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Orbital Phase Continuity Requirements in Triplet States

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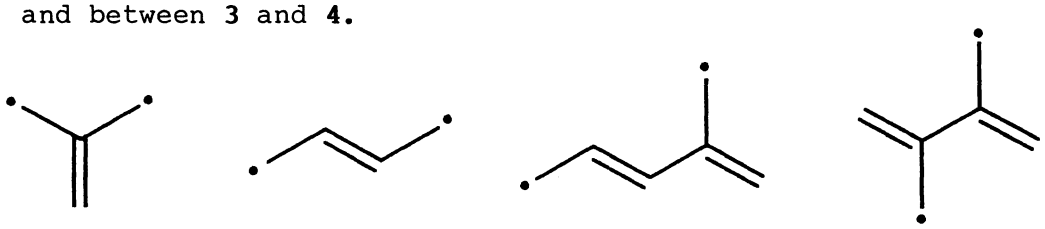
Orbital phase continuity requirements were derived for stabilizing triplet states, and successfully applied to acyclic conjugated diradicals.

Triplet states of molecules are important intermediates in photochemical processes.[1] Triplet diradicals receive an increasing interest as prototypes of high-spin molecules for molecular based magnetic materials.[2] In this letter we will present an orbital phase theory for the stabilities of triplet states and apply it to some conjugated diradicals **1-4**.

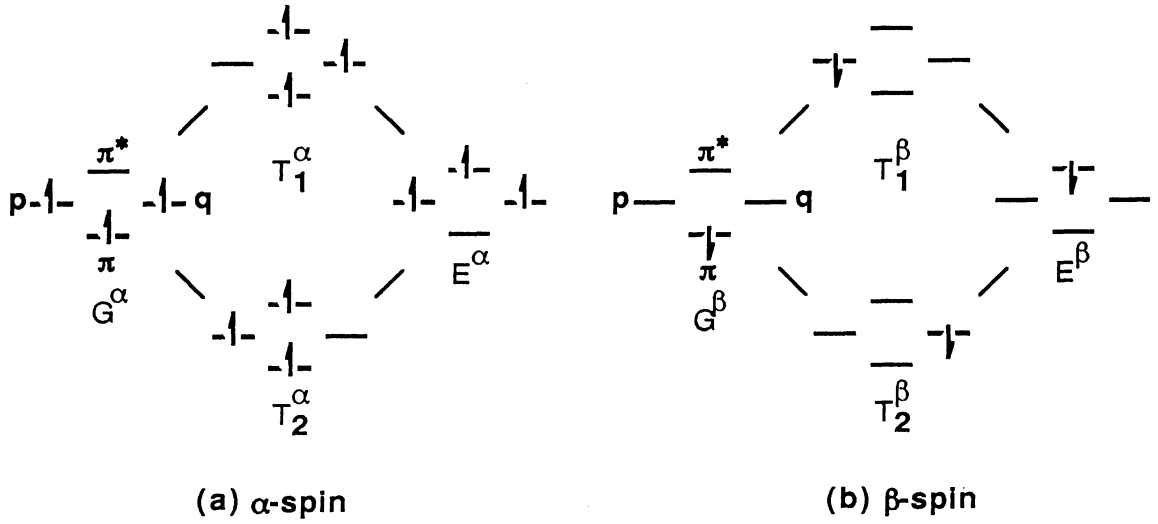
In **1-4**, two radical centers do not effectively interact with each other, but with an intervening conjugated coupler. The coupler is an ethylene unit in **1** and **2**, and a butadiene unit in **3** and **4**. The modes of connection of the radical centers and the couplers are different between **1** and **2**, and between **3** and **4**.



1 **2** **3** **4**

The mechanism of electron delocalization and polarization is illustrated in Scheme 1. An α-spin electron occupies each of the radical orbitals, p and q, and the HOMO (π) of the coupler in the ground configuration (G^{α}). The electron in one of the radical centers (p) shifts to the LUMO (π^*) of the coupler through the interaction of G^{α} and the transferred configuration (T_1^{α}). The G^{α}-T_1^{α} interaction is approximated to the p-π^* interaction. The resulting electron hole in the radical center p is supplied with an electron from π of the coupler through the interaction

of T_1^{α} and the locally-excited configuration (E^{α}), or the π-p interaction. The π-p-π* interaction is involved in the delocalization-polarization process. There is another process involving the G^{α}-T_2^{α}-E^{α} or π-q-π* interaction. As a result, cyclic $[G^{\alpha}\text{-}T_1^{\alpha}\text{-}E^{\alpha}\text{-}T_2^{\alpha}]$ or $[\pi\text{-}p\text{-}\pi^*\text{-}q]$ interaction occurs.



Scheme 1.

For effective occurrence of the cyclic interaction, simultaneous bonding properties are required between any pair of configurations:

$$S(G^{\alpha},T_1^{\alpha})S(T_1^{\alpha},E^{\alpha})S(E^{\alpha},T_2^{\alpha})S(T_2^{\alpha},G^{\alpha}) > 0 \qquad (1)$$

where S is an overlap integral between configurations. The inequality is rewritten as

$$s(p,\pi^*)s(\pi,p)s(q,\pi^*)s(\pi,q) > 0 \qquad (2)$$

where s denotes orbital overlap integral.

Delocalization-polarization mechanism of β-electrons is shown in Scheme 1b. An electron shifts from π to p through the G^{β}-T_1^{β} or π-p interaction. The electron then shifts to π* through the T_1^{β}-E^{β} or p-π* interaction. The G^{β}-T_1^{β}-E^{β} or π-p-π* interaction is involved. The other process involves the G^{β}-T_2^{β}-E^{β} interaction or the π-q-π* interaction. The cyclic $[G^{\beta}\text{-}T_1^{\beta}\text{-}E^{\beta}\text{-}T_2^{\beta}]$ or $[\pi\text{-}p\text{-}\pi^*\text{-}q]$ interaction similarly occurs in the β-spin delocalization-polarization process. The same inequality (2) was obtained.

The inequality requirements can be easily seen to be equivalent to simultaneous satisfaction of the orbital phase continuity conditions: 1) the electron donating orbitals out of phase; 2) the accepting orbitals in phase; 3) the donating and accepting orbitals in phase. The p and q orbitals at the radical centers are the donating orbitals for α-spin and the accepting orbitals for β-spin. The phase conditions are essentially the same as those for cyclic[3] and acyclic[4] closed-shell molecules.

The diradicals **1** and **3** meet the phase requirements in both spin spaces. The orbital phase is continuous. This is not the case with their isomers, **2** and **4**. The phase is discontinuous. Consequently, triplet states of **1** and **3** are thermodynamically stable relative to **2** and **4**, respectively. This agrees with known relative stabilities found in literatures.[5]

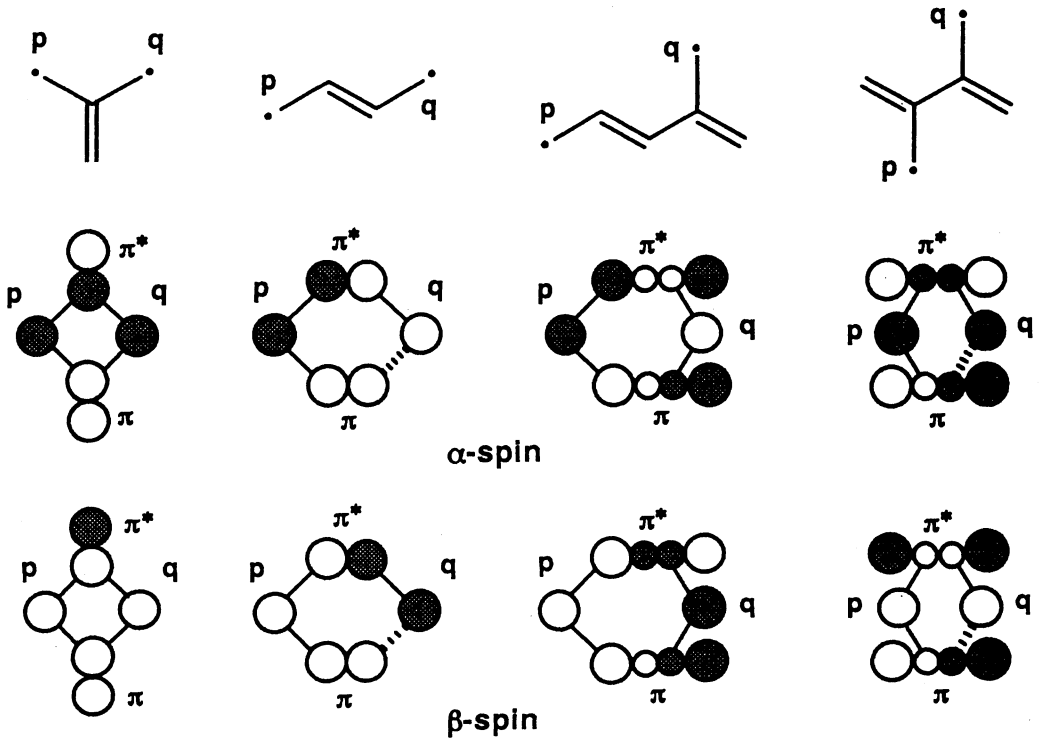


Table 1. Coefficient Ratios of Locally-Excited and Electron-Transferred Configurations to the Ground Configuration

Triplet diradical	E^{α}	T_1^{α}	T_2^{α}	E^{β}	T_1^{β}	T_2^{β}
1	0.49	0.25	0.25	0.50	0.25	0.25
2	0.0	0.15	0.15	0.0	0.13	0.13
3	0.62	0.30	0.17	0.60	0.30	0.17
4	0.0	0.26	0.26	0.0	0.27	0.27

We carried out ab initio UHF calculations[6] on the triplet states of these diradicals. The total wave functions were subjected to the open-shell configuration analysis. The results (Table 1) supported the orbital phase predictions. Contributions of the local-excitation of both spins are significant in **1** (0.49 for E^{α} and 0.50 for E^{β}), whereas absent in **2**. Electron delocalization or mixing of the transferred configurations also prefers **1** (0.25 for both spins) to **2** (0.15 for α and 0.13 for β-spin). This is understood as the results of the orbital phase continuity (**1**) and discontinuity (**2**). The effect of the orbital phase is outstanding in the polarization rather than the delocalization. There are great contributions from the polarization in **3**, but not at all in **4**. This is also understood due to the continuity (**3**) and discontinuity (**4**) of orbital phase.

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