Three-Dimensional Through-Space/Through-Bond Delocalization in Cyclophane Systems: A Molecule-In-Molecule approach

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Supporting Information

**Monomer Wave Functions,
Matrix elements (Table)**

Monomer Wave Functions

The molecular orbitals of the a fragment are written as the linear combination of atomic orbitals (LCAO)

$$\phi_n = \sum_p c_{n,p} \chi_p, \tag{2}$$

where the basis function χ_p is taken to be the p_z atomic orbital on the atom p. The LCAO coefficients $c_{n,p}$ are obtained by solving the restricted Hartree-Fock equation, given by

$$\mathbf{F} c_n = E_n c_n, \tag{3}$$

where $\mathbf{F}$ is the Fock matrix and E_n is the energy of the n-th molecular orbital. The matrix element of the Fock matrix for the Pariser-Parr-Pople Hamiltonian is given by

$$\mathbf{F}_{p,p} = \alpha_{p,p} + (1/2)\gamma_{p,p} P_{p,p} - \sum_{q \neq p} (\gamma_{p,q} q_q - P_{q,q} \gamma_{p,q}), \tag{4a}$$

$$\mathbf{F}_{p,q} = \beta_{p,q} - (1/2)\gamma_{p,q} P_{p,q}, \tag{4b}$$

where the core integral $\alpha_{p,p}$ is the negative value of the valence state ionization potential of the atom p and the $\beta_{p,q}$ the resonance integral between the p_z orbitals on atoms p and q. The $P_{p,q} = 2\sum_n c_{n,p} c_{n,q}$ gives the mobile bond order between atom p and q and $\gamma_{p,q}$ is the electron-electron repulsion integral. The non-nearest-neighbor interactions are taken into account in the PPP model. The $\alpha_{p,p}$, $\beta_{p,q}$ and $\gamma_{p,q}$ integrals can be estimated by semiempirical parameterization shown below. The core integral $\alpha_{p,p}$ can be evaluated by the Slater nuclear charge (z_p) and core charges (ρ_p) according to the semiempirical expression[1]

$$\alpha_{p,p} = -\exp(0.342 z_p + 0.555 \rho_p + 0.758) \tag{5}$$

The resonance integral, $\beta_{p,q}$, can be evaluated by dividing it into σ and π components, defined as:

$$\beta_{p,q} = \beta_\sigma \theta_{z',p} \theta_{z',q} + \beta_\pi (\theta_{x',p} \theta_{x',q} + \theta_{y',p} \theta_{y',q}) \tag{6a}$$

Here $(\theta_{x'p}, \theta_{y'p}, \theta_{z'p})$ and $(\theta_{x'q}, \theta_{y'q}, \theta_{z'q})$ are direction cosine of the p_z orbitals on atoms p and q, with respect to rectangular coordinate system (x', y', z'). The z' axis was defined the axis along the line between atoms p and q. The semiempirical integrals β_π can be evaluated by the Wolfsberg-Helmholtz equation[2]

$$\beta_\pi = KS_{p,q}(\alpha_{p,p} + \alpha_{q,q}) \tag{6b}$$

where K is taken to be 0.460 and $S_{p,q}$ denotes the overlap integral between atoms p and q, the value of $S_{p,q}$ is expressed by an exponential function of the distance $(r_{p,q})$ and the effective nuclear charge (z_r)[1]

$$S_{p,q} = \exp[(-0.1112 r_{p,q} + 0.1339)z_p z_q + (0.0449 r_{p,q} - 0.3759)(z_p + z_q) - 0.8627 r_{p,q} + 2.0631] \tag{6c}$$

and β_σ is evaluated by semiempirical equation

$$\beta_\sigma = \exp(-\varepsilon_\sigma / 2)(-3.546 \times 10^2 \varepsilon_\sigma^4 - 1.418 \times 10^3 \varepsilon_\sigma^3 + 4.255 \times 10^3 \varepsilon_\sigma^2 + 4.255 \times 10^4 \varepsilon_\sigma + 8.512 \times 10^4) \ cm^{-1} \tag{6d}$$

with $\varepsilon_\sigma = 5.385 \ r_{p,q}$/Å. The β_σ is the resonance integral for two end-on p_z orbitals $(z=z')$ which was obtained by fitting observation properties of excimers.[3]

For the electron-electron repulsion integral, $\gamma_{p,p}$, we used the semiempirical expression[1] and $\gamma_{p,q}$ can be evaluated by Mataga-Nishimoto equation[4]

$$\gamma_{p,p} = \exp(0.154 z_p + 0.250 \rho_p + 1.662) \tag{7a}$$

$$\gamma_{p,q} = e^2 / (r_{p,q} + \eta_{p,q}) \tag{7b}$$

where $r_{p,q}$ is the distance between atom p and q and

$$\eta_{p,p} = e^2 / \gamma_{p,p} \tag{7c}$$

$$\eta_{p,q} = 2\eta_{p,p}\eta_{q,q} / (\eta_{p,p} + \eta_{q,q}) \tag{7d}$$

The excited-state wave functions of the fragments are expressed as the linear

combination of the singlet configuration functions corresponding to an excitation from SCF orbital n_1 to n_2 ($^1\psi_N = {}^1\psi_{n1\text{-}n2}$),

$$\Psi_i = \sum_N \xi_{i,N}\, {}^1\psi_N\,. \tag{8}$$

The configuration interaction coefficients, $\xi_{i,N}$, and the excitation energy, ΔE_i, are obtained by solving the following equation

$$A\xi_i = \Delta E_i \xi_i\,, \tag{9a}$$

where the matrix elements of **A** are given by

$$\mathbf{A}_{N,N} = \langle \psi_N | H | \psi_N \rangle - \langle \psi_o | H | \psi_o \rangle = E_{nr} - E_{na} - \langle n_a n_r | n_a n_r \rangle + 2\langle n_a n_r | n_r n_a \rangle \tag{9b}$$

$$\mathbf{A}_{N,M} = \langle \psi_N | H | \psi_M \rangle = 2\langle m_a n_r | m_r n_a \rangle - \langle m_a n_r | n_a m_r \rangle \tag{9c}$$

$$\langle \mu\nu | \lambda\sigma \rangle = \iint \phi_\mu(1)\phi_\nu(2)(1/r_{12})\phi_\lambda(1)\phi_\sigma(2)\,d\tau_1 d\tau_2 \approx \sum_{p,q} C_{\mu,q} C_{\nu,p} C_{\lambda,q} C_{\sigma,p} \gamma_{q,p} \tag{9d}$$

(1) Hida, M. *Dyes and Pigments*. **1995**, *28*, 217.

(2) Wolfsberg-Helmholtz equation

(3) (a) Warshel, A.; Huler, A. *Chem. Phys.* **1974**, *6*, 463. (b) Warshel, A.; Shakked, Z. *J. Am. Chem. Soc.* **1975**, *97*, 5679.

(4) Mataga, N.; Nishimoto, K. Z. *Phys. Chem.* **1957**, *13*, 140.

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Table S1 Matrix Elements (in unit eV) of the Molecule **4** with or without (underline) Double-Bonded Tethers

entry	F	C	V	U	t_e	t_h	CT%
6	3.41	4.47	0.16	-0.03	-0.15	0.06	2.51
<u>6</u>	3.53	4.75	0.11	-0.01	-0.03	0.08	0.74
7	3.43	4.45	0.15	-0.02	-0.18	0.10	4.87
<u>7</u>	3.56	4.79	0.11	-0.01	-0.03	0.07	0.46
8	3.09	4.56	0.19	-0.19	-0.18	0.17	3.12
<u>8</u>	3.24	4.85	0.11	-0.08	-0.04	0.11	0.65
9	3.12	4.58	0.20	-0.19	-0.20	0.22	4.52
<u>9</u>	3.29	4.92	0.10	-0.05	-0.03	0.08	0.36