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Theoretical design of high-spin organic molecules with two-center, three-electron spin-containing units

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ABSTRACT: A series of potentially stable high-spin molecules based on *m*-phenylene and/or *s*-triazine ferromagnetic connectivity coupling units and two-atom three-electron spin centers thioaminyl (—N$^{\cdot}$—S)— and/or hydrazyl (—N$^{\cdot}$—N<) were computationally investigated as novel magnetic material building blocks, using the semiempirical AM1-CI molecular orbital plus configuration interaction (CI) method. Oligoradicals based on these structural units were investigated for various both cyclic and linear connectivities in order to determine the effects of structural variation on the high-spin state preference. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: high-spin organic molecules; two-atom; three-electron spin centers; magnetic materials

INTRODUCTION

The design and synthesis of organic molecules with very high-spin ground states has been and remains a topic of great interest.[1–4] One rational approach to designing high-spin molecules which has been proposed and studied by several groups[5–7] consists of conceptually dividing the molecules into two components: a spin-containing (SC) fragment which provides the unpaired electron and a ferromagnetic coupling (FC) unit which connects radical centers ferromagnetically.

Recent interest in design of organic-based magnetic materials has spurred considerable work on the synthesis and properties of organic open-shell molecules. The highest spin states obtained for purely organic systems have been reported for systems such as polycarbenes and dendridic polyradicals. High-spin polycarbenes[4] have not been considered feasible as realistic components of magnetic materials owing to their high reactivity under non-cryogenic conditions, although recent results suggest some improvements in stability of polycarbenes with appropriate substitution.[4g,h] Even sterically stabilized all-hydrocarbon dendritic polyradicals show instability for larger systems, with some loss of exchange coupling between electrons.[1e] Therefore, the quest for new classes of stable multiradicals with high-spin ground state has been strongly pursued. Although painstaking, the promise of these efforts is spurred by successes such as the solid-state β-phase of the organic radical 1-cyano-4-dithiadiazolyl-2,3,5,6-tetrafluorobenzene that has been recently discovered to exhibit spontaneous magnetization at 36 K.[8]

In this contribution, we describe computational studies of a class of potentially stable high-spin multiradicals that incorporates thioaminyl (—N$^{\cdot}$—S—) and hydrazyl (—N$^{\cdot}$—N<) SC units connected by *m*-phenylene and/or *s*-triazine FCs as shown in the schemes. Free radicals containing the two-atom three-electron thioaminyl[9] and hydrazyl[10] spin centers are exceptionally persistent and can in some cases be isolated as pure radical crystals. Additional requirements for the stabilization of a high-spin ground state in π-conjugated systems are (i) the existence of partially occupied degenerate or near-degenerate molecular orbitals (POMOs) and (ii) strong Coulomb electron–electron interaction within the subspace of near degenerate POMOs that prevents spin pairing and gives rise to preference of the high-spin state.[11] Semiempirical quantum methods have been found to be effective in identifying electronic ground states of open-shell systems with varying structures, connectivities and conformations.[12]

We have applied the semiempirical molecular orbital plus configuration interaction AM1-CI method,[13] to assess ground-state spin multiplicities for a series of putative di- or multiradicals shown in the schemes. Since the prediction of the absolute singlet–triplet gaps of small organic biradicals is seldom feasible even by high quality *ab initio* methods, we concentrated mainly on relative trends associated with variations of SC, FC and connectivity in the series. In addition, we describe the nature of the exchange coupling in terms of energy

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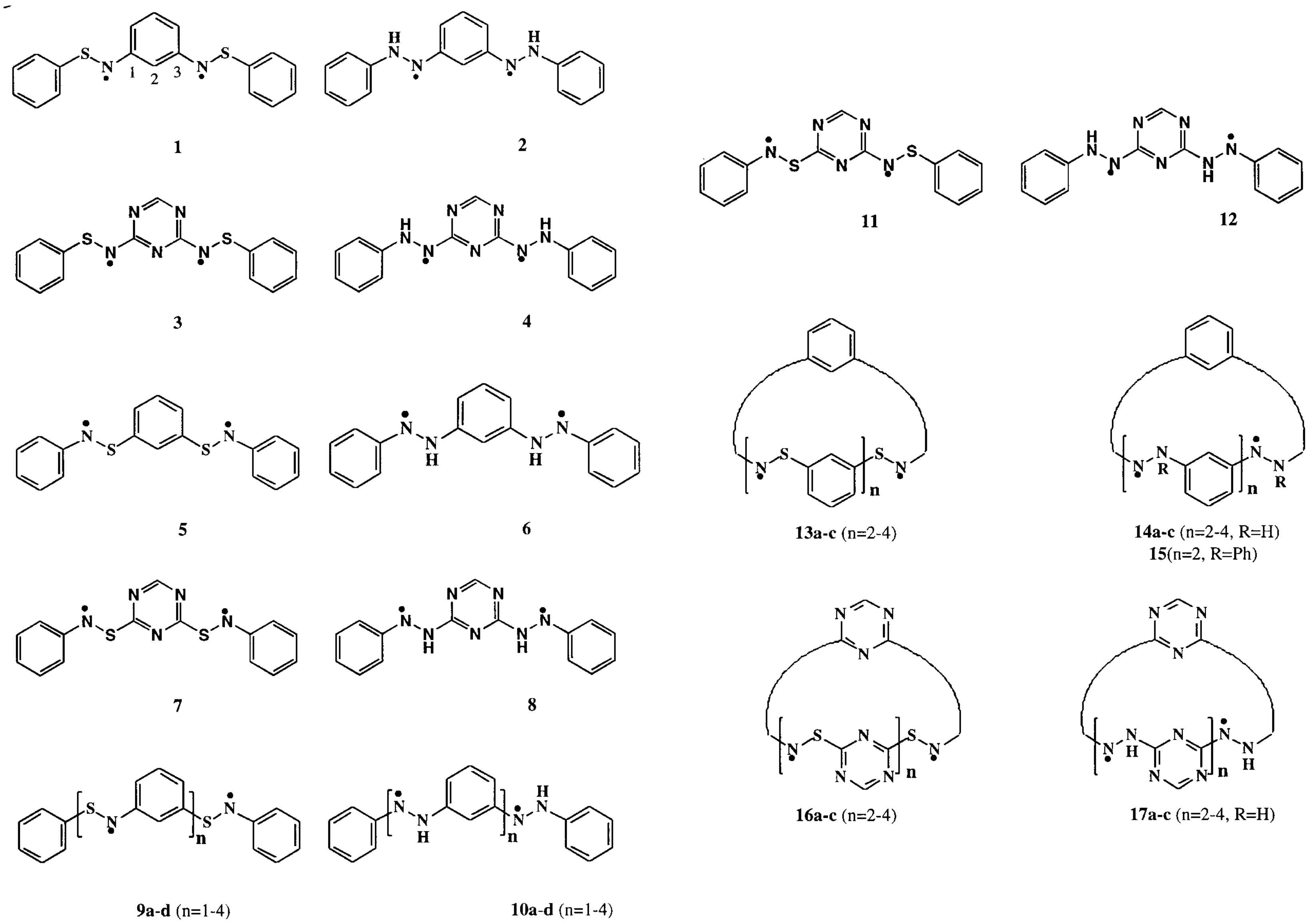

1
2
3
4
5
6
7
8
9a-d (n=1-4)
10a-d (n=1-4)
11
12
13a-c (n=2-4)
14a-c (n=2-4, R=H)
15(n=2, R=Ph)
16a-c (n=2-4)
17a-c (n=2-4, R=H)

Scheme 1

splitting of POMOs and the spin density distributions for the high-spin state.

Limited CI treatments such as those used here can suffer from size extensivity problems, wherein larger molecules are not so completely or precisely described as smaller molecules for the same computational active space. This is a particular problem for *ab initio* methodology. However, as is true for other semiempirical methods, the AM1 limited CI method as we have used it for open-shell molecules has been calibrated[12a–c] using specific active spaces against both experimental results and *ab initio* results. The calibrations have included geometry optimization, ground-state multiplicity determination and the estimation of lowest ground-to-excited state energy gaps $\Delta E_{\mathrm{L-H}}$.[12a–c] The calibration molecules also included systems with considerable heteroatom substitution. Without going into extensive detail, we note that the predictive capability of AM1-CI and closely related methods for ground-state multiplicity *vis-à-vis* known experimental results (such as dinitroxide radicals[12m]) has been extremely good, and that quantitative comparisons of $\Delta E_{\mathrm{L-H}}$ to *ab initio* results have also been family good where the latter numbers are available.[12a–c] Simple variations of technique did not significantly alter the results predicted in this study. Normally, it can be dangerous to alter the standard CI active space used in a semiempirical method that has already been calibrated against *ab initio* results, since the whole calibration procedure might need to be repeated. Still, for a number of the molecules examined in the present study, we found that moderate increases in the active space did not change the computed $\Delta E_{\mathrm{L-H}}$ in any substantial fashion. This finding is in accord with results for other semiempirical studies in which the magnitude of electron correlation is described as not too strongly affecting qualitative ground-state multiplicity for alternant open-shell systems.[12l] Since the results did not vary strongly with CI active space within the constraints of our procedure, only results computed by our previously established procedures are reported.[12a–c,g]

As additional calibration, we note that alteration in connectivity gives reasonable qualitative results when the same AM1-CI methodology is used. For example, planar *para* analogs of the *meta* biradicals described in Scheme 1 are all found to have singlet states, as one would predict by simple connectivity arguments,[1g] and by the precedent of computations[12i] on very closely related biradicals.

Overall, the AM1-CI methodology takes into account the major orbital subspace and configurations that determine ground-state multiplicity and electronic structure for open-shell molecules, insofar as calibration against *ab initio* computation and experiment has determined to date. Extrapolation to larger polyradicals has theoretical pitfalls, but is warranted in the absence of obviously illogical results. Still, the discussion of results given below should be taken in the spirit of explaining trends in computed properties for related sets of molecules, rather than implying that one can expect strict quantitative verification of any given single number.

METHODOLOGY

The series of di- and multiradicals **1**–**17** was obtained by variation not only of the SC (—N$^{\cdot}$—S—, —N$^{\cdot}$—N<; thioaminyl, hydrazyl) and FC (*m*-phenylene, *m*-triazine) units, but also of connectivity. The diradical models **1** and **3** form one pair of symmetrical regioisomers, and models **2** and **4** form a second pair; both pairs utilize the *m*-phenylene FC unit. Analogous pairs of *s*-triazine coupled systems are **5** and **7** plus **6** and **8.** Extended versions of the *m*-phenylene linked systems were studied as linear oligomers (**9** and **10,** $n = 1$–4) and cyclic oligomers (**11**–**13,** $n = 1$–4) as shown in the schemes. We used Spartan (Wavefunction, version 4.1) running on a Silicon Graphics workstation to assemble and pre-optimize the molecules using the AM1 semiempirical all-valence electron Hamiltonian[13] with unrestricted Hartree–Fock (UHF) wavefunctions.

For the diradicals, final geometry optimizations were performed with AM1 multielectron configuration interaction wavefunctions (MECI) using C_{2v} (**1**–**4**) and C_s (**5**–**6;** $n = 1$) symmetry constraints; linear multiradicals (**5** and **6,** $n = 2$–4) were under C_s symmetry constraints. The cyclic multiradicals (**7** and **8,** $n = 2$–4) were optimized with planar constraints for the sake of simplicity in evaluating the connectivity effects in these systems. All MECI optimizations were done using MOPAC93.[14] As reference SCF wavefunction, a restricted open-shell Hartree–Fock (RHF) determinant with single occupancy of all near-degenerate POMOs was used. The CI subspace spanned 121 configurations possessing the lowest energy within six frontier MOs. In addition, we also computed the spin density distribution obtained from the UHF high-spin ground-state wavefunction at the CI equilibrium geometry. UHF wavefunctions typically give spin density magnitudes that are too large and prone to spin contamination by states of higher spin multiplicity, but remain useful to demonstrate qualitative effects of spin polarization in similar molecules.

RESULTS AND DISCUSSION

Various computed properties are given in Tables 1–4: (1) the ground-state spin multiplicity for the bi- and multiradicals including the calculated energy gap $\Delta E_{\mathrm{L-H}}$ between the state of *h*ighest spin multiplicity and the next *l*owest lying state ($\Delta E_{\mathrm{L-H}} > 0$ corresponds to a high-spin ground state); (2) the splitting of the POMO levels ΔE_{POMO} in the reference SCF wavefunction; (3) selected spin densities on each atom of the SC and on positions alternant to the SC (C-2 or N-2 of *m*-phenylene or *m*-triazine moiety, respectively, shown in structure **1**).

Table 1. Stability of triplet ground state ($\Delta E_{\mathrm{L-H}}$), POMO splitting (ΔE_{POMO}) and spin densities on the hypovalent atom (ρN), on the normally valent atom (ρNH/S) of the SC and on the 2-position of the FC (ρC-2 or N-2) for diradical systems ($n = 1$)

	Ph—X—N$^{\bullet}$—Ar—N$^{\bullet}$—X—Ph				Ph—N$^{\bullet}$—X—Ar—X—N$^{\bullet}$—Ph				Ph—N$^{\bullet}$—X—Ar—N$^{\bullet}$—X—Ph			
	Ar = C_6H_4		Ar = C_3N_3H		Ar = C_6H_4		Ar = C_3N_3H		Ar = C_6H_4	Ar = C_3N_3H	Ar = C_6H_4	Ar = C_3N_3H
	X = S	X = NH	X = S	X = NH	X = S	X = NH	X = S	X = NH	X = S	X = NH	X = S	X = NH
Parameter	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9a**[a]	**10a**[a]	**11**[a]	**12**[a]
$\Delta E_{\mathrm{L-H}}$ (eV)	0.39	0.51	0.13	0.25	0.02	0.07	0.01	0.05	0.09	0.16	0.03	0.11
ΔE_{POMO} (eV)	0.24	0.32	0.39	0.45	0.005	0.02	0.08	0.12	0.22	0.24	0.63	0.41
ρX$^{\bullet}$ (N$^{\bullet}$, S$^{\bullet}$)	0.55	0.59	0.41	0.59	0.56	0.59	0.52	0.66	—S—PhN$^{\bullet}$— 0.55 PhN$^{\bullet}$— 0.55	—HNPhN$^{\bullet}$— 0.59 PhN$^{\bullet}$— 0.59	—S—ArN$^{\bullet}$— 0.60 ArN$^{\bullet}$— 0.70	—HN—ArN$^{\bullet}$— 0.52 ArN$^{\bullet}$— 0.68
ρNH/S	0.27	0.19	0.47	0.19	0.28	0.19	0.30	0.12	Ph—$\underline{\mathrm{S}}$— 0.26 —Ar—$\underline{\mathrm{S}}$— 0.26	Ph—$\underline{\mathrm{NH}}$ 0.20 —Ar—$\underline{\mathrm{NH}}$— 0.19	Ph—$\underline{\mathrm{S}}$ 0.28 —Ar—$\underline{\mathrm{S}}$— 0.09	Ph—$\underline{\mathrm{NH}}$ 0.32 —Ar—$\underline{\mathrm{NH}}$— 0.10
ρC-2/N-2[b]	0.67	0.68	0.42	0.21	0.46	0.49	0.46	0.18	0.58	0.60	0.35	0.32

[a] For these asymmetric biradicals, the table shows the results for both the externally delocalized (Ph—X$^{\bullet}$—) and centrally delocalized (—Ar—X$^{\bullet}$—Ph) spin sites.

[b] For all biradicals, this site is at the 2-position of the central, *meta*-substituted ring.

Table 2. Stability of quartet ground state (ΔE_{L-H}), POMO splitting (ΔE_{POMO}) and spin densities on the hypovalent atom (ρN), the normally valent atom (ρNH/S) of the SC, and on the 2-position of the FC (ρC-2 or N-2) ($n = 2$)

Parameter	**9b**	**10b**	**13a**	**14a**	**15**	**16a**	**17a**
ΔE_{L-H} (eV)	0.05	0.09	0.21	0.29	0.25	0.12	0.21
ΔE_{POMO} (eV)	0.35	0.38	0.04	0.007	0.05	0.23	0.31
$\rho N^{\cdot}$	–[a]	–[a]	0.47	0.53	0.55	0.32	0.51
ρNH/S	–[a]	–[a]	0.39	0.23	0.21	0.57	0.27
ρC-2/N-2	–[a]	–[a]	0.57	0.59	0.60	0.35	0.40

[a] Spin densities on monomer units variable owing to non-symmetry of linear oligomer.

Table 3. Stability of quartet ground state (ΔE_{L-H}), POMO splitting (ΔE_{POMO}) and spin densities on the hypovalent atom (ρN), the normally valent atom (ρNH/S) of the SC, and on the 2-position of the FC (ρC-2 or N-2) ($n = 3$)

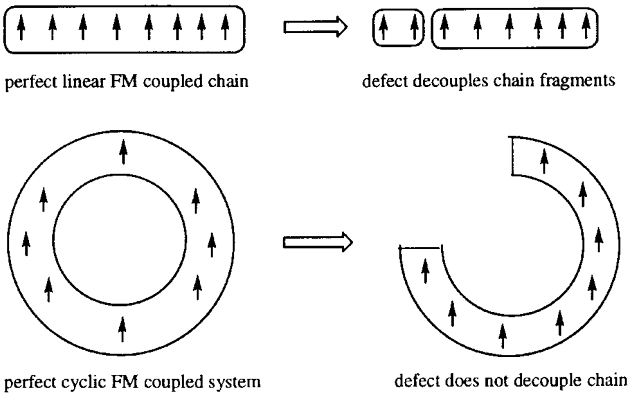
Parameter	**9c**	**10c**	**13b**	**14b**	**16b**	**17b**
ΔE_{L-H} (eV)	0.03	0.05	0.10	0.13	0.09	0.10
ΔE_{POMO} (eV)	0.42	0.44	0.15	0.36	0.33	0.63
$\rho N^{\cdot}$	–[a]	–[a]	0.50	0.58	0.32	0.56
ρNH/S	–[a]	–[a]	0.33	0.21	0.55	0.25
ρC-2/N-2	–[a]	–[a]	0.56	0.60	0.34	0.39

[a] Spin densities on monomer units variable owing to non-symmetry of linear oligomer.

Table 4. Stability of quartet ground state (ΔE_{L-H}), POMO splitting (ΔE_{POMO}) and spin densities on the hypovalent atom (ρN), the normally valent atom (ρNH/S) of the SC, and on the 2-position of the FC (ρC-2 or N-2) ($n = 4$)

Parameter	**9b**	**10c**	**13b**	**14b**	**16b**	**17b**
ΔE_{L-H} (eV)	0.02	0.03	0.08	0.11	0.05	0.07
ΔE_{POMO} (eV)	0.46	0.49	0.11	0.32	0.38	0.56
$\rho N^{\cdot}$	–[a]	–[a]	0.55	0.58	0.43	0.58
ρNH/S	–[a]	–[a]	0.29	0.21	0.45	0.24
ρC-2/N-2	–[a]	–[a]	0.56	0.59	0.35	0.38

[a] Spin densities on monomer units variable owing to non-symmetry of linear oligomer.



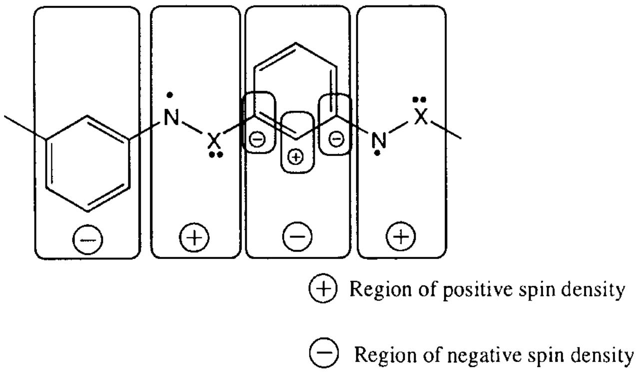
Scheme 2

For the sake of simplicity, we list only the spin densities for the SCs and ρ(C-2 or N-2), since we found these to be the major sites of positive spin density. These variations in spin density can be correlated with the variation of ΔE_{L-H},[12e–h] and the combination of the two results reveals useful trends about the degree of preference of the high spin state as a function of structural variation. From Tables 1–4 it can be seen that all the molecules investigated here are predicted to possess high-spin ground states with $\Delta E_{POMO} \leq 0.63$ eV.

For the various thioaminyl (**1** and **2**) or hydrazyl (**3** and **4**) SCs, the spin densities on the two atoms of the SC have the same sign, but with considerably larger spin densities on the hypovalent nitrogen atoms than on the —S—or—N< atom (see Table 1), regardless of different connectivity patterns. The normally valent atoms therefore tend to insulate the spin-bearing hypovalent sites from delocalization. The choice of connectivity of the FC to the hypovalent or the normally valent atom of the SC strongly affects the spin density ρ(C-2 or N-2) of the FC unit, which is a useful measure of the degree of spin delocalization from the SC on to the FC. When the hypovalent spin density sites are directly attached to the FC, the high-spin state is considerably more favorable than the cases when neither hypovalent site is connected to the FC.[12a,h,i]

The diradicals can be ranked in order of decreasing ΔE_{L-H} as **1** > **9a** > **5** and **2** > **10a** > **6** (Table 1). The decreasing high spin preference with —X—N$^{\cdot}$—Aryl—N$^{\cdot}$—X— > —X—N$^{\cdot}$—Aryl—X—N$^{\cdot}$— > —N$^{\cdot}$—X—Aryl—X—N$^{\cdot}$— connectivity is not just an effect of distance as the hypovalent spin-bearing sites on the SCs become further apart, but is also due to the spin-insulating effects of the normally valent atoms in the SCs. Because spin density does not delocalize well through the —S—and—N< sites in the SCs, less spin density is delocalized on to the FCs in **9a** and **10a,** and even less in **5** and **6,** resulting in a decreasing ΔE_{L-H}. This computational result is supported by the experimental finding that thioaminyl-based diradicals with the connectivity of **5** (—N$^{\cdot}$—S—Aryl—S—N$^{\cdot}$—) do not show triplet behavior.[9g]

ΔE_{POMO} decreases in the series **1**–**2** > **9a**–**10a** > **5**–**6** (Table 1). It may seem paradoxical that the high-spin preference in this series grows smaller as the energetic splitting of the frontier orbitals decreases. However, the decrease in ΔE_{POMO} is an effect of increased insulation of the SCs from one another due to the placement of the spin isolating —S— and —NH— moieties: it is not due to symmetry-imposed effects. As a result, the increasing orbital degeneracy reflects increasing isolation of non-interacting spin orbitals, such that systems **5** and **6** are essentially non-interacting biradical systems. Nominal orbital degeneracy in a system is not sufficient to yield an energetically favorable high-spin state, when an effective



Scheme 3

mechanism for exchange between electrons is not available.

The *s*-triazine FC units give FM coupled behavior for diradicals **3, 4, 7, 8, 11** and **12.** In all cases, the coupling $\Delta E_{\mathrm{L-H}}$ is smaller than that computed for the connectivity analogous *m*-phenylene coupled diradicals. As in the *m*-phenylene coupled analogs, the magnitude of $\Delta E_{\mathrm{L-H}}$ decreases with increasing distance between the hypovalent nitrogen centers, following the order **3** > **11** > **7** and **4** > **12** > **8** for the thioaminyl and hydrazyl SCs, respectively. In the subsequent work on oligomeric species, we chose to study only the *m*-phenylene linear oligomers, because of the lower exchange efficacy of the *s*-triazine units. However, we did study cyclic oligomers incorporating *s*-triazine FCs, because of their potential ability to form chelated or hydrogen-bonded solid-state arrays.

The stability of high-spin ground states ($\Delta E_{\mathrm{L-H}}$) for the linear and cyclic tri-, tetra-and pentaradicals show similar trends to the diradicals as functions of connectivity and SC. All oligomers were formulated using regioregular head-to-tail —Aryl—N$^{\cdot}$—X—Aryl—N$^{\cdot}$—X connectivities, in order to avoid the spin-insulating effects noted above for the —N$^{\cdot}$—X—Aryl—X—N$^{\cdot}$—connectivity. There is some decrease in high-spin preference as oligomer size increases, but it is not clear how much of this trend is due to the inherent uncertainties of using a limited active space for the configuration interaction calculations.[12a,c]

For practical reasons, the cyclic oligoradicals are particularly worthy targets. Rajca[1e] noted that cyclic oligoradicals are more tolerant of SC defects than are linear oligoradicals when the SCs are part of the conjugated system rather than being pendant. As shown in Scheme 2 the cyclic cases allow multiple pathways for electron exchange throughout the molecule, whereas linear oligoradicals are broken into small spin domains by SC defects. In our computations, the cyclic oligoradicals were found to have larger $\Delta E_{\mathrm{L-H}}$ than the corresponding linear forms for the lower degree of polymerization. Multiple factors could contribute to this effect. For linear oligoradicals, spin population tends to concentrate on the terminal units, segregating spin density and leading to a smaller $\Delta E_{\mathrm{L-H}}$. This effect is reduced by an increase in the degree of oligomerization, which leads to a more even spin density distribution in the center of a linear chain resembling that of the cyclic systems. The cyclic system acts like a linear system of infinite length, so long as the cyclic connectivity is nondisjoint and regioregular in a head-to-tail fashion. Also, the cyclic oligomers tend to possess smaller ΔE_{POMO} than corresponding linear oligomers, in part owing to their higher symmetry. Deplanarization of the cyclic oligoradicals could affect these trends in real systems, but the qualitative trends are reasonable and further point to the cyclic systems as desirable synthetic targets.

An interesting and important question for the design of practical ferromagnetic systems concerns whether the nature and magnitude of exchange coupling in the oligoradicals is comparable to those in the diradical models. In considering the trends for both the linear systems **9** and **10** and cyclic oligoradicals **13–17,** there is a substantial drop in $\Delta E_{\mathrm{L-H}}$ on going from the diradical to the higher spin systems. $\Delta E_{\mathrm{L-H}}$ decreases as the degree of oligomerization increases, but the decrease is small in comparison with that on going from the diradical to triradical. A similar trend was found in our original study[12c] of the AM1-CI method as applied to diradicals and oligoradicals, and also by Li *et al.*[12l] in a completely separate semiempirical study of di- and oligoradical systems. Given the variation of the magnitudes of high-spin to low-spin energy gap as a function of structure, the trends in both studies are unlikely to be due solely to methodological artifacts. Qualitatively, these and the previous results show that diradical models are likely to be good qualitative models for the exchange coupling in oligoradicals of similar geometry, but that the magnitude of exchange in the diradical may overestimate the analogous average exchange between any two units in a larger, related polyradical.

For all of the systems studied, if the two-atom SCs are considered as a single unit (since both atoms have spin density of the same sign), a spin density wave is formed in the oligomeric systems. A spin density wave with appropriate connectivity and geometry to avoid spin mismatches (ρ_α–ρ_α spin interactions of the same sign) is expected to exhibit a high-spin ground state for all oligomers, as observed in these calculations (Scheme 3). Such spin-density wave models are known to be in accord with the experimental exchange behavior observed for high spin molecules.[15]

In comparing overall trends, the hydrazyl SC qualitatively delocalizes more spin density on to *m*-phenylene FC units than does the thioaminyl SC. Interestingly, when the *s*-triazine FC is used, the thioaminyl SC is predicted to undergo considerable spin density perturbation, with an increase in unpaired spin upon the divalent sulfur atom attributable to a greater contribution of the —$^{-}$N—S$^{\cdot +}$— resonance structure. The heteroatom substitution in *s*-triazine thus affects the spin density population on the SC. Although an analogous effect is nominally possible for the hydrazyl radical due to resonance admixture of the $—^{-}N—N^{\cdot +}<$ structure, the computations suggest that this does not occur to a significant extent. This result is consistent with the better ability of divalent sulfur to bear a radical cation site in $—^{-}N—S^{\cdot +}—$ than that of trivalent nitrogen in $—^{-}N—N^{\cdot +}<$.

In an effort to model a hydrazyl-based system that is synthetically more realistic, although computationally more complex, than those lacking steric stabilization, we investigated system **15** with *N*-phenyl substitution analogous to that of known stable radicals such as *N,N*-diphenylpicrylhydrazyl. As shown in Table 2, the use of *N*-phenylhydrazyl instead of the simple hydrazyl SC perturbs the degeneracy of POMOs, such that **15** has a slightly larger ΔE_{POMO} and a smaller preference for a quartet ground state than is found for analogous but sterically simpler system **14a.** Still, **15** has a sizable predicted $\Delta E_{\mathrm{L-H}}$ of 0.25 eV, suggesting this system to be a good synthetic target.

In principle, the degree of oligomerization might be further increased while still maintaining a high-spin ground state for both the cyclic and linear oligoradical systems studied here. For example, Patel *et al.*[16] have been investigating liquid crystalline oligoradical systems based on the thioaminyl SC unit. They have also shown computationally that thioaminyl radicals should be attractive synthetic building blocks for molecular magnetic materials. If problems with oligomerization of the radical sites can be overcome in these systems, systems containing the hydrazyl and thiaminyl radicals could serve as useful building blocks for magnetic materials.

CONCLUSION

Stable two-atom three-electron SCs such as thioaminyl and hydrazyl should be useful building blocks in the design of high-spin molecules such as those described above. For diradicals constructed using *m*-phenylene FCs and these SCs, the relative triplet stabilization versus the singlet decreases with an increase of the distance between two hypovalent spin centers carrying the largest spin density, especially when more of the normal valence —S— and —NH— units are interposed between the hypovalent spin-bearing sites. Use of the hydrazyl SC favors more spin density delocalization from the SC on to the 2-position in the FC ring, in comparison with the thioaminyl SC, leading to greater high-spin ground-state preference when hydrazyl is used. This difference would probably be decreased in the experimentally more realistic *N*-phenylhydrazyl systems.

All of the cyclic oligoradicals described here are predicted to be good candidates for stable multiradicals with robust high-spin ground states. The high-spin preference in the cyclic cases appears sufficient not to be overcome by effects of deplanarization. In addition, the cyclic oligoradicals have a greater preference for the high-spin ground state than linear oligoradicals of corresponding length, although the preference is reduced as the degree of oligomerization increases. For all the systems investigated, the magnitude and sign of $\Delta E_{\mathrm{L-H}}$ correlate with variation of spin density on the FC, such that the largest high spin preferences are found when spin density is most delocalized from the SCs on to the linking FCs. Overall, stable high-spin molecules based on these SCs should be attractive targets as part of the design of magnetic materials.

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