferromagnetic coupling in a pendant PPhA based system may be doomed to failure, unless the polymer can be processed or induced into a conformation that allows more polyacetylene backbone conjugation, as might be achieved by stretching the chains through processing. We intend to carry out more rigorous computational

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studies of the PPhA polymers, including molecular dynamics computations, since it is not clear how energetically strong is the inclination toward deconjugation in these systems. Aside from such quantitative energy considerations, we feel that the qualitative possibility of torsion deconjugation in PPhA based systems should be a strong incentive for synthetic workers not to be discouraged by recent lack of ferromagnetic coupling in polyradicals based on PPhA.

Photolytic Polyradical Production

Although the computational study described above suggests difficulties in achieving ferromagnetic coupling in PPhA based polyradicals, experimental work is insufficient to verify the prediction unequivocally. As part of our effort to achieve processibility in polyradicals, we developed photochemical means of producing phenoxyl radicals.[28-29] Our hope is that, through production of a thermally robust, photochemically labile polyradical precursor, we may eventually process a material into thin films, etc., which may be photoactivated to a polyradical. In addition, we may through processing of a precursor be able to induce morphologies more conducive to ferromagnetic exchange.

Figure 5 shows our synthetic scheme for an aryl oxalate derivatized version **15** of the polymer **10**. Full synthetic details will be reported elsewhere, but the overall scheme is an adaptation of known chemistry. Coupling of 4-bromo-2,6-di-*tert*-butylphenol with trimethylsilylacetylene by the method of Pugh and Percec[30] as a route to a polymerizable phenylacetylene monomer was unsatisfactory. However, we found that 4-iodo-2,6-di-*tert*-butylphenol[31] couples readily with trimethylsilyl-acetylene,[30] and may then be functionalized to a diaryloxalate compound by our previously published[29] route. Removal with fluoride ion[32] of the trimethylsilyl protecting group yields a phenyl acetylene that is readily polymerized[22-33] by use of WCl_6 in hot toluene. Final polymer **15** is a brick red, thermally stable powder that is quite stable to decomposition by exposure to room temperature and humidity, and is readily characterized by its infrared spectroscopy. Thirty minutes of quartz-filtered photolysis of **15** in the neat solid at 77 K gives a very intense, gaussian-shaped peak at $g = 2.0039$, consistent with line-broadened polyphenoxyl radicals (Figure 6).

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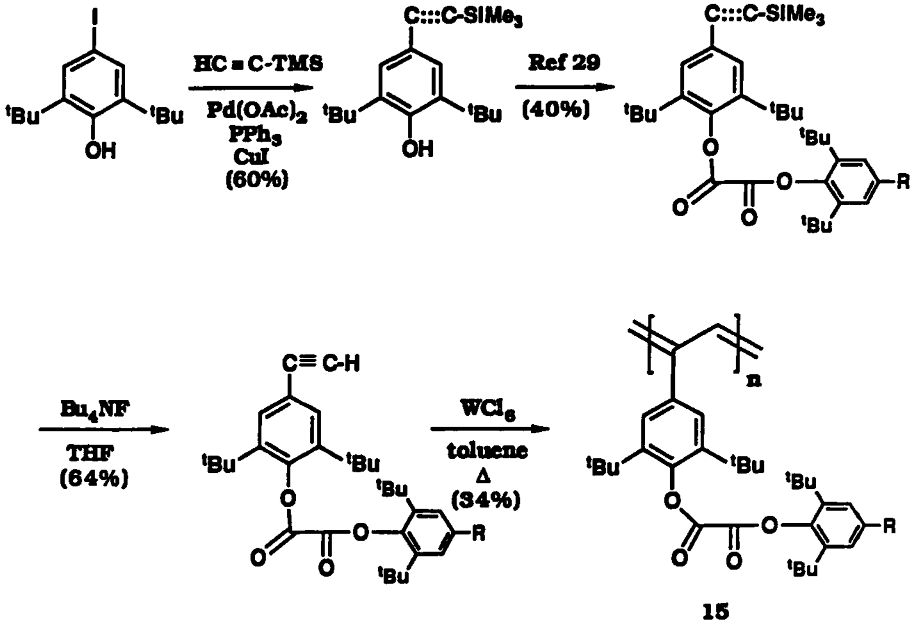

FIGURE 5 Synthesis of photoprecursor **15** to polymer **10**.

This radical signal is persistent for days under vacuum, and is caused by photolysis of a thin layer of surface polymer molecules, as shown by shaking a photolyzed sample, and rephotolyzing to produce additional phenoxyl ESR signal.

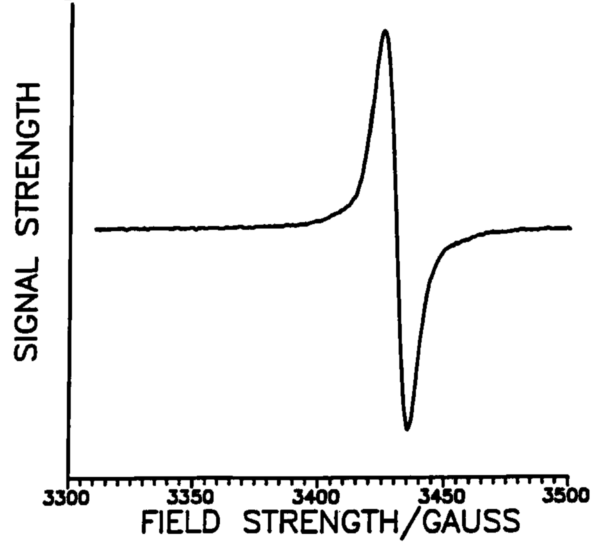

FIGURE 6 ESR spectrum of photolyzed **15** at 77 K, 9.38 GHz.

Overall, the use of photolytic production of polyradicals by strategies such as ours and Iwamura's[34] offers much promise for the processing of fairly robust, nonmagnetic polymeric precursor materials that will allow some control of morphology *before* a polyradical is generated. Such strategies will hopefully allow polyradicals of greater stability to be generated, with greater control of their polymer morphology and (perhaps) their bulk magnetic properties.

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