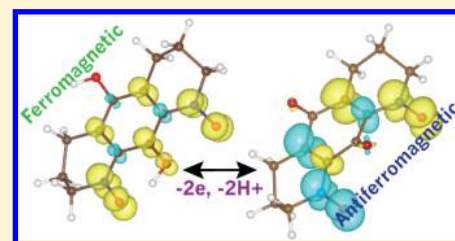


Designing the Redox-Driven Switching of Ferro- to Antiferromagnetic Couplings in Organic Diradicals

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Supporting Information

ABSTRACT: Switching of the magnetic exchange coupling from ferro- to antiferromagnetic or *vice versa* in a single molecule is an appealing but rarely occurring phenomenon in molecular magnetism. Here, we report this for an unprecedented pure organic system, computationally designed by tailoring a conformationally restricted, known nitroxide-diradical (Rajca et al. *J. Am. Chem. Soc.* **2007**, *129*, 10159). This ferro- to antiferromagnetic coupling switching of an “m-phenylene” based diradical is governed by a stereoelectronic effect and controlled by a redox-driven chemical reaction.



Functionalized organic materials have a proven track record in molecular electronics and optoelectronics applications.^{1–4} The current endeavors are to functionalize organic molecular materials by exploiting the spin of the electrons residing in the singly occupied molecular orbitals (SOMOs).^{5,6} The spin of electrons in p-type orbitals of organic radicals is responsible for the magnetic properties in the organic substances.⁵ Such materials could potentially replace the traditional transition metals or rare-earth based atomistic magnetic materials in numerous technological applications.^{6,7} However, obtaining stable organic radicals having ferromagnetic ordering at elevated temperatures is the major challenge in the field.⁷ The discovery of room-temperature ferromagnetic ordering in the stable organic radical solids has added momentum to the research on pure organic molecular magnetism.⁸ Since this discovery, various stable radicals have been synthesized and extensively investigated.^{9–12}

The “m-phenylene” based coupler placed between two radical spin sources triggers a ferromagnetic interaction.^{13,14} This intramolecular magnetic coupling is controlled by several factors such as rotational conformations of the spin sources, spin-delocalization, spin-polarization, aromaticity of the phenyl ring, etc.^{15–18} Various theoretical studies have helped us in understanding and predicting several new diradical systems with strong ferromagnetic character.^{19–21} Apart from continuing development aimed at obtaining enhanced ferromagnetic coupling, the switching of the magnetic properties in a single molecule is another desired phenomenon that promises a potential usefulness in logic devices based on these materials.^{22–25} The switching phenomenon in pure organic systems has been mainly targeted by photoinduced chromophoric systems^{26–30} and temperature-induced,³¹ proton-induced,^{32,33} and reversible cycling chemical reactions.³⁴ A redox-induced spin-crossover for metallo organic systems has

been reported recently.³⁵ However, there is no definite report in the literature about switching the magnetic exchange interactions from ferro- to antiferromagnetic exchange coupling or *vice versa* in metal-free systems.

In this work, we design a redox-driven pure organic magnetic switch that alters the ferromagnetic exchange coupling of an “m-phenylene” based compound to an antiferromagnetic exchange interaction. To study the possibility that such a phenomenon occurs, we have investigated computationally a conformationally restricted nitroso-m-phenylene-nitroso diradical (**1a**, Figure 1). As a proof of concept, we note that a very similar compound has been synthesized by Rajca et al.^{36,37} In the present study, an “m-phenylene” coupler has been tailored by substituting two H atoms at the 2 and 5 positions of the phenylene ring of the coupler by two hydroxyl (–OH) groups.

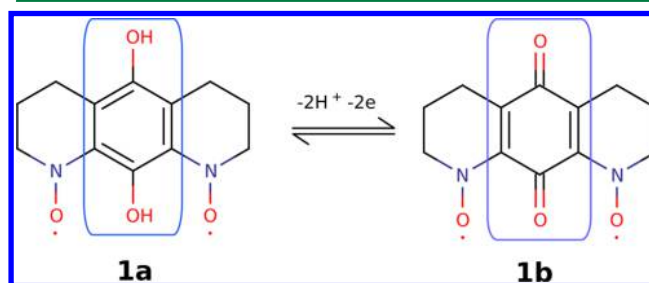


Figure 1. Schematic diagram of redox-induced changes for nitroxide-based, spin-bearing radicals. The molecule within the blue boxes indicates the redox active units. The moiety inside the blue box in **1a** is known as hydroquinone, H₂Q. Similarly, the moiety in **1b** is known as quinone, Q.

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The purpose of this tailoring is to make the phenyl coupler similar to the famous hydroquinone (H2Q) molecule. The latter undergoes a two electron oxidation process to benzoquinone (Q). This oxidation reaction is known to occur reversibly or irreversibly depending on the reaction medium.³⁸ Here, we report that the conformationally restricted nitro-oxide diradicals of the coupler **H2Q** (**1a**) have a strong ferromagnetic coupling, whereas they show a strong anti-ferromagnetic coupling once the moiety is oxidized to the benzoquinone coupler (**1b**).

The molecular geometries of **1a** and **1b** are optimized at the UB3LYP/6-311+G(d,p) level for high-spin (HS) as well as for broken-symmetry (BS) states representing the open-shell singlet. The HS is found to be the ground state for **1a**, and BS is the ground state for **1b**. The lowest potential energy surface (PES) in the geometry optimization for **1a** is found to be always HS, whereas for **1b** the BS state provides the lowest PES. In subsequent magnetic property calculations, the corresponding ground state geometries are used.

Applying Noodleman's broken-symmetry DFT approach,^{39,40} in the strong-localization (weak overlap) limit that could be established by corresponding orbital transformation,⁴¹ the magnetic exchange interactions ($2J$ or ΔE_{S-T}) calculated for **1a** and **1b** are 1202 and -1127 cm^{-1} , respectively. Note that equating $2J$ to ΔE_{S-T} is just a convention and does not imply any assumption regarding the type of magnetic centers. Nevertheless, in the forthcoming discussion, we will provide evidence that the magnetic orbitals are reasonably localized in the NO domains. This means that a strong ferromagnetic interaction is predicted for **1a**, while an equally strong but antiferromagnetic interaction is obtained for **1b**. *These initial results indicate a very special redox-induced magnetic switch, which is associated with significant changes in the magnetic interaction in the ferro- ($S = 1$) to antiferromagnetic ($S = 0$) transition.*

Experimentally, Rajca et al. measured the magnetic exchange coupling constant of the parent compound without any $-\text{OH}$ substitution in the phenyl ring, which is similar to **1a**, and reported $2J \geq 208.5\text{ cm}^{-1}$.^{36,37} In our previous studies, we have noticed that most density functionals (including UB3LYP) overestimate the exchange coupling of the parent diradical by a factor of 2–3.^{42,43} This is not surprising since the magnitude of $2J$ calculated in the BS-DFT approach always strongly depends on the applied functionals although the sign and trends are usually well reproduced.^{44,45} This overestimation is caused by the fact that the unpaired electrons are delocalized beyond the spatial regions of $-\text{NO}^\bullet$ groups and extend over the π -conjugated space. The origin of this problem is the inherent self-interaction error (SIE) in DFT. Hybrid functionals reduce the SIE to some extent; however, they are not completely free from it, and the extent of SIE reduction depends on the applied functional as well as on the molecular topology. In order to confirm the remarkable switching phenomenon predicted from the UB3LYP calculations, we have further applied several wave function based methods. The results are summarized in Table 1. The SCF-type results (ROHF for triplet states, CAS-SCF(2,2) for the singlets) show already the remarkable difference in the magnetic coupling in **1a** and **1b**. It is more pronounced in the sophisticated MR-CI method that accounts for dynamical and nondynamic electron correlations in a systematic manner.^{46–48} Though these calculations predict much smaller values for the magnetic exchange coupling constants for the **H2Q** and **Q**

Table 1. Calculated Magnetic Exchange Coupling Constants for **1a** and **1b**

methods	basis sets	$2J\text{ (cm}^{-1}\text{)}$	
		1a	1b
UB3LYP	6-311+G(d,p)	1202	-1127
CAS-SCF(2,2)	VTZD	205	-71
CAS-SCF(2,2)	VSZDDF	232	-83
MR-CI	VSZDDF	198	-196

couplers, they definitely confirm the switching phenomenon as predicted from the UB3LYP calculations.

The molecular geometry optimization calculations show that one of the nitro-oxide radicals in **1a** is coplanar with the m -phenylene coupler. The dihedral angle between the two $-\text{NO}^\bullet$ radicals with the plane of the phenylene ring are 2° and 30° , respectively. The reason for such asymmetric dihedral angles is the formation of a hydrogen bond between an $-\text{OH}$ and one of the $-\text{NO}^\bullet$ groups. This provides an extra six membered cyclic structure, which increases the coplanarity of the associated $-\text{NO}^\bullet$ group with the coupler, whereas the bare (non-hydrogen bonded) NO has slightly lifted from the plane of the coupler (see **1a** in Figure 2)

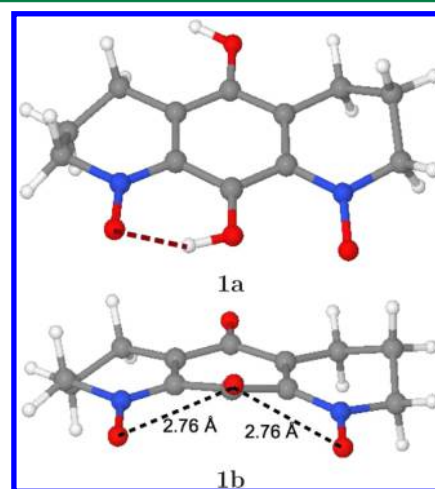


Figure 2. Ball-and-stick model for the optimized geometries of **1a** and **1b**. White spheres denote H atoms; gray, C atoms; blue, N atoms; and red, O atoms.

Consequently, the magnetic exchange interaction in **1a** is expectedly ferromagnetic, and this is confirmed by the calculations. This also corresponds to the general spin-topology rule⁴⁹ and is in agreement with the experimentally observed ferromagnetic exchange interaction of the parent compound without any $-\text{OH}$ substitution in the central phenyl ring.

Why does the exchange interaction switch to antiferromagnetic for moiety **1b**? Upon two electron oxidation, enol to keto conversion occurs within the coupler. This removes the aromaticity of the coupler in **1b** and removes the coplanarity of the nitroxide–phenylene–nitroxide moieties. This is further assisted by the absence of any hydrogen-bond supported coplanarity as in **1a**. This structural change breaks the extended conjugation of the radical electron containing SOMOs as seen in Figure 3. The broken-conjugation indeed alters the spin-interaction pathway which, to a large extent, dominates the coupling.⁵⁰ In this situation, one would expect a very weak magnetic interaction or even no interaction at all between the

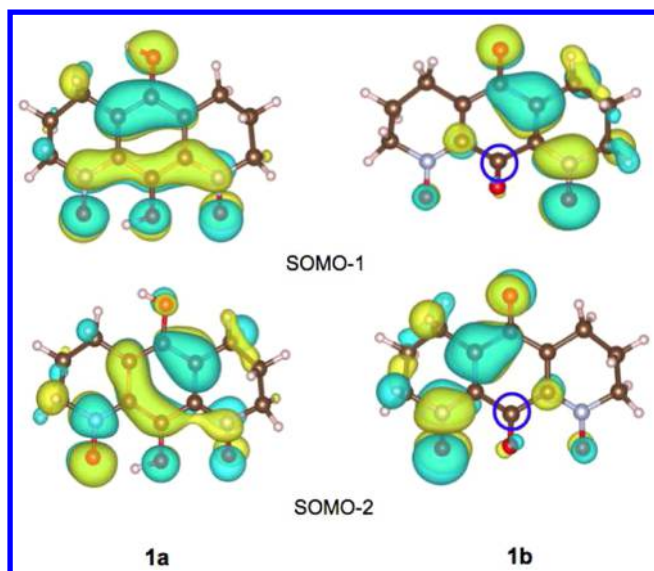


Figure 3. The SOMO-1 and SOMO-2 of **1a** and **1b** in the ground state. The non spin-polarized carbon atom (marked in blue circle) disjoining the SOMOs is responsible for the spin alternation.

two radical centers. Hence, the strong antiferromagnetic exchange interaction predicted for **1b** is quite unexpected. To obtain insight into this interesting result, we have investigated several similar systems of the type $R-H_2Q-R$ and $R-Q-R$, where R = nitronyl–nitroxide (NN), imino–nitroxide (IN), and oxy-verdazyle (o-Ver) radicals. The calculated magnetic exchange interactions evaluated at the UB3LYP level switch from 9.03 to -0.44 , 35.35 to 4.15, and 57.56 to 1.92 cm^{-1} for enol to keto, respectively, for the above-mentioned species. While the B3LYP values may not be accurate enough, the emerging trend is very clear, and one can safely state that, in these cases, no substantial conversion of ferro- to antiferromagnetic exchange occurs, which leaves **1b** as a special and, so far, unique case.

To understand the unique features of **1b**, we analyzed in detail the electrostatic potential (ESP) of both **1a** and **1b** and found that the molecular topology of the latter is strongly influenced by the electrostatic interactions between the oxygen atoms. A strong repulsive potential develops between the oxygen atoms of the keto and $-NO$ groups. This is easily recognized in the calculated ESP iso-surface reported in Figure 4.

The electrostatic interactions also contributed to destroy the π -conjugation in the coupler and enforce the two almost degenerate SOMOs of **1a** to become disjoint at one of the keto-C atoms in **1b** (see Figure 3). This localizes the unpaired α - and β -spin electrons separately on each side of the molecular C_2 axis, which results in a partial lifting of the near degeneracy of the two SOMOs. Hence, the exchange interaction mechanism works in **1b** in a manner different from that in **1a**. In **1a**, the through bond, π -conjugation plays a major role for the magnetic coupling, whereas in **1b** a through space magnetic interaction dominates which is mediated by the strong repulsive electrostatic forces. Therefore, this through space interaction is responsible for the strong antiferromagnetic interaction in **1b**.

Thus, the switching of the magnetic exchange interaction from **1a** to **1b** is mechanistically understood. However, its device applications require further work especially to under-

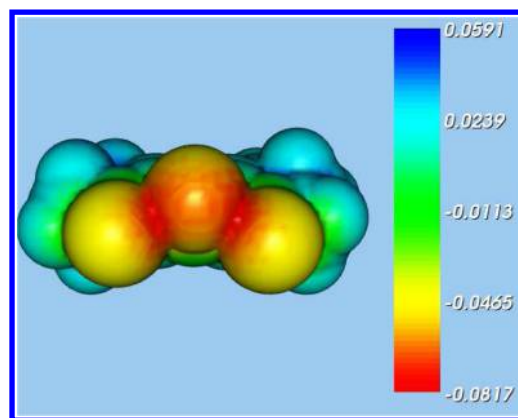


Figure 4. Isosurface of electrostatic potentials computed from the B3LYP electron density of **1b**. A large negative potential (red) develops between the oxygen atoms.

stand fabrication of these *concept molecules* using appropriate polymeric anchor or spin-trapping methods in solution or solid-solution matrix. In the spin-trapped solution matrix, **1a** could store magnetic information as an “ON” state at the (high-spin) ground state while **1b** could store information as an “OFF” state in the (low spin) ground state. Thus, here, the switching information (fortunately magnetic as well) could be encoded in the two stable thermodynamic states of **1a** and **1b**. However, the fate of these separate thermodynamic states is an issue at the elevated temperature, which requires further studies as well. The operating principle of our proposed switch is somewhat different from the conventional data storage mechanism, where two magnetization states are locked by a potential energy barrier height that is proportional to the square of the total spin and its magnetic anisotropy. To retrieve magnetic information from high-spin molecule **1a**, relaxation dynamics of its magnetization could be used. To obtain further insight into the intramolecular magnetic properties, the zero-field-splitting (ZFS) parameters D and E of **1a** have been calculated. The calculated D and E/D are -0.311 cm^{-1} and 0.208, respectively. The contribution of spin–spin coupling part in D is -0.158 cm^{-1} , while the spin–orbit coupling part is -0.153 cm^{-1} . These contributions are much smaller than the exchange coupling of 198 cm^{-1} as computed with MR-CI, but nonetheless, they will have a stabilizing influence on the spin state.

In conclusion, a redox-driven magnetic switch based on purely organic substances has been predicted where the conversion from ferromagnetic to antiferromagnetic exchange interaction is noticeably large. Moreover, it has been shown that the stereoelectronic effect plays a key role in this switching phenomenon.

■ ASSOCIATED CONTENT

● Supporting Information

Computational methods, optimized structures, total energies for all the species in hydroquinone (H_2Q) as well as in quinone (Q) form. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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