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MOLECULAR ORBITAL (MO) THEORY FOR MAGNETICALLY INTERACTING ORGANIC COMPOUNDS. AB-INITIO MO CALCULATIONS OF THE EFFECTIVE EXCHANGE INTEGRALS FOR CYCLOPHANE-TYPE CARBENE DIMERS

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A generalized molecular orbital (GMO) theory for magnetically interacting organic compounds has been presented. The theory is applied to the calculations of the effective exchange integrals (Jab) for the cyclophane-type carbene dimers whose para and ortho-isomers have the high-spin ground state. The calculated Jab-values are consistent with observations.

Designing of high-spin (HS) molecules has been accepting continuing interest in relation to the syntheses of organic magnetic materials such as organic ferromagnets.[1-9] Recently, Iwamura and his collaborators[9] have synthesized the cyclophane-type diphenyl carbene dimers (I) illustrated in Fig.1. The ground state of the para (Ip) and ortho (Io) dimers was found to be quintet, while the meta (Im) dimer was to be singlet. Iwamura and his collaborators have successfully interpreted the observed trends on the basis of McConnell's model[1] which describes the spin-density-product (SDP) type interactions between the face-to-face radicals. However, the magnitudes of the effective exchange integrals (Jab) still remained unknown. We wish to present a generalized molecular orbital (GMO) theory for magnetically exchange-interacting organic molecules, to calculate the Jab-values for these species.

The exchange coupling between localized spins in molecular systems can be described by the total spin form of the Heisenberg (HB) Hamiltonian[1-12]

$$\mathbf{H}(\mathrm{HB}) = -2 \sum_{a>b} \mathrm{Jab}\ \mathbf{Sa}\cdot\mathbf{Sb} \qquad (1)$$

where Jab is the effective exchange integral between the radical sites with total spin operators **Sa** and **Sb**. The exchange split energy levels for the dimers are therefore given by

$$^{2i+1}\mathrm{E}(\mathrm{HB}) = -\mathrm{Jab}\,[\, i(i+1) - \mathrm{Sa}(\mathrm{Sa}+1) - \mathrm{Sb}(\mathrm{Sb}+1)\,] \qquad (2)$$

where Sa and Sb are the magnitudes of spins **Sa** and **Sb**, respectively, and where i is the magnitude of the total spin operators **S** of the systems.

$$i = (\mathrm{Sa}-\mathrm{Sb}),\ (\mathrm{Sa}-\mathrm{Sb})+1,\ \ldots,(\mathrm{Sa}+\mathrm{Sb}) \qquad (3)$$

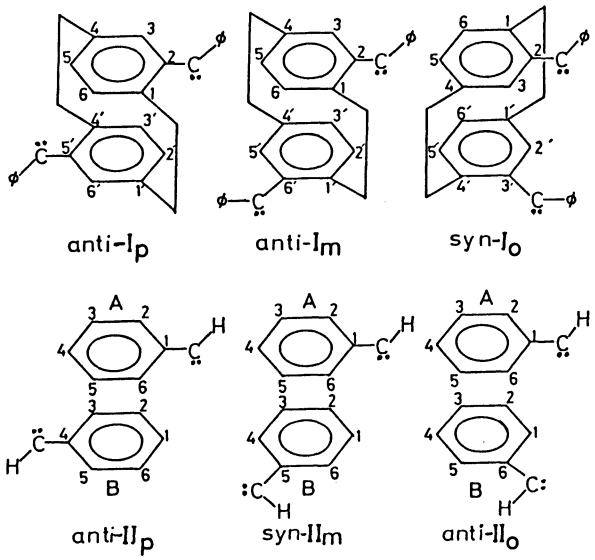

Fig. 1. Molecular structures of cyclophane-type diphenylcarbene dimers (Ip-Io) in Ref. 9, where p, m, and o denote the para-, meta-, and ortho-dimers, respectively. IIp, IIm, and IIo are stacked phenylcarbene dimers at the intermolecular distance 3 Å. II is taken as a model of I.

in which we set Sa = n/2 + m and Sb = n/2 so that i = m, m+1, ..., (m+n). The Jab-value has hitherto been regarded as an empirical parameter which is to be determined so as to reproduce the magnetic properties of molecules and molecular assemblies.

Here we attempt to calculate the effective exchange integral within the ab-initio symmetry-projected unrestricted Hartree-Fock (PUHF) approximation. To this end, the singlet state (m=0) is first examined. The UHF molecular orbitals for the singlet ground state of magnetic species[1-9] are generally given by[13-15]

$$\psi_n^{\pm} = \cos\theta_n \, \phi_n \pm \sin\theta_n \, \phi_n^* \quad (n=1,2, \ldots) \tag{4}$$

where ϕ_n and ϕ_n^* denote the n-th bonding and antibonding approximate natural orbitals. Then, the singlet UHF solution is described by a superposition of the (n+1) PUHF solutions[15] as

$$^1\Psi(\mathrm{UHF}) = |\psi_1^+\bar{\psi}_1^-\psi_2^+\bar{\psi}_2^- \cdots \psi_n^+\bar{\psi}_n^-| = \sum_{i=0}^{n} C(2i+1) \; ^{2i+1}\Phi(\mathrm{PUHF}) \tag{5}$$

where $C(2i+1)$ and $^{2i+1}\Phi(\mathrm{PUHF})$ denote the expansion coefficient and wavefunction, respectively, for the spin eigenstate (2i+1). The total energy and total spin eigenvalue of the UHF solution can be rewritten with those of the (n+1) PUHF solutions as

$$^1E(\mathrm{UHF}) = \sum_{i=0}^{n} C^2(2i+1) \; ^{2n+1}E(\mathrm{PUHF}), \tag{6a}$$

$$^1\langle\hat{S}^2\rangle\,(\mathrm{UHF}) = \sum_{i=0}^{n} C^2(2i+1)\, i(i+1), \tag{6b}$$

where

$$\sum_{i=0}^{n} C^2(2i+1) = 1. \tag{6c}$$

The spin contamination is negligible for the highest spin state (2n+1) since

$$^{2n+1}E(\mathrm{UHF}) \cong {}^{2n+1}E(\mathrm{PUHF}), \tag{7a}$$

$$^{2n+1}\langle\hat{S}^2\rangle\,(\mathrm{UHF}) \cong {}^{2n+1}\langle\hat{S}^2\rangle\,(\mathrm{PUHF}). \tag{7b}$$

In order to calculate the Jab-value, the ^{1}UHF (Eq. 6a) and $^{2n+1}$UHF (Eq. 7a) energy levels are formally rewritten by using the HB energy levels given by Eq. 2

$$^{1}E(UHF) = \sum_{i=0}^{n} C^{2}(2i+1)\{ -Jab [i(i+1) - 2(n/2)(n/2+1)] \}$$
$$= - Jab\ ^{1}\langle \hat{S}^{2} \rangle (UHF) + Jab\ n(n/2+1), \quad (8a)$$

$$^{2n+1}E(UHF) = - Jab\ n(n+1) + Jab\ n(n/2+1). \quad (8b)$$

The effective exchange integral Jab is then obtained from Eqs. 8a and 8b as

$$Jab = [\ ^{1}E(UHF) - ^{2n+1}E(UHF)\ ] / [\ n(n+1) - ^{1}\langle \hat{S}^{2} \rangle (UHF)\ ]. \quad (9a)$$

The Jab value by the PUHF solution can thus simply be calculated from the total energies of the highest spin (HS) and singlet (i=0) UHF solution themselves.

The GMO (PUHF) plus HB model can be applied to general open-shell systems. The effective exchange integral Jab for the system is similarly calculated from the difference between the total energies of the highest (HS=2(m+n)+1) and lowest (LS=2m+1) spin states as

$$Jab = [\ ^{LS}E(X) - ^{HS}E(X)\ ] / [\ ^{HS}\langle \hat{S}^{2} \rangle (X) - ^{LS}\langle \hat{S}^{2} \rangle (X)\ ] \ (X=PUHF, MR\text{-}CI) \quad (9b)$$

where the spin contamination effects for the LS state have been ignored just as in the case of the singlet state. Equations 9a and 9b are applicable to beyond-HF theories such as the multireference (MR) CI[16] and the Møller-Plesset perturbation theories,[17] both of which involve the dynamical correlation correction to the PUHF solution.

The above theory has been applied to cyclophane-type carbene dimer models (II) shown in Fig. 1. The STO-3G basis set was used for calculation. Table 1 summarizes the Jab-values obtained for the model systems in the ground and locally excited (*) states. Figure 2 illustrates the AO coefficients of the up-spin HOMO for the para-dimer IIp.

From Table 1 and Fig. 2 three conclusions can be drawn as follows:

Table 1. Effective exchange integrals (cm^{-1}) for stacked phenyl carbenes calculated by the GMO (STO-3G) method

System[a]	Sa	Sb	Conf.[b]	Jab
IIp	1	1	anti	288.9
IIm	1	1	syn	-297.0
IIp*	2	1	anti	5.57
IIm*	2	1	syn	-15.8

a) *; $\pi\pi^{*}$-excited state. b) Conformation of the upper and lower carbene groups (Fig. 1).

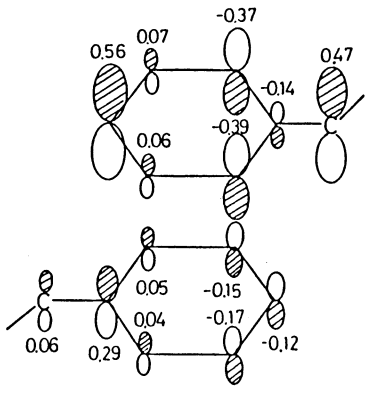

Fig. 2. AO coefficients of the up-spin highest occupied MO (HOMO) of IIp.

(1) The HS state is the ground state for the para (IIp) dimer, while for the meta (IIm) dimer the LS state is the ground state. The calculated results are compatible with the experimental results for cyclophane-type diphenyl carbene dimers (Ip and Im).[9] This indicates that the face-to-face interaction between the benzene rings determines the Jab values.

(2) The above tendency for the relative stabilities of the LS and HS states remains true also for the locally excited (*) states of II, which are constructed of the $\pi\pi^*$ excited quintet (Sa=2) and ground triplet (Sb=1) phenyl carbenes.

(3) The π-magnetic up-spin electron of one (A) of the triplet phenyl carbenes is significantly delocalized over the other (B), indicating a charge transfer (CT) from A to B. Obviously the reverse delocalization of down-spin electrons from B to A is also operative. These are responsible for the orbital-overlap term,[11] which favors the LS ground state over the HS one even in the HS dimer IIp (Ip).

The GMO results indicate that the HS exchange coupling is significant in the ortho- and para-phenyl carbene dimers II without the polymethylene bridges which are crucial for the geometry fixation in the case of the dimer I. The sign of Jab is thus sensitive to the stacking mode of the phenyl groups. This in turn suggests that HS dimers or clusters can be formed if the stacking of diphenyl carbenes in the solid state are adequately controlled by the Langumuir-Blodgett method.[18]

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