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Conformational Analysis of Singlet−Triplet State Mixing in Paternò−Büchi Diradicals

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Abstract: Conformational dependence of spin−orbit coupling (SOC) in flexible Paternò−Büchi (PB) diradicals has been studied with high-level ab initio methods using both (i) one-electron spin−orbit Hamiltonian with parametrized (effective) nuclear charges in conjunction with a state-averaged MCSCF wave function as implemented by Robb in Gaussian 98 and (ii) complete one- and two-electron SOC with a fully optimized MCSCF triplet wave function and frozen core singlet as implemented by Furlani in the GAMESS computational package. The ab initio results revealed two distinct areas of elevated SOC values, one corresponding to the region whereby a *cisoid* conformation in the C−C−O−C fragment brings the two odd-electron orbitals closer to each other, and the other area corresponding to the partially eclipsed conformation lacking direct overlap between the spin centers. In this second region the 1,4-electronic communication is mediated by the oxygen's 2p-lone pair, which is suitably oriented to play the role of a "relay-antenna". The other critical factor affecting the rate of intersystem crossing (ISC)—singlet−triplet energy separation—was computed utilizing a multireference CASSCF-MP2 method to include dynamic correlation effects. The largest singlet−triplet energy gap, approximately 2 kcal/mol, was found for a gauche conformer (also a minimum SOC conformation). Rotation about the central C−O bond either toward the fully eclipsed (0°) or the partially eclipsed (120°) conformations decreases the singlet−triplet gap while increasing the value of the SOC matrix element. These computational findings support the Griesbeck model for stereochemistry of triplet PB reactions and provide a rigorous basis for predicting the probability of ISC in diradicals separated by a partially conjugated spacer.

Introduction

Paternò−Büchi (PB) reaction,[1] i.e., the [2+2] cycloaddition of electronically excited carbonyl compounds to alkenes, is a versatile photochemical process that yields four-membered oxygen heterocycles, oxetanes. The reaction occurs both in the singlet and triplet manifold, with the triplet mechanism known to proceed via 1,4-diradicals detected experimentally in transient spectroscopy studies.[2,3] Recent renewed interest in the triplet reaction was prompted by observations of unusual stereoselectivity in PB cycloadditions, leading to the emergence of the Griesbeck model.[4] The model contends that it is the spin−orbit coupling (SOC)-controlled intersystem crossing (ISC) that determines the stereochemical outcome. The observed difference in stereochemistry of singlet vs triplet reactions supports the model.[4b,5]

It is generally accepted that ISC in short (1,3 and 1,4) triplet diradicals is controlled by spin−orbit coupling and there is some evidence that SOC dominates over electron−nuclear hyperfine coupling (HFC) even in longer 1,*n*-diradicals.[6] Unlike HFC, spin−orbit coupling is strongly conformationally dependent as shown in several studies that addressed structural effects on SOC in triplet organic species.[7] Such conformational dependence in trimethylene (and radical pairs) was semiquantitatively described with a simple parametric equation $B(R)|S|\sin\varphi$, involving the overlap and the sine of the angle between the odd-electron orbitals, and a function slowly changing with distance.[7i] Conformational behavior of SOC in the next polymethylene, tetramethylene, is by far more complex[7k] and does not seem to

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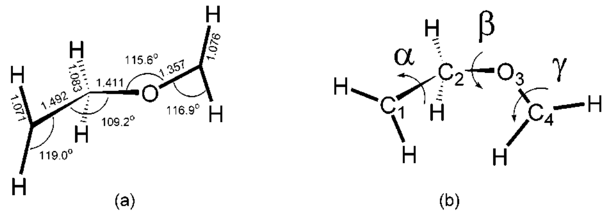

Figure 1. The MP2/6-311+G(d) initial geometry and the torsional angles convention.

follow the simple parametric scheme. Introduction of oxygen with its lone pairs further complicates the situation. Experimentally, triplet lifetimes of PB diradicals are considerably shorter than that of their corresponding all-carbon analogues. Caldwell suggested that the reason for that is (i) a decreased average distance between the unpaired electrons due to the following resonance: $C^{\uparrow}-C-\ddot{O}-C^{\uparrow} \leftrightarrow C^{\uparrow}-C-O^{\uparrow +}-C^{-}$ and (ii) an increase in SOC due to conformations, which provide an angle of approximately 90° between the oxygen 2p orbital and the half-filled p orbital at the adjacent terminus.[3c,d]

Prediction of ISC-reactive conformations relies heavily on a clear understanding of conformational dependence of spin−orbit coupling. In view of our own interest in the parametrization of SOC in conformationally flexible triplet species, we carried out a systematic ab initio study of conformational behavior of spin−orbit coupling in PB diradicals, with the primary goal of establishing a rigorous basis for identifying the ISC-reactive conformations.

Computational Details

Ab initio computations were carried out by using the Gaussian 98[8] and GAMESS[9] programs on a dual R10000 mips processor SGI Octane workstation equipped with 1GB memory. The initial geometry of triplet 3-oxabutane-1,4-diyl, $^{\bullet}CH_2CH_2OCH_2^{\bullet}$, constrained to C_s symmetry in an anti-conformation with flat methylenes rotated by 90° out of the CCOC plane, was optimized at the MP2/6-311+G(d) level of theory. The relevant geometrical parameters are presented in Figure 1a. Spin−orbit coupling was then mapped out as a function of three torsional angles: α (rotation about C1−C2 bond), β (C2−O3), and γ (O3−C4), with conformations designated as ($\alpha;\beta;\gamma$), Figure 1b. The points were computed for every 15°, although in some regions of conformational space a finer grid of 10° or even 5° was used.

For computing SOC matrix elements we utilized and compared two approaches: (i) one-electron spin−orbit Hamiltonian with parametrized (effective) nuclear charges in conjunction with a state-averaged MCSCF wave function as implemented by Robb in Gaussian 98, and (ii) complete one- and two-electron SOC with a fully optimized MCSCF triplet wave function and a frozen core singlet as implemented by Furlani in GAMESS. In both cases an active space of 6 electrons in 6 orbitals was utilized to include the two odd electrons and two oxygen lone pairs.[10] The Gaussian 98 module for computing spin−orbit integrals (L319) was modified to update the effective nuclear charges.[11]

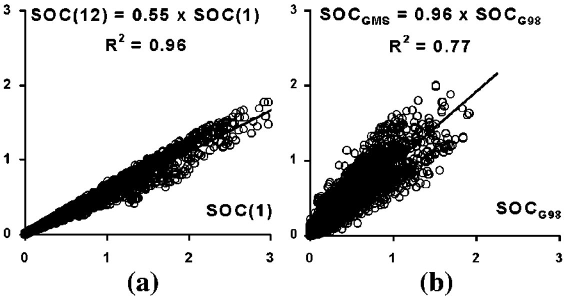

Figure 2. (a) Correlation between one-electron, SOC(1), and one- and two-electron, SOC(12), values computed by GAMESS; (b) correlation between GAMESS (SOC_{GMS}) and Gaussian 98 (SOC_{G98}) results (cm^{-1}).

Two issues are worth noting here: (i) the effect of including the two-electron operator and (ii) comparison of the results obtained with GAMESS vs Gaussian 98. Figure 2a shows that SOC computed with a full one- and two-electron Breit−Pauli Hamiltonian, SOC(12), is about 55% of the corresponding one-electron values, SOC(1). This supports the notion that the two-center one- and two-electron terms approximately cancel for lighter elements,[12] and justifies the effective charge approach.[13] The uniform 45% decrease in SOC(1) values is mainly due to *one-center* two-electron contributions. Since such contributions come primarily from the integrals involving two core (i.e. 1s) and two valence orbitals, we expected their conformational behavior to be no different from that of the one-electron (two valence orbitals) contributions. A good correlation between the two data sets ($R^2 = 0.96$) supports this conclusion.

Gaussian 98 values deviate from SOC(12) computed by GAMESS only by 4% on average, with $R^2 = 0.77$, Figure 2b. Although the correlation in this case is not perfect, this result indicates that the computationally much less expensive state-averaged MCSCF approach with effective nuclear charges as implemented in Gaussian 98 produces sensible results. The final SOC values presented in Figure 3 are obtained using GAMESS with a full one- and two-electron approach, which in our experience required approximately 3−4 times more CPU time per single point.

Singlet−triplet energy separations were computed with Gaussian 98 at a multireference CASSCF(6,6)-MP2 level of theory, utilizing the 6-311+G(d) basis set. For the importance of dynamic correlation see ref 14.

Results and Discussion

The SOC Map. In the *cisoid* conformation of the C−C−O−C fragment the dependence of spin−orbit coupling has a clear maximum at (105;0;30)−Figure 3a, green arrow (the second peak corresponds to the enantiomer). As β is increased, the maximum on the SOC surface slowly shifts in the direction of smaller values of α (the C1 odd-electron orbital "follows" the C4-orbital). When β increases to 60−75° the total SOC value drops below 0.5 cm^{-1}, at which point another maximum (red arrow) grows in (Figure 2d). This second area of enhanced SOC reaches its maximum at $\beta \approx 110°$.[15] Further rotation into the transoid conformation, $\beta \rightarrow 180°$, gradually decreases SOC to near zero (Figure 2g,h).

Figure 3i ($\gamma = 15°$) clearly shows these two areas of elevated SOC values. Expectedly, all the geometries of maximum SOC have their odd-electron orbitals nearly perpendicular (within ±10°). The reverse is not generally true because for any given value of β one can find an infinite number of ($\alpha;\gamma$) combinations such that the angle between the

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[10] Active space of 4-in-4 was clearly not sufficient; increasing it to 8-in-8 did not produce noticeable changes in calculated SOC values.

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[15] In both areas of elevated SOC the maximum values are observed for $\gamma = 20° \pm 10°$ and $\alpha = 90° \pm 20°$.

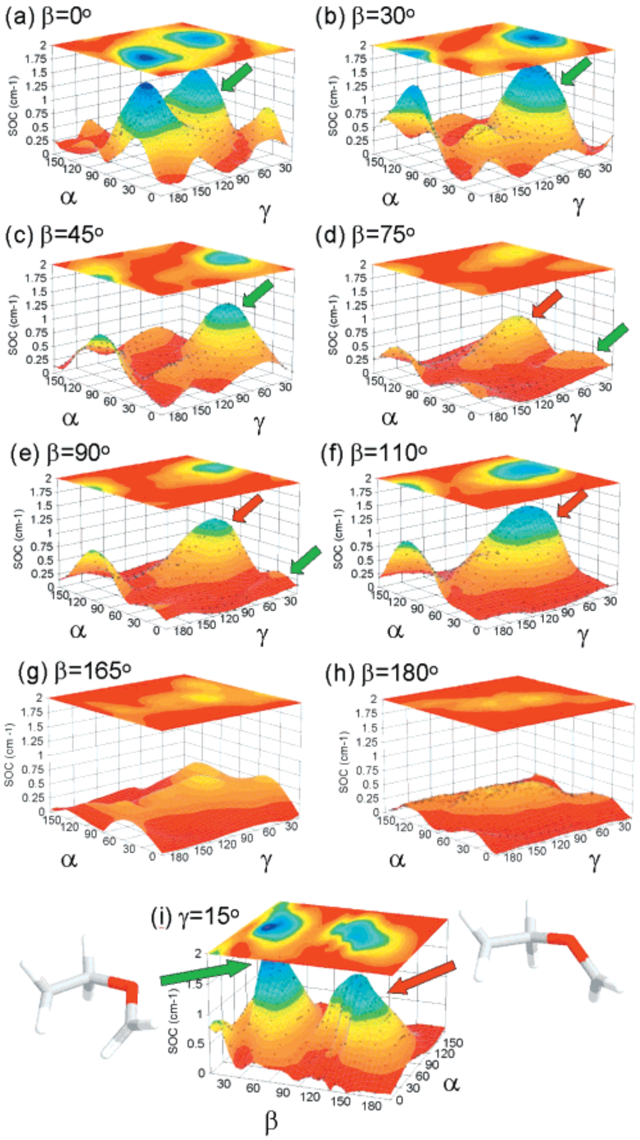

Figure 3. Selected 3-D sections of the four-dimensional SOC dependence in PB diradical.

two odd-electron orbitals is 90°. Additionally, unlike in the simple trimethylene case, direct application of the Carlacci−Doubleday formula,[7e] $B(R)|S|\sin\varphi$, does not help to adequately describe the second area of enhanced SOC.

To understand this more complex conformational dependence of SOC, one needs to examine how the spin density is propagating through the molecular network. Our rationale is that due to favorable overlap with the C4 orbital at small γ, oxygen's lone pair (2p) develops some odd-electron character[16] and thus plays the role of a relay-antenna, so that the situation is really reminiscent of the maximum SOC conformation in trimethylene,[7e] Figure 4.

This is in keeping with Caldwell's resonance prediction, with the reservation that the oxygen 2p orbital is actually almost *parallel*, not perpendicular to the half-filled p orbital at the adjacent terminus. The effect of overlap between the two odd-electron orbitals on SOC is in producing a more zwitterionic (in Salem terminology[7a]) singlet state. Our analysis indicates that indirect overlap, i.e., mediated by the oxygen lone pair, can be just as important. Partial build up of spin density on oxygen in conformations of small γ also contributes to the increase in SOC because of the difference in nuclear charges, $(Z_O/Z_C)^2_{eff} = 2.37$.[11]

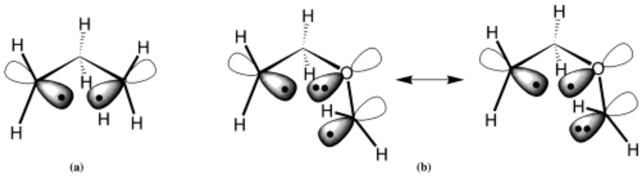

Figure 4. (a) Maximum SOC conformation in trimethylene; (b) the second ($\beta \sim 110°$) maximum SOC conformation in the PB diradical.

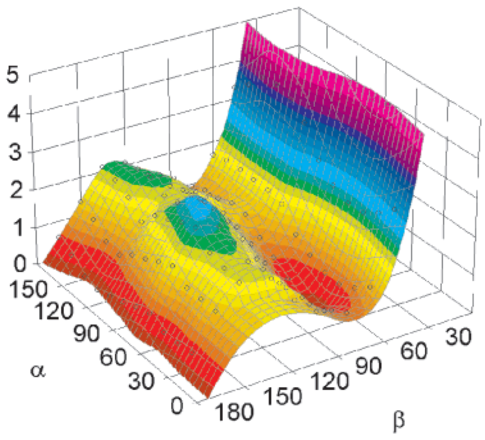

Figure 5. Triplet PES (kcal/mol) CASSCF(6,6)-MP2/6-311+G(d).

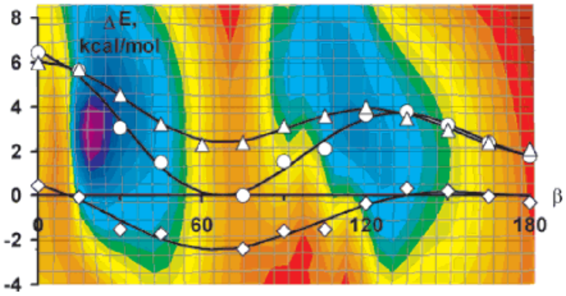

Figure 6. Triplet (△) and singlet (○) CASSCF(6,6)-MP2 energies and triplet−singlet energy separation (◇) as a function of β. The superimposed background color-codes corresponding changes in SOC as a function of β (γ is fixed at 15°, α is vertically spanning 30° to 150°)

Triplet PES and Singlet−Triplet Energy Separation. Figure 5 shows the triplet PES obtained at a multireference level of theory for the same (rigid scan) geometries as for scanning the SOC. As expected, the surface has two minima/valleys corresponding to the *gauche*- and *anti*-conformations. The high-energy value in the vicinity of $\beta = 0°$ is an artificial effect of the rigid scan due to the steric crowding in the cisoid conformation. The actual (relaxed) energy barrier for the cisoid conformation on the triplet energy surface is about 4 kcal/mol—see Figure 6.

For probing the singlet−triplet energy gap computationally we reoptimized the triplet geometry of PB diradicals via a *relaxed* scan for β values spanning 0−180° every 15° at the MP2/6-311+G(d) level and obtained triplet and vertical singlet energies for these geometries with the CASSCF-MP2 method (active space of 6-in-6, same basis set). Figure 6 shows that the *gauche* conformation of the triplet ($\beta \approx 70°$, which also is a minimum SOC conformation) is separated from the singlet surface by approximately 2 kcal/mol.

The barriers on the triplet PES, about 4 kcal/mol for $\beta = 0°$ and 2 kcal/mol for $\beta = 120°$, can be readily overcome at room temperature. The β rotation toward either of the barriers reduces the singlet−triplet energy separation, increasing the probability of ISC. The spin−orbit coupling matrix element is also increased as indicated by the superimposed background image of the SOC map. The most favorable conditions for ISC are predicted for $\beta = 15−25°$ and also in the vicinity of 120°. Rotation into the *anti*-conformation coupled with ISC should

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[16] NBO population analysis shows considerable depletion of electronic density in the oxygen 2p orbital for conformations with small γ, coupled with an increase of spin density. For γ approaching 90°, i.e., overlap with the oxygen sp lone pair, the effect is less pronounced.

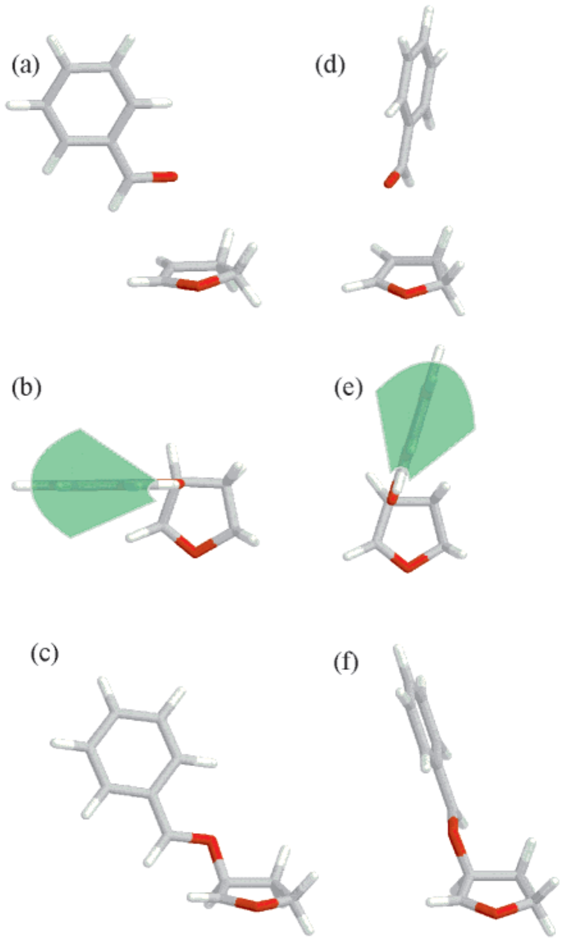

Figure 7. Schematic representation of the approach and the AM1 geometries of triplet PB diradicals in the benzaldehyde addition to dihydrofuran: (a−c) the *exo-gauche*; (d−f) the *exo-anti*.

lead to C2−O3 fragmentation, whereas twisting the *gauche* in the direction of a *fully eclipsed* conformation is expected to produce a singlet diradical, predisposed to ring closure.

Stereochemical Implications. Although there is still no direct experimental evidence to rule out initial C−C bonding in some PB reactions, it is now generally accepted that the "perpendicular" approach, i.e., the attack by the *oxygen's* half-filled n-orbitals, is the most favorable at least for the additions of carbonyl compounds to electron-rich alkenes.[17] For the characteristic case of benzaldehyde additions to dihydrofuran, the two less hindered approaches are depicted in Figure 7, parts a and d, with the phenyl group facing away from the direction of the attack. The green segments in the top views for the *gauche* (b) and *anti* (e) arrangement semiqualitatively denote such areas of unimpeded approach. The AM1-optimized geometries of the respective triplet PB diradicals are shown in Figure 7c,f. In terms of the three dihedral angles ($\alpha;\beta;\gamma$) the *gauche* conformer can be described as (116;70;1), while the *anti* is (118;168;2). As suggested by our SOC conformational analysis, the spin−orbit matrix element for both conformers is small. By analogy with 3-oxabutane-1,4-diyl (Figure 6), the rocking motion or the rotation about the newly formed O−C bond should increase the SOC values while closing the singlet−triplet energy gap. It is evident that out of the four possible motions enhancing ISC (*gauche* or the *anti* rotating *counterclockwise* or *clockwise*), only *gauche* rotating *clockwise* is a productive channel. The oxetane, which is produced as a result of such a motion, has the phenyl group *in an energetically less favorable* endo-configuration, predicted by the model and observed experimentally. Another experimental result, the low quantum yields commonly observed in PB reactions, is also in keeping with this conceptually simple mechanistic rationale, since the second area of elevated SOC values in the vicinity of partially eclipsed conformation seems to provide a nonproductive triplet-to-singlet decay channel.

To conclude, our study supports the Griesbeck model of ISC-controlled stereochemistry of PB reactions while offering a more quantitative description of conformational behavior of spin−orbit coupling and singlet−triplet energy separation in Paternò−Büchi diradicals.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. This paper is dedicated to Professor Howard E. Zimmerman on the occasion of his 75th birthday.

Supporting Information Available: Computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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