Coupling between Two NO Radicals Linked through Electron-Rich Rings

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Abstract: The characters of coupling between two doublet NO radicals linked through electron-rich rings have been studied. The results demonstrate that the molecules have triplet ground states, and ferromagnetic coupling exists in these molecules.

Keywords: Electron-rich ring, ferromagnetic coupling, NO radical.

Design and synthesis of organic molecules in very high-spin ground states are current subjects of great importance[1-4]. A key to the rational design of these molecules is the ability to control spin-spin coupling of unpaired electrons. One strategy being currently pursued[5] is that a high-spin molecule can be divided into two components: the spin-containing fragment (SC) and the ferromagnetic coupling unit (FC). The SC is simply any structure that provides the unpaired electrons, and the FC is a general structural unit that ferromagnetically couples any two or more SCs. As has been stressed previously[6], FC is the key element in the design of new organic magnetic molecules. In the past years numerous works have devoted to searching FCs[5-9].

Our recent work[10] has demonstrated that the electron-rich rings, furan ring, thiophene ring, or pyrrole ring, can ferromagnetically couple two triplet biradicals, bicarbenes or binitrenes. In this paper we have studied the coupling between two doublet NO radicals linked through the electron-rich rings(**Figure 1a**), and taken further steps to investigate the characters of electron-rich rings as FCs. A series of model molecules are proposed, and depicted in **Figure 1b**. These molecules are composed of two doublet NO radicals (SCs) and one of the electron-rich rings (FCs). To evaluate the effectiveness of the FCs, the singlet-triplet (S-T) energy splittings of the molecules have been calculated at the UHF/6-31G* level.

The interaction of the two SCs can be described by the Heisenberg Model[11]. This spin-only Hamiltonian is defined in terms of the individual spin operaters S_1 and S_2 of

the interacting subunits and a magnetic exchange parameter, J, and can be written as Eq.(1),

$$H=-2J\mathbf{S}_1\bullet\mathbf{S}_2 ,\qquad\qquad(1)$$

where J embodies all of the spatial information of the wavefunction, *i.e*., the through-space and through-bond interactions which actually determine the ground-state spin preference. Representative biradical eigenfunctions are given in Eqs.(2)-(3), and the energies, E_S, of biradical states with spin total angular momentum S are given in Eq. (4) and **Figure. 2**,

$$TW=| 1/2\rangle| 1/2\rangle ,\qquad\qquad(2)$$
$$SW=2^{-1/2}(| 1/2\rangle| -1/2\rangle - | -1/2\rangle| 1/2\rangle) ,\qquad(3)$$
$$E_S=-J[S(S+1)-3/2] ,\qquad\qquad(4)$$

where TW and SW are the triplet and singlet wavefunction, respectively. From Eq.(4) we can obtain,

$$\Delta E_{ST}=E_S-E_T=2J\qquad\qquad(5)$$

The sign and the magnitude of J can be determined by using the S-T energy splitting, ΔE_{ST}, so a potential FC can be fully characterized: If $\Delta E_{ST}>0$, then $J>0$, TW is the ground state, and high-spin, or ferromagnetic, coupling occurs; while if $\Delta E_{ST}<0$, then $J<0$, SW is the ground state, and low-spin, or antiferromagnetic, coupling occurs. The energy splitting identifies the strength of the spin coupling through the FC.

Figure 1.a) Design of triplet ground-state biradicals.
b) Schematic representations of model molecules(X=O, S, NH).
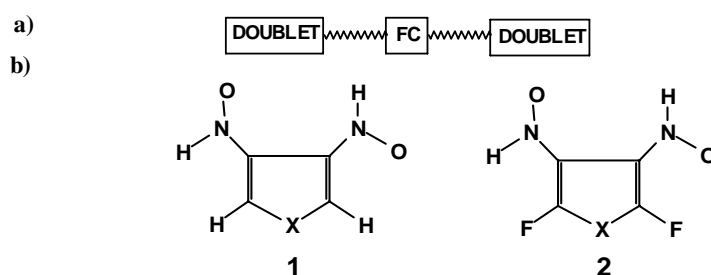
Figure 2. Heisenberg energy level diagrams for two interacting NO radicals.
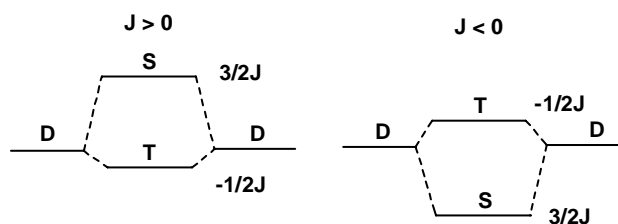
Total energies of the singlet state, E_S, and triplet state, E_T, and the singlet-triplet energy splitting, ΔE_{ST}, have been calculated for these molecules. The results are in **Table 1**.

The singlet-triplet splittings of these molecules are positive, so the ground states are triplet. Ferromagnetic coupling exists in these molecules. Incorporating the coupling between two biradicals, bicarbenes or binitrenes, linked through electron-rich rings, we can find that the electron-rich rings are indeed FCs.

Table 1. Energies(a.u.) and ΔE_{ST}(kJ/mol) of the model molecules

Species		Energy		ΔE_{ST}
		LS(S=0)	HS(S=1)	
X=O	1	-486.9764	-487.0950	311.38
	2	-684.6455	-684.7782	348.40
X=S	1	-809.6581	-809.7646	279.61
	2	-1007.3061	-1007.4298	324.77
X=NH	1	-467.1868	-467.2802	245.22
	2	-664.8471	-664.9593	294.58

The fluorine-substitutions have no influence on the nature of the coupling. This result demonstrates ferromagnetic coupling through electron-rich ring is probably produced by π electrons, and σ electrons play almost no role in the coupling. Energy splittings, ΔE_{ST}, of the fluorine-substitutions are larger than those of their original molecules, so ferromagnetic coupling in the fluorine-substitutions is stronger than in the original molecules.

The results also demonstrate that the spin density of NO radical equals unit, and concentrates almost entirely on atom O, so the unpaired electron on NO radical is localized.

UHF/6-31G* calculations have been performed to determine the character of coupling between two doublet NO radicals linked through the electron-rich rings. Our results suggest that the electron-rich ring is a potential FC. This implies that two SCs can be linked through the electron-rich ring ferromagnetically. This conclusion provides an instructive idea for the design of new organic ferromagnetic molecular materials.

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