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Design of High-Spin Molecules Incorporating Charged Plus Neutral Spin Centers

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ABSTRACT

A series of diradicals comprised of m-phenylene exchange coupling units and spin-bearing centers of the same (homo-spin) and different (hetero-spin) types were compared, using the semiempirical AM1-CI molecular orbital method. Two meta-coupled neutral (or charged) hetero-spin centers result in a high-spin ground state, while coupling of one neutral and one charged spin center gives rise to a low-spin ground state in the cases studied. The latter result is ascribed to the large splitting of partially occupied molecular orbitals by substitution, leading to dominance of purely ionic resonance structures in the singlet states of the monocharged "hetero-spin" cases. Effects of substitution and HOMO–LUMO splitting may be evaluated by computational methods to identify systems where resonance effects may override spin parity effects. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:161–167, 1998

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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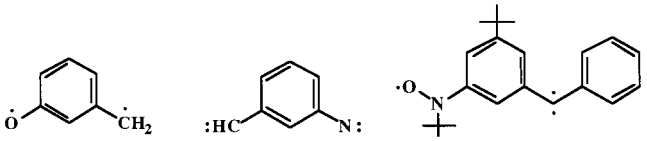
INTRODUCTION

High-spin molecules have attracted much interest because they could serve as building blocks for magnetic materials [1]. It has been noted that high-spin molecules may be considered as being comprised of two components: a spin-containing (SC) fragment or spin center, which provides the unpaired electron, and a ferromagnetic coupling (FC) unit, which connects radical centers through interelectronic exchange [2]. Considerable experience has shown that [1,3] *m*-phenylene is one of the most effective FC units, at least for exchange coupling of homo-spin centers, by which we mean that all SC units are the same. The ferromagnetic coupling mechanism of high-spin molecules with neutral hetero-spin centers has been less studied, with only a few known diradical examples such as **1** [3a], **2** [3b], and **3** [3c] having different types of SCs. Diradicals or related non-Kekulé molecules with one charged spin center plus one neutral spin center or with two charged SCs of different types have been subjected to little scrutiny to the best of our knowledge. We were interested in probing whether one would expect exchange coupling effects to be different in such hetero-spin-coupled systems. Therefore, we carried out computations on a series of diradicals having *m*-phenylene FC units that couple hetero-spin centers, and com-

pared them with analogs possessing homo-spin centers (see Figure 1).



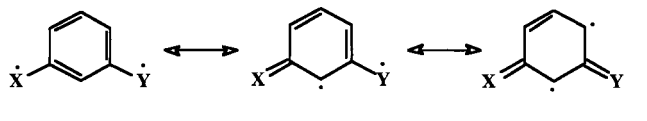
S = 1 S = 2 S = 3/2

1 **2** **3**

The requirements for the stabilization of a high-spin ground state in π-conjugated systems are (1) the existence of partially occupied degenerate or near-degenerate molecular orbitals (POMOs) and (2) strong Coulomb electron–electron interaction within the subspace of near-degenerate POMOs that prevents spin pairing and makes a pseudo-Hund's rule effective. The ground-state spin multiplicities and relative stabilities of diradicals can be computed in terms of energy gaps between ground states and first excited states $\Delta E_{T\rightarrow S}$, with $\Delta E_{T\rightarrow S} > 0$ corresponding to a triplet ground state. The intent of this study is to investigate the dependence of $\Delta E_{T\rightarrow S}$ upon replacement of neutral with charged SCs in diradical systems.

METHODOLOGY

The investigated diradical model systems are shown in Figure 1. A number of those with homo-spin centers have been investigated experimentally [1,3] or by computational [4] methods. These known systems comprise calibration tests of our methodology. A variety of model SCs were used to vary structurally the archetypal *m*-xylylene diradical **4a** to form neutral homo-spin center diradicals (**4b–e**) and hetero-spin center diradicals (**5a–d**). In addition, homo-spin center diradicals with two charged SCs (**6a–e**), and hetero-spin center diradicals with one charged SC (**7a–e**) were considered. Finally, a set of diradical cases with *two* different, charged SCs (**8a–d**) were considered as hetero-spin doubly ionic systems.



(i) (ii) (iii)

X = Y = CH_2 (**4a**), O (**4b**), NOH (**4c**), NH (**4d**), PH (**4e**)

Y = CH_2, X = O (**5a**), NHO (**5b**), NH (**5c**), PH (**5d**)

X = Y = $^+NH_2$ (**6a**), ^+OH (**6b**), ^+SH (**6c**), ^-BH (**6d**), ^-CHO (**6e**)

Y = CH_2, X = $^+NH_2$ (**7a**), ^+OH (**7b**), ^+SH (**7c**), ^-BH (**7d**), ^-CHO (**7e**)

X = ^+SH, Y = $^+NH_2$ (**8a**); X = ^+SH, Y = ^+OH (**8b**);

X = ^+OH, Y = $^+NH_2$ (**8c**); X = ^-CHO, Y = $^-BH_2$ (**8d**)

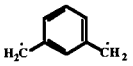
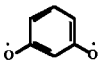
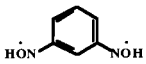
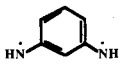
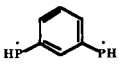
FIGURE 1 *Meta*-linked diradical systems investigated by semiempirical AM1-CI method.

We used Spartan 4.1 [5] running on a Silicon Graphics workstation to assemble and preoptimize the molecules using triplet UHF wave functions with the AM1 semiempirical all-valence electron Hamiltonian [6]. The same geometry was subsequently used for both triplet- and singlet-state energy calculations. Planarized structures are used as constraints for the above-mentioned symmetries. Where symmetrical structures were possible, geometry optimization was performed under C_{2V} and C_S symmetry, respectively. These constraints are consistent with our goal to investigate the semiquantitative nature of exchange coupling in these systems and to classify them as robust triplets, robust singlets, or near-degenerate systems.

Final geometry optimization at the multielectron configuration interaction (MECI) level was done using MOPAC 93 (v. 1.0) [7], using the same geometric constraints as described earlier. A restricted open-shell Hartree-Fock reference SCF wave function with single-electron occupancy of the near-degenerate POMOs was used. The MECI computations consider 121 configurations of lowest energy within an orbital subspace of six frontier MOs. Similar AM1-MECI procedures have previously been established by us and others to give predictions in good accord with experimental results for neutral diradical and diradicaloid systems [4c–f,8].

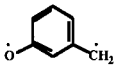
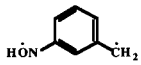
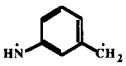
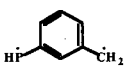
Since the exact prediction of the absolute singlet–triplet energy gaps of small organic diradicals can be problematic even with high-quality ab initio methods, we concentrate mainly on the relative trends associated with the variation of the spin center as given in Figure 1. What semiempirical methods lack in complete precision, they gain through allowing semiquantitative surveys of whole classes of related molecules. So long as experimentally realistic systems resemble the geometry and connectivity of the systems computed, the singlet–triplet energy gaps given herein should be appropriate for relative comparisons. Likewise, due to the tendency of UHF wave functions to overestimate quantitative effects of spin polarization, we will focus on qualitative variation of spin density in hetero-spin center diradicals vs. homo-spin center ones, rather than considering the Mulliken populations output by MOPAC to predict experimental spin densities.

TABLE 1 Calculated Results for Neutral Diradicals with Homo-Spin Centers

	$\Delta E_{T\rightarrow S}$(eV)	ΔE_{POMO}(eV)	ρ_{spin} on SC	ρ_{spin} on C-2
	0.49	0.001	0.91	0.74
4a				
	0.31	0.43	0.38	0.95
4b				
	0.11	0.10	N 0.44 O 0.51	0.57
4c				
	0.81	0.10	0.68	0.86
4d				
	0.21	0.08	0.87	0.63
4e				

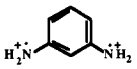
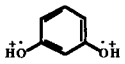
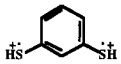
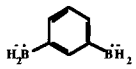
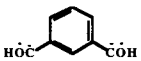
$\Delta E_{T\rightarrow S}$ (eV) is the triplet–singlet (T → S) energy splitting for the molecule shown, ΔE_{POMO} is the energy splitting between partially occupied frontier MOs, ρ_{spin} on SC is UHF computed spin density on the spin-bearing unit, and ρ_{spin} on C-2 is the computed spin density on C-2.

TABLE 2 Calculated Results for Neutral Diradicals with Hetero-Spin Centers

	$\Delta E_{T\rightarrow S}$ (eV)	ΔE_{POMO} (eV)	ρ_{spin} on SC	ρ_{spin} on C-2
	0.54	0.70	C 0.91 O 0.36	0.83
5a				
	0.25	0.32	C 0.91 N 0.45,O 0.50	0.67
5b				
	0.81	0.36	C 0.91 N 0.66	0.80
5c				
	0.41	0.42	C 0.90 P 0.85	0.70
5d				

$\Delta E_{T\rightarrow S}$ (eV) is the triplet–singlet (T → S) energy splitting for the molecule shown, ΔE_{POMO} is the energy splitting between partially occupied frontier MOs, ρ_{spin} on SC is UHF computed spin density on the spin-bearing unit, and ρ_{spin} on C-2 is the computed spin density on C-2.

TABLE 3 Calculated Results for Diradicals with All Charged Homo-Spin Centers

	$\Delta E_{T\to S}$ (eV)	ΔE_{POMO} (eV)	ρ_{spin} on SC	ρ_{spin} on C-2
	0.36	0.89	0.61	0.84
6a				
	0.49	0.49	0.29	0.83
6b				
	0.16	0.45	0.90	0.60
6c				
	0.24	0.66	0.47	0.80
6d				
	0.14	0.78	C 0.37 O 0.28	0.72
6e				

$\Delta E_{T\to S}$ (eV) is the triplet–singlet (T → S) energy splitting for the molecule shown, ΔE_{POMO} is the energy splitting between partially occupied frontier MOs, ρ_{spin} on SC is UHF computed spin density on the spin-bearing unit, and ρ_{spin} on C-2 is the computed spin density on C-2.

RESULTS AND DISCUSSION

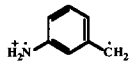
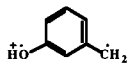
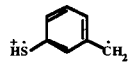
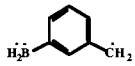
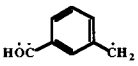
Calculated results are listed in Tables 1 through 5. Energy gaps between triplet and singlet (T-S) states ($\Delta E_{T\to S}$), the splittings between partially occupied MOs (ΔE_{POMO}), and the spin density populations on the exocyclic SCs (ρ_{spin} on SC) and on each endocyclic C-2 position (ρ_{spin} on C-2) are given. We shall see that the latter spin density population is a useful reflection of the degree of spin delocalization from the SC into the FC. Table 1 shows that triplet ground states are obtained for all the diradicals **4a–e.** $\Delta E_{T\to S}$ for **4a** (0.49 eV = 11.3 kcal/mol) and **4b** (0.31 eV = 7.2 kcal/mol) are in good agreement with ab initio level results [4a,b]. In addition, **4a** is known experimentally to have a triplet ground state [3h]. Experimental evidence also supports triplet ground states for derivatives of diradicals **4c–e** [3i–k]. Therefore, we feel that the other computed T-S splittings listed in Tables 1 through 5 can be assumed for the sake of discussion to be of similar semiquantitative quality.

It can be seen from Tables 1 through 5 that all calculated diradicals with homo-spin centers (**4a–e, 7a–e**) are predicted to have triplet ground states ($\Delta E_{T\to S} > 0$); that is, ferromagnetic coupling is obtained. In addition, the neutral (**5a–d**) and doubly charged (**8a–d**) hetero-spin center diradicals also are predicted to have triplet ground states. However, the diradicals with one neutral and one charged hetero-spin center (**7a–e**) are predicted to have singlet ground states ($\Delta E_{T\to S} < 0$), corresponding to antiferromagnetic coupling. This difference constitutes a notable change from the usual dominance of ferromagnetic coupling by *m*-phenylene that is based upon simple parity arguments.

When neutral spin centers are used to substitute a single $\cdot CH_2$ SC unit in **4a** to form neutral hetero-spin center diradicals **5a–d,** the degeneracy of POMOs is lifted compared to **4a** due to the effect of the heteroatoms (see Table 2). Nevertheless, the ΔE_{POMO} splittings found for **5a–d** are still less than the typical threshold (1.5 eV) [9] past which the triplet state is considered to be destabilized relative to the singlet state. As a result, despite the POMO non-degeneracy, the parity-induced exchange preference for a high-spin state in these systems is retained. Experimental support for this generalization is given by the high-spin ground state of hetero-spin diradical **1,** despite the fact that this diradical can be formulated to have zwitterionic resonance structures [10].

The spin populations on the exocyclic SC units of the hetero-spin center remain quite comparable

TABLE 4 Calculated Results for Diradicals with One Charged Hetero-Spin Center

	$\Delta E_{T\to S}$ (eV)	ΔE_{POMO} (eV)
 **7a**	-0.45	1.89
 **7b**	-1.09	2.40
 **7c**	-0.56	2.20
 **7d**	-0.90	2.19
 **7e**	-0.86	2.12

$\Delta E_{T\to S}$ (eV) is the triplet–singlet (T → S) energy splitting for the molecule shown, and ΔE_{POMO} is the energy splitting between partially occupied frontier MOs.

to the populations found in the same SC unit of the corresponding homo-spin center. For example, ρ_{spin} on the oxygen SC of homo-spin diradical **4b** is 0.38, and on the oxygen SC of hetero-spin diradical **5a,** it is 0.36.

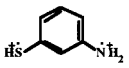
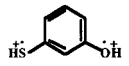
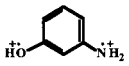
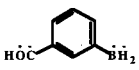
According to the spin density distribution of **5a,** larger spin densities are found mainly on the exocyclic CH_2 and endocyclic C-2 position, hence the trimethylenemethane-like resonance structure types (ii)–(iii) in Figure 1 are predominant for **5a.** By analogous consideration of ρ_{spin} results, type (iii) is the main resonance structure for **4b.** In fact, for **4b,** the oxygen SC "leaks" much of its spin density into the ring system in order to form C = O double bonds, a phenomenon that is supported by ab initio computations for **4b** [11]. For **5b–d,** spin density results suggest that they have the resonance natures that are quite similar to those of analogous homo-spin diradicals **4c–e.** All resonance structures (i)–(iii) in Figure 1 are consistent with the delocalization for **4c–e** and **5b–d.**

Since all the charged homo-spin center diradicals (**6a–e**) are computed to have triplet ground states, the charged SC are also considered as potential spin centers for design of high-spin building blocks, even though Table 3 shows that the charged diradicals have appreciable ΔE_{POMO} compared with ΔE_{POMO} for the neutral diradicals in Table 1. The spin density distributions for **6a–e** suggest that only the SH^+ SC concentrates the majority of spin density onto itself, such that resonance structure (i) in Figure 1 is predominant for **6c.** For the other charged diradicals, ρ_{spin} mainly resides on central phenylene FC unit, so that resonance structures (ii)–(iii) predominate. This situation would presumably be somewhat altered in experimentally realistic systems that would allow greater delocalization of both the charge and spin densities for analogs of **6a–e,** leading to dilution of the exchange interactions and a decrease in $\Delta E_{T\to S}$ [4e]. Still, the usual parity-based expectation of a high-spin ground state for a *meta*-linked diradical is verified for the homo-spin double-charged systems **6a–e,** whatever the apparent resonance structure or exact spin density distribution.

By comparison, the hetero-spin center diradicals with one charge (**7a–e**) all are computed to be singlet ground states. This is simplistically ascribable to the larger splitting of POMOs in these, which favors spin pairing in the lower-spin state. From Table 4, ΔE_{POMO} = 1.9–2.4 eV for **7a–e,** compared to $\Delta E_{POMO} < 1.0$ eV for all the triplet ground-state diradicals. In a qualitative sense, these results may also be explained by the dominance of ionic over diradical resonance structures in the singlet states of the hetero-spin systems that have one charge. For example, the $^1A'$ state of neutral diradical **5a** can be formulated as either a diradical or a zwitterion. This neutral hetero-spin system is computationally found by either the present method or by post–Hartree-Fock ab initio methods [11] to have a diradical singlet state with considerable mixing of configurations in the C. I. wave function and a triplet ground state in accord with parity rules. Therefore, **5a** is correctly described as a diradical. This correlation of strong configurational mixing with diradical nature in singlet states has been discussed by one of us in previous work [4c]. The other neutral homo-spin and neutral hetero-spin singlet states also have strongly diradical-type singlet states.

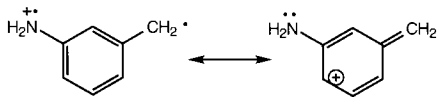
However, the hetero-spin singly charged diradicals **7a–e** were found to have singlet states with one dominant, closed shell configuration. This result supports the dominance of ionic resonance character in these singlet ground states, despite the fact that diradical resonance structures can be formulated for them. In short, this is a case where perturbation of orbital near degeneracy through substitution confounds an overly simplistic parity analysis. Similar effects of varying substitution have been computationally explored for heterocyclic systems whose

TABLE 5 Calculated Results for Charged Diradicals with Hetero-Spin Center

	$\Delta E_{T\rightarrow S}$ (eV)	ΔE_{POMO} (eV)	ρ_{spin} on SC	ρ_{spin} on C-2
 **8a**	0.26	0.66	S 0.92, N 0.59	0.74
 **8b**	0.26	0.52	S 0.95, O 0.25	0.71
 **8c**	0.29	0.79	N 0.64, O 0.26	0.84
 **8d**	0.15	0.43	N 0.67, O 1.02 B 0.01	0.44

$\Delta E_{T\rightarrow S}$ (eV) is the triplet–singlet (T → S) energy splitting for the molecule shown, ΔE_{POMO} is the energy splitting between partially occupied frontier MOs, ρ_{spin} on SC is UHF computed spin density on the spin-bearing unit, and ρ_{spin} on C-2 is the computed spin density on C-2.

dominant nature as diradical, ionic, or hypervalent resonance structures is unclear upon simple inspection [4c].

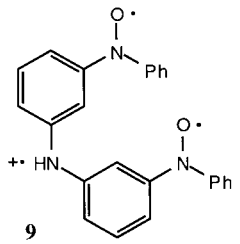


7a (diradical) **7a (ionic)**

In the large majority of cases studied experimentally and computationally to date, *meta*-coupled diradicals have high-spin ground states. The strength of this preference has typically been explained by parity models, as mentioned earlier. But recently, a number of apparent violations of the parity expectations (often termed violations of Hund's rule of high-spin multiplicity) have been delineated [12]. Some of these have been caused by torsional deplanarization of the exocyclic SC units (Table 5). The parity approaches typically assume that all intramolecular exchange interactions are of similar magnitude in a planar or nearly planar system. When planarity cannot be achieved, a diradical with apparent high-spin parity may have nearly degenerate triplet/singlet states, or a singlet ground state. Experimental examples have been found for sterically congested, stabilized variants of **4c** [13,14], and computational justification of the mechanisms for the disfavoring of the triplet state has been given for these cases [15].

In the present study, planarity is artificially enforced, so the finding of a low-spin ground state for **7a–e** is due to electronic factors, not torsional alteration of exchange between the SC units through the FC unit. In an analogous case investigated both experimentally and computationally, West et al. [16] found that the neutral 2,6-pyridinediyl unit acts as a typical ferromagnetic linker in accord with parity expectations but that the protonated 2,6-pyridiniumdiyl unit acts as an antiferromagnetic linker, helping to fuel the notion that simplistic parity approaches confounded in some charged open-shell systems. Another related example was given by Yoshizawa et al. [17] in a semiempirical PM3-CI survey of organic open-shell systems. These workers noted that "heteroatomic systems" **9** incorporating two neutral nitroxides and a charged $NH^{\cdot+}$ unit is computed to have a low-spin ground state, in contrast to the high-spin ground state of a set of related systems that incorporated only charged SCs or only neutral SCs. They went on to argue that this apparent anomaly was explained by the increased HOMO–LUMO splitting in the Hückel MOs for the system, but they did not extrapolate their result. We feel that our results generalize the notion that a combination of charged with neutral SCs will not invariably be successful for design of high-spin organic molecules, but rather that considerable caution and computational/theoretical consideration should be given in choosing such systems as potential building blocks for bulk magnetic materials. In particular, the effects of

HOMO–LUMO splitting and of alternate, ionic resonance structures must be weighed against the parity-based arguments, in deciding whether novel substitution patterns will still be consistent with a truly diradical structure.



9

SUMMARY

Based on our calculated results, high-spin ground-state ferromagnetic coupling for diradicals with hetero-spin centers can be best achieved for two neutral or two charged radical spin-bearing units connected by planar ferromagnetic exchange coupling unit. Coupling of one neutral and one charged hetero-spin center is often predicted to result in a low-spin ground state, even when a nominally ferromagnetic exchange coupling connectivity is used.

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