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Acid−Base-Driven Multilevel Switching of Electronic Coupling in 2,4-Dimethylene Five-Member Heterocycles

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The ground state multiplicity of 2,4-dimethylene five-member heterocycles is dependent on the protonation of the heteroatom. The relative singlet and triplet energy at π-CASSCF-optimized geometries varies and is dependent on the number of protons attached to the heteroatom. The 2,4-dimethylenecyclopentadiene anion ($X = CH^-$) and the 2,4-dimethylenepyrrole anion ($X = N^-$) are ground state singlets while the 2,4-dimethylenecyclopentadiene ($X = CH_2$) and 2,4-dimethylenepyrrole cation ($X = NH_2^+$) are ground state triplets. The neutral 2,4-dimethylenepyrrole ($X = NH$) is a ground state triplet with a weaker preference than that calculated for the 2,4-dimethylenepyrrole cation. Similarly, the protonated 2,4-dimethylenefurane ($X = OH^+$) is a strongly preferred ground state triplet while the neutral 2,4-dimethylenefurane ($X = OH$) has a weaker preference for the triplet ground state. Analogous relationships exist for the systems with the third-row elements. These properties of the 2,4-dimethylene five-member heterocycles allow for the construction of molecular organic ferromagnets with pH-controlled magnetism.

The rapidly expanding field of high-spin organic molecules as components of molecular ferromagnets has evolved from its initial infancy of preliminary discoveries to the stage where the advance is driven by search for new molecular topologies and building blocks. The need for more robust, potent, and versatile structures has prompted the synthesis of structures with new strategies for high-spin coupling of radical sites,[1] introduction of aromatic heterocycles as ferromagnetic coupling units, and the investigation of new radical units.[2−11]

Ferromagnetic coupling units (FCs) are fundamental building blocks of organic ferromagnets and have been defined as structural units that links two or more paramagnetic centers and enforce a high spin coupling between (among) them. While many types of radical units have been described (benzyl radicals,[12] carbenes,[13] nitrenes, nitroxides, and nitronyl nitroxides,[14] phenoxyls, etc.), FCs are less accessible and their structures are governed by strict and limiting rules. The coupling properties of *alternant* hydrocarbon FCs can be reasonably well predicted based on their connectivity. Heteroatoms are known to modify an FC's properties such as its spin state, although rules governing the effects of such substitution remain elusive.[2−10] A potentially important mitigant of heteroatom-substituted FC efficacy is the protonation state of the heteroatom. Dougherty and co-workers have shown that the protonated state of an analogue of 2,6-dimethylenepyridine has been shown to favor the low-spin ground state in contrast to the high-spin ground state of the free base.[10] Despite this observation, the concept of pH controlled FCs has received limited treatment, and a comprehensive description of the effects of protonation on FC efficacy has yet to be developed.

We now report on the numerical prediction of acid- and base-driven switching of the spin-coupling properties of *nonalternant* 2,4-dimethylene five-member heterocycles **1a−n**. In the limiting case, 2,4-dimethylenepyrrole and phosphole can be switched from the strong FC **1e** and **1l** to weak FC **1d** and **1k** to antiferromagnetic coupling units (AFCs) **1c** and **1j via** appropriate (de)protonation (Scheme 1, Figure 1). The weakly ferromagnetic **1d** and **1k** have tautomeric forms **3a** and **3c**, respectively, which are strongly antiferromagnetic. Similarly, the FCs **1b** and **1i** can be deprotonated to weak AFCs **1a** and **1h**, respectively, and reprotonated to strong AFCs **2b** and **3b**.

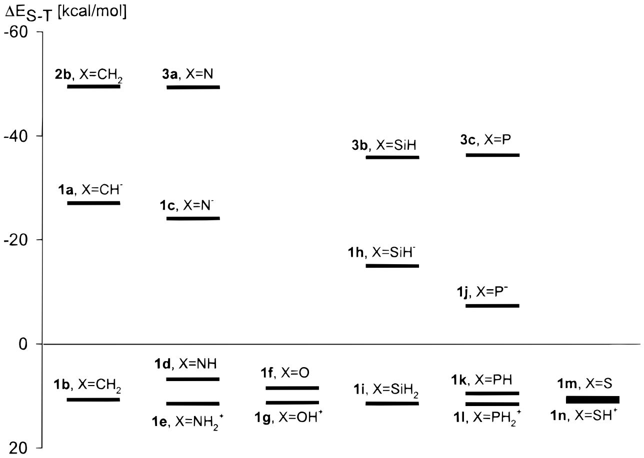
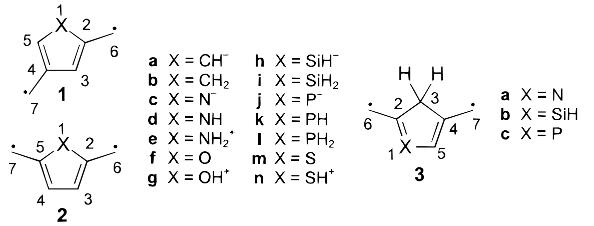


Figure 1. Relative ΔE_{S-T} for **1**, **2b**, and **3**.

SCHEME 1



Previous calculations of singlet−triplet gaps for 2,5-dimethylene five-member heterocycles **2** showed a strong dependence

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TABLE 1: Singlet−Triplet Energy Gaps for 1, 2b, and 3

entry	X[a]	ΔE_{S-T} (kcal mol^{-1})	entry	X[a]	ΔE_{S-T} (kcal mol^{-1})
2b	CH	−49.4	**3b**	SiH	−35.9
1a	CH^-	−27.1	**1h**	SiH^-	−15.0
1b	CH_2	10.8	**1i**	SiH_2	11.5
3a	N	−49.3	**3c**	P	−36.3
1c	N^-	−24.1	**1j**	P^-	−7.3
1d	NH	6.7	**1k**	PH	9.5
1e	NH_2^+	11.5	**1l**	PH_2^+	11.6
1f	O	8.5	**1m**	S	10.3
1g	OH^+	11.3	**1n**	SH^+	11.1

[a] The "+" and "−" represent total, rather than localized, charges.

TABLE 2: Singlet and Triplet Energies for Tautomeric Pairs of 1, 2, and 3

entry	X	E_S (hartree)	E_T^{rel} (kcal mol^{-1})	E_T (hartree)	E_T^{rel} (kcal mol^{-1})
2b	CH_2	−269.764 98	0[a]	−269.686 21	49.4[a]
1b	CH_2	−269.686 56	49.2[a]	−269.703 67	38.5[a]
3a	N	−285.767 83	0[b]	−285.689 31	49.3[b]
1d	NH	−285.690 66	48.4[b]	−285.701 44	41.7[b]
3b	SiH	−520.754 82	0[c]	−520.697 67	35.9[c]
1i	SiH_2	−520.733 63	13.3[c]	−520.751 90	1.8[c]
3c	P	−572.023 75	0[d]	−571.965 96	36.3[d]
1k	PH	−571.891 94	82.7[d]	−571.907 13	73.2[d]

[a] Relative to **2b**($1^1A'$). [b] Relative to **3a**($1^1A'$). [c] Relative to **3b**($1^1A'$). [d] Relative to **3c**($1^1A'$).

of ΔE_{S-T} on the heteroatom present and on the degree of protonation at the heteroatom. The preference for the singlet ground state was increased when the heteroatom was protonated. We attributed this trend to stronger electronegativity of the protonated heteroatom compared to the unprotonated one, which resulted in electron density distribution stabilizing the singlet state compared to the triplet state. The ΔE_{S-T} in the 2,4-substituted series **1** and **3** also strongly depends on these factors; however, the effect is opposite to that reported for **2**. Contrary to **2**, the triplet state in **1** and **3** is more stable with the increased electronegativity of X.

Full geometry optimization was applied at the π-CASSCF level with the 6-31G* basis set as implemented in GAMESS and PC GAMESS. The active space included all π electrons, eight electrons and seven π orbitals for **1c**, **1d**, **1f**, **1g**, **1h**, **1j**, **1k**, **1m**, and **1n**, and six electrons and six π orbitals for the remaining compounds. All heavy atoms were held in one plane by enforcing C_s symmetry for **1b−n** and **3**. Previously reported calculations of **1a** and **2b** were run with C_{2v} symmetry.[8]

The calculations resulted in the prediction of the triplet ($1^3A'$) ground state for compounds devoid of an overall negative charge (**1b**, **1d−g**, **1i**, **1k−n**) (Table 1).[15] Anionic compounds **1c**, **1h**, and **1j** had singlet ($1^1A'$) ground states. The results of similar calculations of **1a** and **2b**, also ground state singlets, have been previously reported.[8] Compounds **3** are structurally similar to **2b** and predictably all have singlet ground states. Qualitatively, our results for **1f** agree with the INDO/S-CI calculations by Lahti, Rossi, and Berson, who predicted that the $1^3A'$ state would lie below the $1^1A'$ state.[16] Also, nitroxide analogues of **1m** have been shown experimentally to have triplet ground state, in agreement with our calculations.[17]

The data reported in this work represent six sets of compounds that differ in their degree of protonation (Figure 1). In all cases, the increase in group electronegativity of X in **1** stabilizes the triplet state relative to the singlet.[18] This effect is observed as four distinct trends. (i) *Protonation of a common heteroatom*: this results in increased localization of p electrons at X by the formation of chemical bonds (**1a** → **1b**, **1c** → **1d** → **1e**, **1f** → **1g**, **1h** → **1i**, **1j** → **1k** → **1l**, **1m** → **1n**). (ii) *Changes in heteroatom electronegativity with conserved protonation*: the increased electronegativity causes better localization of both the s and π electrons (**1a** → **1d** → **1g**, **1b** → **1e**, **1c** → **1f**, **1h** → **1k** → **1n**, **1i** → **1l**, **1j** → **1m**). (iii) *Changes of the heteroatom within a group with conserved protonation*: this results in poorer overlap of the heteroatom's valence p orbitals with the π system. (iv) *Proton tautomerism*: the proton shift from atom 3 to atom 1 in **1** results in transfer of well-localized s electrons to atom 1 (**2b** → **1b**, **3a** → **1d**, **3b** → **1i**, **3c** → **1k**).

The first set of modifications renders a family of molecular magnetic switches that change their ground state character upon (de)protonation. When X contains carbon or silicon, there are two possible degrees of protonation: neutrals (**1b**, **1i**) and monoanions (**1a**, **1h**). Better localization of the s electrons in **1b** and **1i** than the π electrons in **1a** and **1h** at X causes increased stabilization of the triplet state compared to the singlet state.[19] Reprotonation of **1a** and **1h** may occur at X with the formation of **1b** and **1i**, respectively, or may occur at atom 3, in which cases compounds **2b** and **3b** will be created. Protonation at atom 3 in **1** causes the electron density to depart from X, resulting in the stabilization of the singlet state. Comparison of absolute energies of isomeric compounds (Table 2) reveals that the most stable states are the singlets of **2b** and **3b**.

Substitution of nitrogen and phosphorus at X allows for the construction of three-level switches with zero, one, and two protons at the heteroatom. Removal of all protons from X (**1c**, **1j**) releases the electron density at X for donation into the π system thus stabilizing the singlet state and destabilizing the triplet in comparison to **1d** and **1k**, respectively. The monoprotonated species **1d** and **1k** have moderately stabilized triplet ground states, but the electron densities from the 2p orbital of **1d** and the 3p orbital of **1k** are still available for redistribution throughout the p system. Additional protonation of the heteroatom in **1e** and **1l** causes this electron density to strongly localize at X and further stabilizes the triplet state relative to the singlet. Thus, the protonation at X allows for the change of the character of the ground state and the occurrence of the switching behavior in **1**.

The impact of the second protonation on ΔE_{S-T} is much smaller than that of the first one, which is contrary to our original expectations. The difference between electron donation from the s lone pair in **1c** and **1j** and from the s X−H bond in **1d** and **1k** is relatively small compared to the substantial effect of the removal of the p orbital from the p system in **1e** and **1l**. Contrary to the pyrrole and phosphole compounds, the protonation of furan and thiophene derivatives **1f** and **1m** to **1g** and **1n** provides only marginal enhancement of ΔE_{S-T}.

The tautomeric effects in the nitrogen and phosphorus series are analogous to those in the carbon and silicon. The singlet ground states of **3a** and **3c** are of lower energy than both the ground, triplet, and the singlet states of **1d** and **1k**. Therefore, these systems are capable of tautomerization from **1d** and **1k** to **3a** and **3c**.[20] We also predict similar tautomeric effects in **1g** and **1n**.

Analysis of charge redistribution upon the change of multiplicity (Figure 2) shows that the signs of the charge changes in **1** are the same as those in **2** at corresponding atoms. However, the observed trends of charge redistribution in **1** are opposite to those found in **2**. The calculations predict that in **1** atoms C2 and X become more negative in the triplet state while C3 and C6 are more positive. The changes at C4, C5, and C7 are similar to those at C2, X, and C6, respectively, even though these pairs

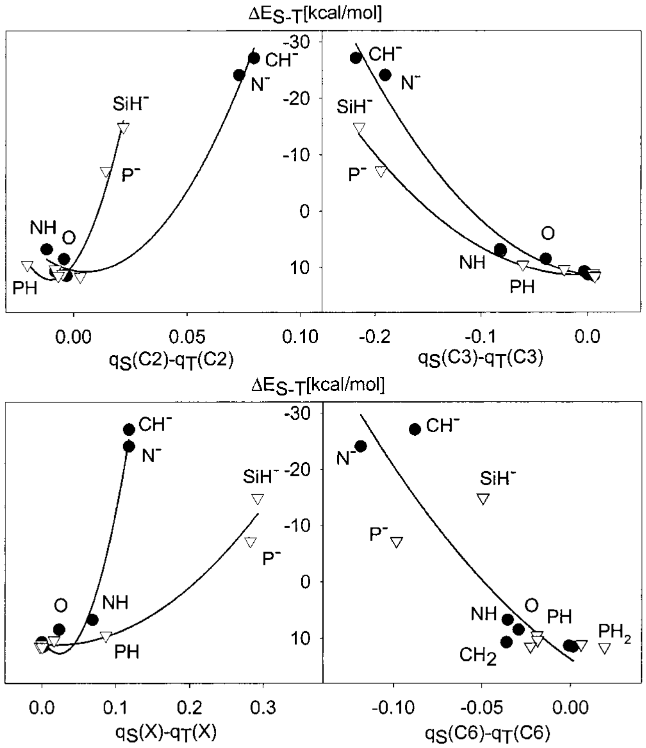

Figure 2. Lowdin charge redistribution upon change of the state multiplicity for representative sites in **1**.

are not related by symmetry as in **2**.[21] The trends of the changes in charge redistribution within **1** have slopes opposite to those found in **2**. The differences in localized charge between singlet and triplet states become less pronounced with the triplet state becoming more stable relative to the singlet, and in limiting cases these differences approach zero. A possible explanation of the difference in trends lies in the reversed polarization of the molecule, as the heteroatom in **1** is located on the opposite side of the ring. This reversed polarization is closer to the stereoelectronic demand of the triplet state, thus stabilizing it relative to the singlet. High group electronegativity of X disallows charge redistribution in the singlet state increasing its energy.

Trilevel protonation in the nitrogen and phosphorus series provides the capability for changing the character of the system from FC to AFC. Developers of materials based on these FCs must be mindful of the role that tautomerism plays in modulating the singlet−triplet gap. In **1**, the ΔE_{S-T} is controlled by group electronegativity of X, and its effect is opposite to that found in **2**. The progress in ΔE_{S-T} suggests a limit of electronic coupling at about 12 kcal/mol.

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Supporting Information Available: CASSCF-optimized Cartesian coordinates, energies, and Lowdin charges for all reported structures with charts of ΔE_{S-T} vs charge redistribution for all heavy atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) While the comparison of ΔE_{S-T} is acceptable, at this junction we cannot comment on the exact effect on individual states as the size of the active space of the MCSCF calculations is not consistent (eight electrons on seven orbitals for **1a** and **1h** vs six electrons on six orbitals for **1b** and **1i**).

(20) The quantitative comparison of the absolute energies of **1d** and **3a**, and **1k** and **3c,** has to be treated with caution because the active spaces in the respective pairs of compounds are different (eight electrons and seven orbitals for **1d** and **1k**, six electrons and six orbitals for **3a** and **3c**). We do not expect qualitative changes in the order of state energies.

(21) The full list of Lowdin charges is included in the Supporting Information.