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Possible Photoinduced Spin Transitions in Bis(phenylmethylenyl)[2.2]paracyclophanes. A Spin−Orbit Coupling Study

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A possible mechanism for the spin transitions in various stacking conformations of bis(phenylmethylenyl)-[2.2]paracyclophanes, which have close-lying lowest singlet, triplet, and quintet spin states, is theoretically investigated by using diphenylcarbene dimers as models. Spin−orbit coupling (SOC) matrix elements, which play an essential role in the spin transition phenomena, are calculated with the effective one-electron spin−orbit Hamiltonian. The SOC between the first excited singlet state and the first excited triplet state and that between the first excited triplet state and the lowest quintet state are strong. The SOC between the first excited quintet state and the first excited triplet state and that between the first excited triplet state and the lowest singlet state are also strong. These results demonstrate that the spin conversion between the low-spin singlet state and the high-spin quintet state can occur via the first excited intermediate-spin triplet state. We propose that possible photoinduced spin-crossover phenomena can be observed in these organic molecular systems.

Introduction

Spin-crossover complexes[1] have extensively been studied since Cambi et al. discovered thermally induced spin transitions in iron(III) complexes.[2] Gütlich, Hauser, and collaborators observed in an Fe(II) spin-crossover system that a green light (514.5 nm) switches the LS state ($S = 0$) to the HS state ($S = 2$)[3] and a red light (820 nm) changes the HS state to the LS state[3c,4] The former phenomenon is now called the LIESST (light-induced-excited-spin-state-trapping) effect and the latter is called the reverse-LIESST effect.[1] The proposed mechanism for the spin transition phenomena involves two intersystem crossing processes via the intermediate spin (IS) state with $S = 1$,[3b] as shown in Figure 1. The spin allowed $^1A_1 \rightarrow {}^1T_1$ excitation with a lifetime typically of nanoseconds occurs upon irradiation with a green light and the fast $^1T_1 \rightarrow {}^3T_1 \rightarrow {}^5T_2$ transitions populate the metastable $^5T_2$ state (LIESST effect). Irradiation with a red light induces the $^5T_2 \rightarrow {}^5E$ spin-allowed transition and turns the ^5E state to the $^1A_1$ state via the $^3T_1$ state (reverse-LIESST effect). In this mechanism, spin−orbit coupling (SOC) plays an essential role in the transition between the LS (HS) state and the IS state since SOC induces a spin-mixed state[5] that permits the transitions between different spin states.

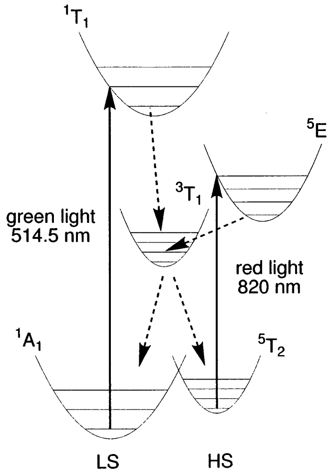
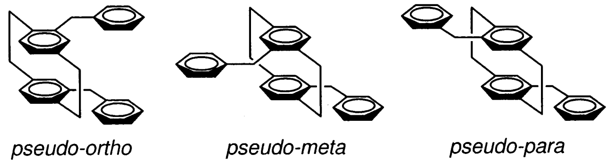


Figure 1. Schematic representation of the mechanism of the light-induced-excited-spin-state-trapping (LIESST) and the reverse-LIESST effects in a spin-crossover system.

SCHEME 1



Designing molecule-based magnetic compounds[6] is one of the most exciting issues in the border of chemistry and physics. Since the experimental verification by Itoh[7a] and Wasserman et al.,[7b] various organic magnetic compounds have been synthesized. Iwamura and collaborators[8] synthesized a series of bis(phenylmethylenyl)[2.2]paracyclophanes illustrated in Scheme 1. These cyclophane molecules involve two carbenic carbon atoms and they have close-lying lowest singlet, triplet, and quintet spin states. They concluded from electron spin resonance analyses that the ground states of the *pseudo-ortho* and *pseudo-para* forms are quintets, while the ground state of the *pseudo-meta* form is a singlet. These experimental results can be rationalized by McConnell's model.[9] This useful model predicts that the *pseudo-ortho* and *pseudo-para* forms should have ferromagnetic interaction, whereas the *pseudo-meta* form should have antiferromagnetic interaction. Yamaguchi et al.[10] estimated the effective exchange integrals of phenylcarbene clusters (dimer and trimer) with various conformations at the approximately projected unrestricted Hartree−Fock level of theory and concluded that (i) the *geminal* form, which has not yet been synthesized, and the *meta* form have singlet ground

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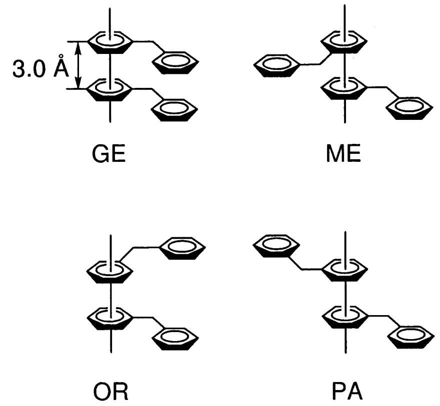


Figure 2. Conformations of DPC dimer in this study.

states, while the *ortho* and *para* forms have quintet ground states and (ii) suitable stacking modes of triplet carbene is indispensable for ferromagnetic interactions. Their computational results for the dimers are fully consistent with the experimental observations.[8] Yoshizawa and Hoffmann[11] showed that McConnell's model that is based on a spin polarization mechanism can be interpreted from the viewpoint of molecular orbital interactions between stacked hydrocarbon molecules in general.

As mentioned above, bis(phenylmethylenyl)[2.2]paracyclophanes have two carbenic carbon atoms and their singlet, triplet, and quintet spin states lie close in energy. Thus, these organic molecules and the spin-crossover complex mentioned above have some resemblance with respect to the magnetic structures. The SOC in carbene is quite strong, and therefore spin-crossover phenomena can be observed in these organic molecules. In molecular crystals, effects of the surrounding molecules around the relevant one are important in inducing photoinduced cooperative phenomena. However, in this study we confined our discussions to the spin transitions in a single molecule as a first approximation. We investigated the SOC in the pseudo-*geminal*, pseudo-*ortho*, pseudo-*meta*, and pseudo-*para* conformations of bis(phenylmethylenyl)[2.2]paracyclophane using four diphenyl carbene dimers (DPCDs) depicted in Figure 2. We call the *geminal* form GE, the *ortho* form OR, the *meta* form ME, and the *para* form PA. We propose from computational results a mechanism for a possible photoinduced spin-crossover effect in bis(phenylmethylenyl)[2.2]paracyclophanes.

Computational Details

We optimized the structure of DPC in the triplet state under C_2 symmetry using the hybrid HF/density functional theory (DFT) B3LYP method[12] with the double-ζ 6-31G* basis set of Pople and collaborators.[13] In this calculation we used the Gaussian 98 program package.[14] We adopted the optimized structure to construct the dimers (DPCDs) assuming the distance between the two benzene planes to be 3.0 Å. We carried out complete-active-space self-consistent field (CASSCF) calculations[15] to obtain reference wave functions that are used for SOC calculations. The low-lying singlet and triplet states, and the lowest quintet state of the cyclophane molecules are dominated by electron configurations that consist of possible occupations of four electrons in the four orbitals coming from the p orbitals on the two carbenic carbon atoms; however, we cannot express excited quintet states using only such electron configurations. In aromatic molecules, all π orbitals are usually included in active-space orbitals, but in this case, it is impossible to do so because DPCDs have 24 π orbitals on the benzene rings involved. In this work, we added two orbitals energetically just below and above the four orbitals coming from the two carbenic carbon atoms as active-space orbitals for our calculations to consider excited quintet states derived from the electron transitions from a π orbital on a benzene ring to a p orbital on a carbenic carbon atom. Our choice of six active-space orbitals is depicted in Figure 3. These active-space orbitals are localized on carbenic carbon atoms and a benzene ring. pσ1 and pπ1 (pσ2 and pπ2) represent two p orbitals on the carbenic carbon atom of the upper (lower) DPC. bp1 and bp2 are one of the π orbitals on a benzene ring.

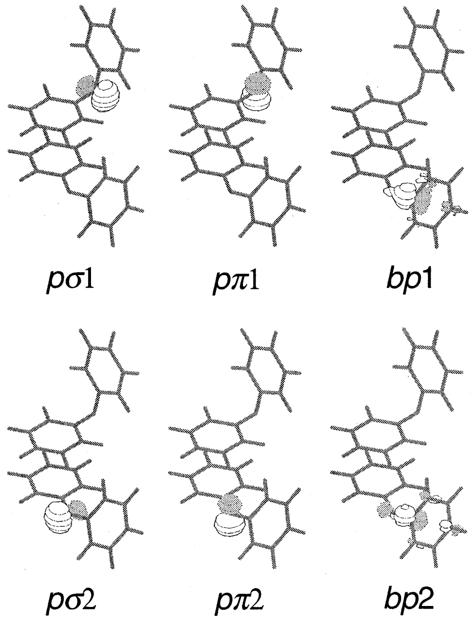


Figure 3. Active-space orbitals used in our calculation.

Using these six orbitals as active-space orbitals, we obtained reference wave functions in the quintet state at the CASSCF-(6,6)/6-31G* level of theory and estimated the SOC with the approximate one-electron spin−orbit Hamiltonian[16] given in eq 1:

$$H_{\mathrm{SO}} = \frac{\alpha^2}{2}\sum_i\sum_k\left(\frac{Z_k^*}{r_{ik}^3}\right)(\mathbf{S}_i\cdot\mathbf{L}_{ik}) = \sum_i h_i(Z^*) \qquad (1)$$

$$\frac{\alpha^2}{2} = \frac{e^2h}{4\pi m_e^2c^2}\,(\alpha^{-1} = 137.036)$$

where $\mathbf{L}_{ik}$ and $\mathbf{S}_i$ are the orbital and spin angular momentum operators for electron i in the framework of the nuclei indexed k, respectively, and Z_k^* is the effective nuclear charge, an empirical parameter set in the approximate spin−orbit Hamiltonian. We used an effective nuclear charge (Z_k^*) of 3.6 for carbon according to Koseki, Schmidt, and Gordon.[16] We performed SOC calculations using the GAMESS program package.[17] Our calculations of spin−orbit coupling matrix elements express the degree of coupling between the singlet and triplet states and between the triplet and quintet states. These matrix elements are written as eqs 2−1 and 2−2:

$$\langle H_{\mathrm{so}}\rangle_s^{1-3} = \langle {}^3\Psi(\mathbf{M}_{\mathrm{s}})|H_{\mathrm{so}}|{}^1\Psi\rangle \qquad (2\text{-}1)$$

$$\langle H_{\mathrm{so}}\rangle_{s,s'}^{3-5} = \langle {}^5\Psi(\mathbf{M}_{\mathrm{s}})|H_{\mathrm{so}}|{}^3\Psi(\mathbf{M}_{\mathrm{s'}})\rangle \qquad (2\text{-}2)$$

where ${}^1\Psi$, ${}^3\Psi$, and ${}^5\Psi$ are the many-body wave functions in the singlet, triplet, and quintet states, respectively, and M_s is the spin magnetic quantum number. Since the spin sublevels are generated by SOC, the root-mean-square coupling constant given in eqs 3-1 and 3-2 is a reasonable measure of the strengths of the singlet−triplet and triplet−quintet interactions.

$$\mathrm{SOC}(1-3) = [\sum_s \{\langle H_{\mathrm{so}}\rangle_s^{1-3}\}^2]^{1/2} \tag{3-1}$$

$$\mathrm{SOC}(3-5) = [\sum_{s,s'} \{\langle H_{\mathrm{so}}\rangle_{s,s'}^{3-5}\}^2]^{1/2} \tag{3-2}$$

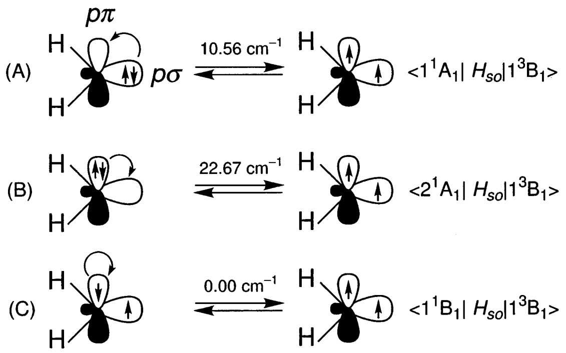
Results and Discussion

Spin−Orbit Coupling Matrix Elements. Let us first look at the SOC in carbene CH_2 to aid our understanding. The SOC in biradicals has been extensively investigated by Michl and collaborators;[19] in ref 19b, the basis set dependencies of convergency and quantitative estimation of SOC in carbene and silylene were investigated in detail. They suggested that at least a double-ζ basis set is needed for semiquantitative discussions.[19b] We calculated the strengths of the SOC in carbene, which has a planer C_{2v} geometry, using the wave function in the triplet state obtained at the CASSCF(2,2)/6-31G* level of theory and the approximate one-electron spin−orbit Hamiltonian of eq 1. We chose two p orbitals (pσ orbital with a_1 label, parallel to the trigonal carbene plane and pπ orbital with b_1 label, perpendicular to the carbene plane) on the carbenic carbon atom as active-space orbitals. We considered three singlet states, 1^1A_1 ($(p\sigma)^2$), 2^1A_1 ($(p\pi)^2$), and 1^1B_1 ($(p\sigma)^1(p\pi)^1$), and one triplet state, 1^3B_1 ($(p\sigma)^1(p\pi)^1$), in this calculation. Calculated SOC values and corresponding singlet−triplet spin transitions are depicted in Scheme 2. These values are in good agreement with the values obtained with the CASSCF(6,6) wave function.[19b] We see in Scheme 2 that the SOC between the closed-shell singlet states (1^1A_1 and 2^1A_1) and the 1^3B_1 triplet state are very large, but that between the 1^1B_1 open-shell singlet state and the 1^3B_1 triplet state is nearly zero. We can rationalize these results from orbital-symmetry discussions.[5a,20] Using eq 1, we can write the SOC matrix elements between the singlet and triplet states in the form of eq 4.

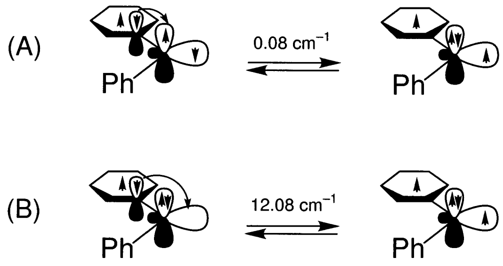
$$\langle {}^3\Psi|H_{\mathrm{SO}}|{}^1\Psi\rangle = \frac{\alpha^2}{2}\sum_i \begin{Bmatrix} \langle\alpha\alpha|\mathbf{S}_i|\{1\}/\{\sqrt{2}(\alpha\beta-\beta\alpha)\}\rangle \\ \langle\{1\}/\{\sqrt{2}(\alpha\beta+\beta\alpha)\}|\mathbf{S}_i|\{1\}/\{\sqrt{2}(\alpha\beta-\beta\alpha)\}\rangle \\ \langle\beta\beta|\mathbf{S}_i|\{1\}/\{\sqrt{2}(\alpha\beta-\beta\alpha)\}\rangle \end{Bmatrix} \times \left\langle {}^3\Phi\left|\sum_k\left(\frac{Z_k^*}{r_{ik}^3}\mathbf{L}_{ik}\right)\right|{}^1\Phi\right\rangle \tag{4}$$

The spin part of eq 4 gives a nonzero value, and therefore, the space part determines whether the SOC is zero or not. Since $\mathbf{L}_x$, $\mathbf{L}_y$, and $\mathbf{L}_z$ behave like the rotation operators, $\mathbf{R}_x$, $\mathbf{R}_y$, and $\mathbf{R}_z$, respectively, the direct product of the orbital symmetry labels must contain the irreducible representation to which the rotation operators belong in order to give nonzero SOC values. From the character table of C_{2v} point group, we see that the rotation operators belong to A_2, B_1, and B_2. In (A) and (B) of Scheme 2, the direct product of the orbital symmetry labels $a_1 \times b_1$ is B_1, and therefore these interactions give nonzero SOC values. But in (C) of Scheme 2 the direct product of the orbital symmetry labels $b_1 \times b_1$ is A_1, and such an interaction leads to a zero SOC value.

SCHEME 2



SCHEME 3



Let us next look at the SOC between the singlet states and the triplet states which derive from the electron transitions from one of the π orbitals on the benzene rings to one of the p orbitals on the carbenic carbon atom in DPC. We chose two p orbitals on the carbenic carbon atom and one of π orbitals on the benzene ring as active-space orbitals. The SOC values in DPC between the closed-shell ^1A singlet states (corresponding to the 1^1A_1, and 2^1A_1 states of carbene) and the 1^3B triplet state (corresponding to the 1^3B_1 state of carbene) are large, being similar to those in carbene. The SOC value in DPC between the open-shell 1^1B singlet state (corresponding to the 1^1B_1 state of carbene) and the 1^3B triplet state is nearly zero. We give in Scheme 3 the SOC values and the corresponding spin transitions. Part A shows the electron transition from the p_z orbital on the benzene ring's carbon atom neighboring to the carbenic carbon atom to the pπ orbital on the carbenic carbon atom, and (B) shows the electron transition from the p_z orbital on the benzene ring's carbon atom neighboring to the carbenic carbon atom to the pσ orbital on the carbenic carbon atom. The electron transition in (A) gives a SOC value of 0.08 cm^{-1}, while that in (B) gives a SOC value of 12.08 cm^{-1}. Let us consider why the SOC value in (B) is larger than that in (A). A nonzero angular momentum expectation value (the space part of eq 4) is produced along the normal to the plane defined by a pair of p orbitals when they are perpendicularly oriented, while a maximum expectation value is obtained when the orbitals are mutually perpendicular.[21] The pπ orbital on the carbenic carbon atom is parallel to the p_z orbitals on the carbon atoms neighboring to the carbenic carbon atom, so the angular momentum expectation value (the space part of eq 4) is small. As a result, the SOC in (A) is small. On the other hand, the pσ orbital is perpendicular to the p_z orbitals, and therefore we expect that the space part of the SOC matrix element in eq 4 should be large. So, the SOC in (B) is larger than that in (A).

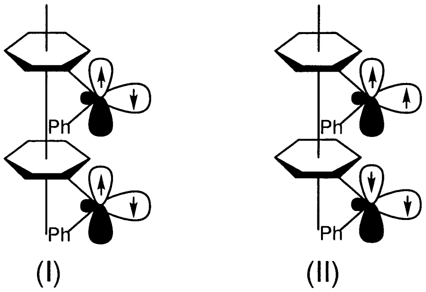
Electron Configurations of DPCDs. Let us consider the electron configurations of DPCDs. From spin−orbit-coupling configuration interaction (SOC-CI) calculations, we concluded

TABLE 1: Dominant Electron Configurations in DPCDs

state	configuration
lowest singlet	$(p\sigma 1)^1(p\sigma 2)^1(p\pi 1)^1(p\pi 2)^1$
first excited singlet	closed shell[a]
	$(p\sigma 1)^2(p\sigma 2)^1(p\pi 2)^1$
lowest triplet	$(p\sigma 1)^1(p\sigma 2)^1(p\pi 1)^1(p\pi 2)^1$
first excited triplet	$(p\sigma 1)^2(p\sigma 2)^1(p\pi 2)^1$
	$(p\sigma 1)^1(p\pi 1)^1(p\pi 2)^2$
lowest quintet	$(p\sigma 1)^1(p\sigma 2)^1(p\pi 1)^1(p\pi 2)^1$
first excited quintet	$(bp1)^1(p\sigma 1)^2(p\sigma 2)^1(p\pi 1)^1(p\pi 2)^1$
	$(bp1)^1(p\sigma 1)^1(p\sigma 2)^1(p\pi 1)^2(p\pi 2)^1$

[a] $(p\sigma 1)^2(p\sigma 2)^2$, $(p\pi 1)^2(p\pi 2)^2$, and $(p\sigma)^2(p\pi)^2$.

SCHEME 4



that the electron configurations of DPCDs in the singlet, triplet, and quintet states are summarized in Table 1. All DPCDs have nearly the same electron configurations in each spin state. The lowest singlet, triplet, and quintet states are all composed of the electron configuration of $(p\sigma 1)^1(p\pi 1)^1(p\sigma 2)^1(p\pi 2)^1$. In the lowest triplet state, a DPC unit of DPCD has the 1^1B state and the other unit has the 1^3B state. In the lowest quintet state, all electron spins on the carbenic carbon atoms are parallelly aligned. In the lowest singlet state, we can consider two possible spin configurations, as shown in Scheme 4. Configuration (I) is viewed as a combination of the open-shell singlet (OSS) states of DPC, and (II) is viewed as an antiferromagnetic combination of the triplet state. We concluded that configuration (II) represents the lowest singlet state because the 1^3B triplet state of DPC is energetically more stable than the singlet states.[18] The first excited singlet state is mainly composed of the closed-shell singlet states: $(p\sigma 1)^2(p\sigma 2)^2$, $(p\sigma 1)^2(p\pi 2)^2$, etc. The first excited triplet state is composed of the electron configurations of $(p\sigma 1)^2(p\sigma 2)^1(p\pi 2)^1$ and $(p\pi 1)^2(p\sigma 2)^1(p\pi 2)^1$, in which a DPC unit has the closed-shell singlet state and the other unit has the 1^3B triplet state. The first excited quintet state is composed of $(bp1)^1(p\sigma)^3(p\pi 1)^1(p\pi 2)^1$ and $(bp1)^1(p\sigma 1)^1(p\sigma 2)^1(p\pi)^3$, which correspond to the electron transition from a π orbital on a benzene ring to the orbitals on a carbenic carbon atom.

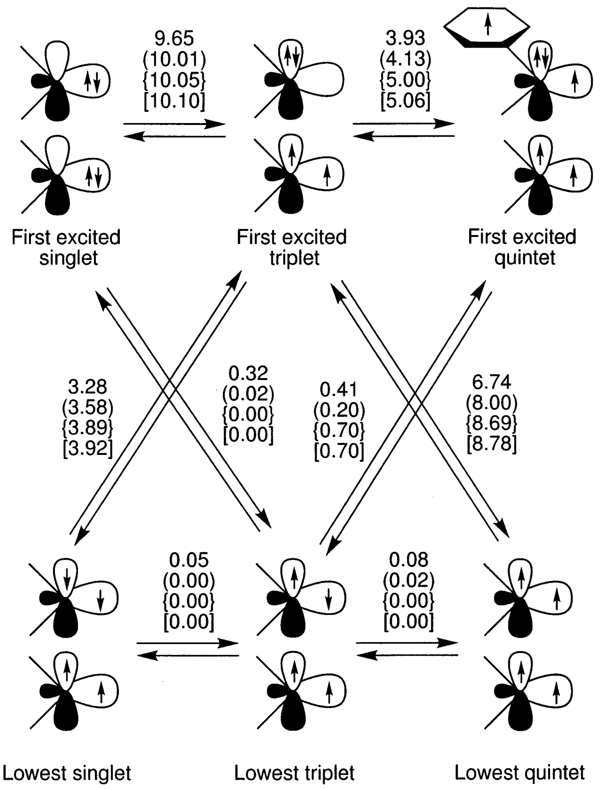


Figure 4. Electronic configurations and the SOC values of GE, OR (in parentheses), ME (in middle parentheses), and PA (in large parentheses). Units are in cm^{-1}.

SOC in DPCDs. Let us look at the SOC in DPCDs. Calculated SOC values and corresponding spin configurations of DPCDs are shown in Figure 4. Only the spin configurations that play an important role in the spin transition processes are shown in this illustration. We see from Figure 4 at first that the SOC values do not depend on the conformation of the monomeric unit. This means that the strengths of the SOC in DPCDs are significantly dependent on those of the monomeric DPC unit itself. Small SOC values between the lowest singlet state and the lowest triplet state (0.05 cm^{-1} for GE, 0.00 cm^{-1} for OR, 0.00 cm^{-1} for ME, and 0.00 cm^{-1} for PA) and between the lowest triplet state and the lowest quintet state (0.08 cm^{-1} for GE, 0.02 cm^{-1} for OR, 0.00 cm^{-1} for ME, and 0.00 cm^{-1} for PA) indicate that such spin transitions are unlikely to occur. Both of the spin transitions derive from the spin inversion in the same orbital, and they are forbidden because spin−orbit coupling is forbidden between the states of the same electron configuration.[5a,22] This can explain the reason the SOC between the lowest spin states are small. On the contrary, the spin transitions from the first excited triplet state to the lowest (the first excited) singlet state should occur because of the large SOC values. In the former transition, the SOC values are 3.28 cm^{-1} for GE, 3.58 cm^{-1} for OR, 3.89 cm^{-1} for ME, and 3.92 cm^{-1} for PA. In the latter transition, the values are 9.65 cm^{-1} for GE, 10.01 cm^{-1} for OR, 10.05 cm^{-1} for ME, and 10.10 cm^{-1} for PA. Both of the transitions derive from the electron transition from the pσ orbital to the pπ orbital on a carbenic carbon atom, and these transitions are allowed.[22] From the viewpoint of monomeric unit, we can view these spin transitions as the transitions from the 1^1A singlet state to the 1^3B triplet state in DPC, and the SOC between the 1^1A state and the 1^3B state is very large (11.82 cm^{-1}). The SOC values between the first excited singlet state and the first excited triplet state are quantitatively in good agreement with those in DPC. We expect that the SOC values can be estimated from the SOC analyses of the monomeric unit qualitatively. Taking the large 1^1A-1^3B SOC value in DPC (11.82 cm^{-1}) into account, the large SOC values between the first excited triplet state and the lowest quintet state (6.74 cm^{-1} for GE, 8.00 cm^{-1} for OR, 8.69 cm^{-1} for ME, and 8.78 cm^{-1} for PA) are reasonable. The SOC value in DPC (11.82 cm^{-1}) is close to those in DPCDs ($\sim$9 cm^{-1}). The spin transition from the first excited singlet state to the lowest triplet state in each conformation is viewed as follows: the spin transition from the 1^1A singlet state (or the 2^1A singlet state) to the 1^1B singlet state occurs in a DPC unit and the transition from the 1^1A singlet state to the 1^3B triplet state occurs in the other DPC unit. The former transition is spin-allowed, but the transition gives a zero SOC value. As a whole, the spin transition between the first excited singlet state and the lowest triplet state is forbidden. Thus, the SOC value for such a

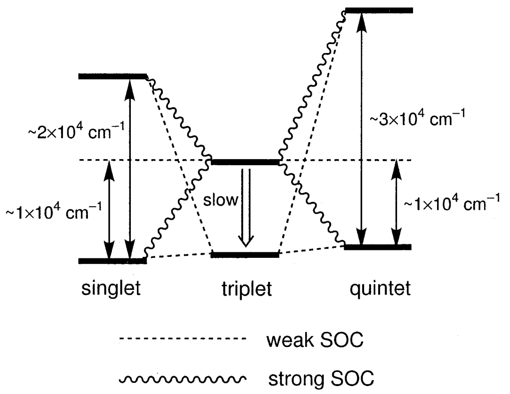


Figure 5. Diagram of the SOC in DPCDs. The wavy (dotted) lines indicate that the SOC between two states linked by the lines are strong (weak).

transition is small in each conformation (0.32 cm^{-1} for GE, 0.02 cm^{-1} for OR, 0.00 cm^{-1} for ME, and 0.00 cm^{-1} for PA).

Let us finally look at the SOC between the first excited quintet state and the lowest triplet state (the first excited triplet state). In each conformation the SOC value between the first excited quintet state and the first excited triplet state is quite large (3.93 cm^{-1} for GE, 4.13 cm^{-1} for OR, 5.00 cm^{-1} for ME, and 5.06 cm^{-1} for PA), but that between the first excited quintet state and the lowest triplet state is not so large (0.41 cm^{-1} for GE, 0.20 cm^{-1} for OR, 0.70 cm^{-1} for ME, and 0.70 cm^{-1} for PA). These results are reasonable in view of Scheme 3. The spin transition from the first excited triplet state to the first excited quintet state is viewed as the electron transfer from the p_z orbital on the benzene ring's carbon atom neighboring to a carbenic carbon atom to the $p\sigma$ orbital on the carbenic carbon atom in DPC. The spin transition from the lowest triplet state to the first excited quintet state is viewed as the electron transfer from the p_z orbital on the benzene ring's carbon atom neighboring to a carbenic carbon atom to the $p\pi$ orbital on the carbenic carbon atom in DPC. The SOC value in the former case (12.08 cm^{-1}) is larger than that in the latter case (0.08 cm^{-1}). Thus, the SOC values for the transition from the first excited quintet state to the first excited triplet state are larger than those for the transition to the lowest triplet state. The spin transition from the first excited quintet state to the first excited triplet state is more likely to occur than that from the first excited quintet state to the lowest triplet state.

A Possible Mechanism for the Spin Transitions in Bis(phenylmethylenyl)[2.2]paracyclophanes. Taking our results discussed above into account, we propose a mechanism for the spin transitions in bis(phenylmethylenyl)[2.2]paracyclophanes. A diagram of the SOC in the singlet, triplet, and quintet states of DPCDs is shown in Figure 5. The wavy lines indicate that the SOC between the two states is strong and the dotted lines indicate that the SOC between the two states is weak. In all DPCDs, the SOC between the lowest singlet state and the lowest triplet state and that between the lowest triplet state and the lowest quintet state are weak, and consequently, the lowest states should be metastable at low temperature. Therefore once spin states are changed, the spin states after the change keep the spin states. In contrast, the SOC between the first excited singlet state and the first excited triplet state is strong. The SOC between the first excited triplet state and the lowest quintet state is also strong. Therefore the LS → HS transition should occur by the photoexcitation from the lowest singlet state to the first excited singlet state, which is then converted to the lowest quintet state via the first excited triplet state. According to CASSCF/SOC−CI calculations, the excitation energy is about 2×10^4 cm^{-1} that corresponds to a green light. Using a green light we might induce the LS → HS transition in bis(phenylmethylenyl)[2.2]paracyclophanes (LIESST-like effect).

The SOC between the first excited quintet state and the first excited triplet state is strong, and that between the first excited triplet state and the lowest singlet state is also strong. Therefore the HS → LS transition should occur by the photoexcitation from the lowest quintet state to the first excited quintet state, which is converted to the lowest singlet state via the first excited triplet state. The excitation energy is about 3×10^4 cm^{-1} (reverse-LIESST-like effect) and irradiation with UV light can cause the electron transfer from the π orbital on one of the benzene rings to the p orbital on a carbenic carbon atom.

We calculated the oscillator strength (f) for the spin-allowed transition from the first excited triplet state to the lowest triplet state in each conformation to look at whether it occurs or not and found that it is not possible because f is smaller than 10^{-5}. We estimated the energy differences between the lowest triplet state and the first excited triplet state to be about 1×10^4 cm^{-1}. Therefore a light with a wavenumber of about 1×10^4 cm^{-1} (near-infrared) might cause the spin transitions in bis(phenylmethylenyl)[2.2]paracyclophanes. Our computational results suggest that the excitation from the lowest quintet (singlet) state to the first excited triplet state can induce the HS × LS transition if such an excitation is possible.

Concluding Remarks

We investigated the spin−orbit coupling (SOC) in *pseudo-geminal*, *pseudo-ortho*, *pseudo-meta*, and *pseudo-para* bis(phenylmethylenyl)[2.2]paracyclophanes using reasonable models, diphenylcarbene dimers (DPCDs). Using the effective one-electron spin−orbit Hamiltonian, we estimated the strengths of SOC, which plays an essential role in the spin transitions between different spin states ($\Delta S = 1$). Our conclusions are as follows: (i) The spin transitions via the lowest triplet state are unlikely to occur; (ii) on the other hand, the spin transitions via the first excited triplet state are very likely and should play an important role in the LS ↔ HS spin transitions in bis(phenylmethylenyl)[2.2]paracyclophanes; (iii) these results are rationalized from SOC analyses of the monomeric unit DPC; (iv) the SOC values of DPCDs do not depend on the conformations of the monomeric units. We propose from these results a mechanism for the possible LS ↔ HS spin transitions in bis(phenylmethylenyl)[2.2]paracyclophanes. The SOC−CI calculations suggest that the excitation energies from the lowest singlet state to the first excited singlet state and those from the lowest quintet state to the first excited quintet state are about 2×10^4 cm^{-1} (green) and 3×10^4 cm^{-1} (UV), respectively, in all conformations, and we might induce the LS ↔ HS transitions using photoexcitation. Spin-crossover phenomena (both LIESST and reverse-LIESST effects) can occur in these organic molecules.

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