937

Ground State Spins of Bicarbenes and Binitrenes, Coupled through Electron-Rich Rings

Hai Quan HU, Yong Jun LIU, Da Cheng FENG, Cheng Bu LIU*

Institute of Theoretical Chemistry, Shandong University, Jinan 250010

Abstract: The ground state spins coupled through electron-rich rings of bicarbenes and binitrenes have been studied at UHF/6-31G* level. The results demonstrate that ferromagnetic coupling exists in these molecules, and electron-rich rings are the potential ferromagnetic coupling units.

Keywords: Electron-rich ring, ferromagnetic coupling, bicarbene, binitrene.

The rational design and synthesis of magnetic organic molecular materials has received much attention in the past few years[1-4]. One strategy being currently pursued[5] is shown schematically in **Figure 1a**. 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], the key element in the design of new organic magnetic molecules is the FC.

In this paper a series of model molecules are proposed. These molecules are composed of two triplet biradicals (SCs), bicarbenes or binitrenes, and one electron-rich ring (FC), furan ring, thiophene ring, or pyrrole ring (**Figure 1b**). To evaluate the effectiveness of the FCs, the singlet-quintet (S-Q) energy splittings of the molecules have been calculated, and the character of the electron-rich rings as FCs has been studied.

The model molecules are depicted in Figure 2. Their geometries have been optimized at the UHF/6-31G* level.

The interaction of the two SCs can be described by the Heisenberg Model7. This spin-only Hamiltonian is defined in terms of the individual spin operaters S1 and S2 of the interacting subunits and a magnetic exchange parameter, J, and can be written as Eq.(1),

$$H = -2J S_1 \cdot S_2 \qquad (1)$$

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 tetraradical eigenfunctions are given in Eqs.(2)-(4), and the

energies, E_S, of tetraradical states with spin total angular momentum S are given in Eq. (5) and **Figure 3**,

$$QW = |1> |1>, \tag{2}$$
$$TW = 2^{-1/2}(|1> |0> - |0> |1>), \tag{3}$$
$$SW = 3^{-1/2}(|1> |-1> - |0> |0> + |-1> |1>), \tag{4}$$
$$E_S = -J[S(S+1)-4], \tag{5}$$

where QW, TW, and SW are the quintet , triplet , and singlet wavefunction, respectively. From Eq.(5) we can obtain,

$$\Delta E_{SQ} = E_S - E_Q = 6J \tag{6}$$

The sign and the magnitude of J can be determined by using the S-Q energy splitting, ΔE_{SQ}, so a potential FC can be fully characterized: If $\Delta E_{SQ} > 0$, then $J > 0$, QW is the ground state, and high-spin, or ferromagnetic, coupling occurs; while if $\Delta E_{SQ} < 0$, 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) Schematic for design of high-spin molecules.

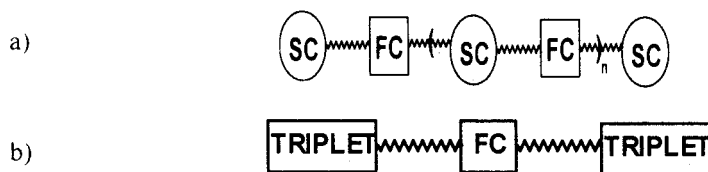b) Design of quintet ground-state tetraradicals.

a)

b)

Figure 2. Schematic representations of model molecules

(X=O, S, NH; Y=H,F).
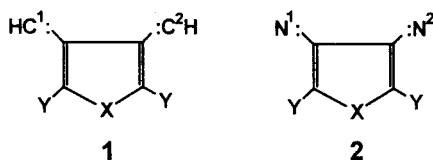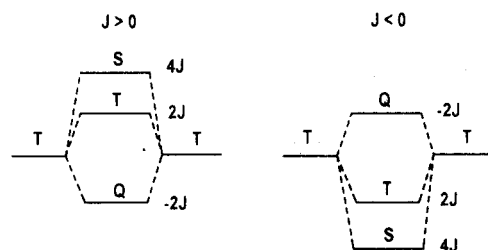

1   **2**

Figure 3. Heisenberg energy level diagrams for two interacting biradicals.

Total energies of the singlet state, E_S, and quintet state, E_Q, and the singlet-quintet energy splitting, ΔE_{SQ}, have been calculated for these molecules. The results are in **Table 1**.

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

Species		Energy		ΔE_{SQ}
		LS(S=0)	HS(S=2)	
X=O,Y=H	1	-304.1234	-304.1974	194.22
	2	-336.0291	-336.2743	643.71
X=S,Y=H	1	-626.7816	-626.8634	214.73
	2	-658.7605	-658.9408	473.37
X=NH,Y=H	1	-284.3153	-284.3742	154.64
	2	-316.3016	-316.4561	405.59
X=O,Y=F	1	-501.7612	-501.8903	338.92
	2	-533.7053	-533.9610	671.28
X=S,Y=F	1	-824.3704	-824.5415	449.17
	2	-856.4423	-856.6119	445.17
X=NH,Y=F	1	-482.0084	-482.0657	150.47
	2	-513.9985	-514.1413	374.98

The singlet-quintet splittings of these molecules are positive, so the ground states are quintet. Ferromagnetic coupling exists in these molecules. The electron-rich rings are indeed FCs. The results also demonstrate that all atoms C^1, C^2, N^1, and N^2 have almost two spin densities, so the two unpaired electrons on biradical are localized.

The fluorine-substitutions have no influence on the nature of the coupling. The result demonstrates ferromagnetic coupling through electron-rich ring is probably produced by π electrons, and σ electrons play almost no role in the coupling.

UHF/6-31G* calculations have been performed to determine the ground state spins coupled through the electron-rich ring of bicarbenes or binitrenes. Our results suggest that the electron-rich ring is the 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.

Acknowledgment

References

1. A.Raja. *Chem.Rev.*, **1994**,*94*,871.
2. O.Kahn. *Molecular Magnetism*.VCH Publisers:Berlin,**1993**.
3. D.A.Dougherty. *Acc.Chem.Res.*, **1991**,*24*,88.
4. L.Ducasse,A.Fritsch, *Chem.Phys.Lett.*, **1998**,*286*,183.
5. S.J.Jacobs,D.A.Shultz,R.Jain,J.Novak,D.A.Dougherty,
   J.Am.Chem.Soc.,**1993**,*115*,1744.
6. S.K.Silverman,D.A.Dougherty,*J.Phys.Chem.*,**1993**,*97*,13273.
7. K.Itoh. *Pure Appl.Chem.*,**1978**,*50*,1251.