

Effect of Donor–Acceptor Substitution on Intersystem Crossing Rates of 1,3-Diaryl-1,3-cyclopentenediyl Triplet Biradicals

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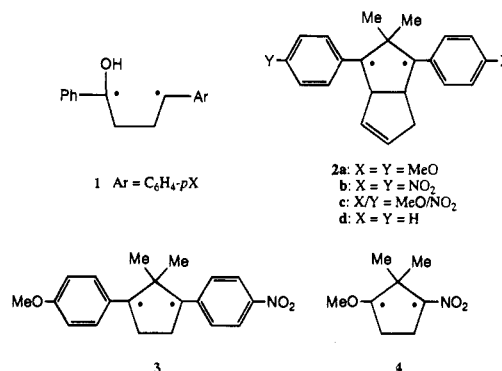
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This work provides experimental evidence, supported by model calculations, that the long-sought polar effect on carbon-centered triplet biradicals is, and should be, virtually nonexistent. Triplet biradicals with small distances between their unpaired electrons commonly have lifetimes governed by the rate of intersystem crossing (ISC), ${}^3\tau \approx 1/k_{\text{ISC}}$, and spin–orbit coupling (SOC)¹ is the main mediator for their spin inversion process. A set of simple rules, which allow us to predict the influence of conformational and electronic properties of biradicals on SOC, was first developed by Salem and Rowland.²

The design of experiments to test these rules has met with partial success.^{3–6} However, experimental evidence for the second rule is still scanty: it predicts that the rate of ISC in homosymmetric biradicals will increase in proportion to the zwitterionic character of the lowest singlet state wave function, S_0 . 2,2-Dimethyl⁵ and symmetrical 1,3-diaryl⁶ substitution of 1,3-cyclopentenediyl biradicals has a substantial effect on ISC rates, which indicates that a slight increase in ionic character of the wave function is sufficient to induce a large increase in ISC rates, as stated by the second rule.

Intuitively, one would expect that a large increase of the zwitterionic character should be caused by introduction of a donor substituent at one of the radical centers and an acceptor substituent at the other.^{2,4} Several such systems have been studied, but the ISC rates measured were not in line with this expectation. On the contrary, Caldwell found that the lifetimes of the Norrish type II triplet biradicals **1** in heptane tended to increase with increasing dipolar (push–pull) substitution.^{4b,e} Unfortunately, clearcut interpretation of these data was hampered by the difficulty in differentiating between conformational and electronic effects, which operate simultaneously in the open-chain biradicals **1**. The effects of substituents on conformational

distributions, on the dynamics of their interconversion, and, hence, on the contributions of various conformations to the overall rate constants of ISC are difficult to evaluate. A strong sensitivity of the SOC matrix elements to the geometry in open-chain biradicals is predicted by Salem's first rule² and is borne out by *ab initio* calculations.⁸



Biradicals with well-defined geometries are required to assess the purely electronic influence of unsymmetrical substitution on triplet lifetimes, and we have extended our previous study⁶ of the cyclic biradicals **2a,b** to the donor–acceptor substituted system **2c**. The triplet biradicals **2** were generated by direct excitation of the conveniently available⁹ azo or housane precursors, and their lifetimes were measured by flash photolysis. The present set of biradicals **2** provides the first direct comparison of all three relevant substitution patterns, i.e., donor–donor, acceptor–acceptor, and donor–acceptor. The lifetimes of the triplet biradicals are given in Table 1. Since the lifetime of the unsymmetrical biradical **2c** falls between those of the two symmetrical reference molecules **2a** and **2b**, donor–acceptor substitution does not significantly accelerate ISC.¹⁰

Does the present finding contradict the second rule of Salem and Rowland? The answer is No! The error lies in the intuitive expectation (expressed above) that a polarizing perturbation will substantially enhance the zwitterionic contributions to the lowest singlet wave function, S_0 . More detailed treatments of the two-electron/two-orbital model for biradicals by Michl and co-workers¹² have exposed the fact that a polarizing perturbation will induce substantial admixture of zwitterionic contributions only when the energy of the lower zwitterionic state drops below that of the covalent state. In this model, moreover, SOC

(8) Furlani, T. R.; King, H. F. *J. Chem. Phys.* **1985**, *82*, 5577. Carlucci, L.; Doubleday, C., Jr.; Furlani, T. R.; King, H. F.; McIver, J. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 5323. Morita, A.; Kato, S. *J. Phys. Chem.* **1993**, *97*, 3298.

(9) Synthesis: Adam, W.; Harrer, H.; Nau, W. M.; Peters, K. *J. Org. Chem.* **1994**, *59*, 3786. The unsymmetrical azoalkane and housane precursors of **2c** are actually 1:1 mixtures of two regioisomers with respect to interchange of the substituents X and Y. The transient absorption of the resulting mixture of regioisomers **2c** cleanly obeyed first-order decay kinetics.

(10) In fact, the lifetime of **2c** can be predicted within the limits of experimental error by defining additive increments for the effects of the nitro and methoxy substituents: $\log(k/k_{\text{ref}}) = \sum c_i$, where $1/k_{\text{ref}}$ is the lifetime of the parent biradical **2d** and c_i are the increments for the substituents. From the lifetime of **2a**, we obtain $c_{\text{MeO}} = +0.202 \pm 0.015$, and from that of **2b**, $c_{\text{NO}_2} = -0.267 \pm 0.014$. Hence, the lifetime of **2c** is predicted to be 2040 ± 200 ns, consistent with the experimental value given in Table 1.

(11) (a) Bonačić-Koutecký, V.; Koutecký, J.; Michl, J. *Angew. Chem.* **1987**, *99*, 216; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 170. (b) Michl, J.; Bonačić-Koutecký, V. *Electronic Aspects of Organic Photochemistry*; Wiley: New York, 1990; Chapters 4.4–6. (c) Michl, J. In *Theoretical and Computational Models for Organic Chemistry*; Formosinho, S. J., Csizmadia, I. G., Arnaut, L. G., Eds.; Kluwer: Dordrecht, 1991; p 207. (d) Michl, J. *J. Mol. Struct. (Theochem.)* **1992**, *260*, 299. (e) The parameters are defined as in ref 12a: polarizing perturbation (basis energy difference), $\delta_{\text{AB}} = h_{\text{A}} - h_{\text{B}} + (J_{\text{AA}} + J_{\text{BB}})/2$; covalent perturbation (resonance integral), $\gamma_{\text{AB}} = 2h_{\text{AB}} + (A_{\text{A}}/A_{\text{B}})^* + (B_{\text{B}}/B_{\text{A}})$; exchange integral, $K_{\text{AB}} = (A_{\text{A}}/B_{\text{B}})$; $K'_{\text{AB}} = [(J_{\text{AA}} + J_{\text{BB}})/2 - J_{\text{AB}}]/2$.

(1) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ 1969; p 183.

(2) Salem, L.; Rowland, C. *Angew. Chem.* **1972**, *84*, 86; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

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(5) (a) Adam, W.; Reinhard, G.; Platsch, H.; Wirz, J. *J. Am. Chem. Soc.* **1990**, *112*, 4570. (b) Engel, P. S.; Lowe, K. L. *Tetrahedron Lett.* **1994**, 2267.

(6) Adam, W.; Fröhlich, L.; Nau, W. M.; Wirz, J. *J. Am. Chem. Soc.* **1993**, *115*, 9824. In this work, a correlation of calculated NBMO energy gaps with ISC rates was noted that was in line with Salem's second rule if allowance was made for the known⁷ tendency of the AM1 model to underestimate *through-space* relative to *through-bond* coupling. In the meantime, we have established that a direct correlation of the experimental data with STO-3G *ab initio* calculations exists (unpublished results).

(7) Comments by Prof. T. Bally, University of Fribourg, on the paper of Rauhut, G.; Clark, T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1783.

Table 1. Substituent Effects on Triplet Lifetimes ($^3\tau$) of Biradicals **2**

biradical	$^3\tau$ (ns) ^a	biradical	$^3\tau$ (ns) ^a
2a	690 ± 40 ^b	2c	1840 ± 40 ^c
2b	6000 ± 300 ^{b,c}	2d	1750 ± 20 ^b

^a Excitation of the azoalkane in degassed benzene at ~25 °C with a XeF excimer laser (351 nm, 25 ns, 150 mJ); the transient decays were monitored at 580 nm for **2b** and **2c** and at 320 nm for **2a** and **2d**. Errors are standard deviations of the mean (≥8 data points each). ^b Ref 6. ^c Also observed upon 351-nm excitation of the housane.

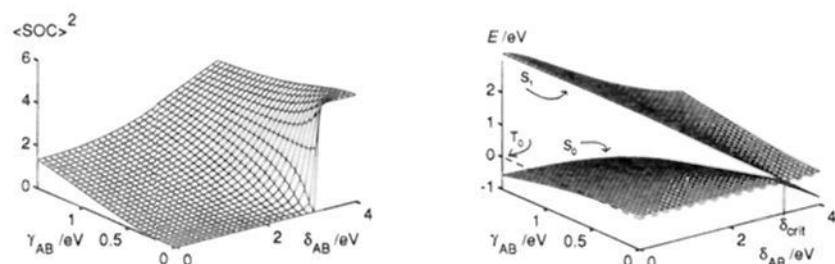


Figure 1. Dependence of the square of the T_0 – S_0 SOC matrix elements (left, arbitrary scale) and the energies of the S_0 and S_1 states relative to $E_T \equiv 0$ (right) on the parameters δ_{AB} , which expresses the basis energy difference, and γ_{AB} , which represents the interaction between the nonbonded, localized orbitals A and B. The parameters $K_{AB} = 0.01$ eV and $K'_{AB} = 1.6$ eV were fixed.

between the T_0 and S_0 wave functions in perturbed biradicals will be directly proportional to the coefficient of the highest-energy zwitterionic wave function, $^1|A^2 + B^2\rangle$, in the singlet state.^{12c} We refer to a localized basis set of two spatially separated NBMO's, A and B. The dependence of the SOC matrix elements on the relevant electronic parameters^{12a,e} K_{AB} , K'_{AB} , γ_{AB} , and δ_{AB} can then be evaluated simply by diagonalization of the 3×3 Hamiltonian matrix, eq 1,^{12a} for the singlet states (diagonal elements are relative to $E_T \equiv 0$)

$$\begin{array}{l} |A^2 - B^2\rangle \\ |A^2 + B^2\rangle \\ |AB\rangle \end{array} \left| \begin{array}{ccc} 2K'_{AB} & \delta_{AB} & 0 \\ \delta_{AB} & 2(K'_{AB} + K_{AB}) & \gamma_{AB} \\ 0 & \gamma_{AB} & 2K_{AB} \end{array} \right| \quad (1)$$

Inspection of eq 1 immediately leads to the (perhaps counterintuitive) conclusion^{12a,c} that polarizing perturbations δ_{AB} induce first-order mixing of the zwitterionic wave functions $^1|A^2 - B^2\rangle$ and $^1|A^2 + B^2\rangle$ only; first-order coupling of the highest-energy ionic wave function $^1|A^2 + B^2\rangle$ to the lowest-energy covalent (dot–dot) wave function $^1|AB\rangle$ is induced only by the covalent perturbation (resonance integral), γ_{AB} . Hence, the electronic contribution to SOC is much more sensitive to covalent than to polarizing perturbations. A sample calculation is displayed in Figure 1. With a localized basis set of two spatially separated NBMO's, A and B, the exchange integral K_{AB} will be quite small (AM1 calculations¹³ on model system **3** afford 0.01 eV) and the quantity K'_{AB} fairly large (1.6 eV). Figure 1 shows the variation of the energies of the two lowest singlet states (right) and of the square¹⁴ of the S_0 – T_0 SOC element (left) upon variation of γ_{AB} and δ_{AB} .

The resonance integral γ_{AB} is quite small for cyclopentane-1,3-diyls due to the near cancellation of *through-space* and *through-bond* couplings (AM1 calculations¹³ on model system **3** afford 0.02 eV).⁵ The relevant portion of the diagram will, therefore, be near the right-wing front edge. The clearcut

message from such a treatment is that nonsymmetrical substitution, which is reflected in the model by an increase of the parameter δ_{AB} , does not lead to a significant increase in the weight of the zwitterion contributions to S_0 and hence has no influence on SOC, until the perturbation δ_{AB} approaches the critical value of $\delta_{crit} = 2[K'_{AB}(K'_{AB} - K_{AB})]^{1/2}$ for S_0 – S_1 crossing (see Figure 1). Before this critical point is reached, the covalent configuration (dot–dot) dominates the ground state wave function S_0 , whereas beyond this critical point, it is a linear combination of the zwitterionic configurations (hole–pair).¹² Note that the triplet state is nearly degenerate with the lowest singlet state as long as $\delta_{AB} < \delta_{crit}$. In the two-electron model, $E_S - E_T \approx 2K_{AB}$ for small values of γ_{AB} ; the AM1 model gives $E_S - E_T = 0.01$ eV for **3**. Therefore, the energy of the lowest singlet state will rapidly drop below that of the triplet state when the perturbation δ_{AB} exceeds δ_{crit} .

The rise in SOC along the left-wing front edge of Figure 1 illustrates the sensitivity towards the parameter γ_{AB} , which increases with the donating ability of the substituents.⁶ On exchange of one of the donors by an acceptor substituent (**2a** → **2c**), the marginal increase of SOC expected from the larger value of δ_{AB} is overcompensated by the decrease of SOC due to the lower value of γ_{AB} which results from the introduction of the acceptor substituent. The net result is thus a longer triplet lifetime (Table 1). Since the slope along the γ_{AB} axis is much steeper than that along the δ_{AB} axis, the polarizing perturbation, δ_{AB} , may be ignored, and the changes in $\log(k_{ISC})$ can be interpreted as an additive effect of donor (faster ISC) and acceptor (slower ISC) substitution.⁶ The same approach appears to hold for the Norrish type II biradicals studied by Caldwell.⁴

Semiempirical calculations (AM1)¹³ on the planar model system **3** confirm that the state S_0 remains overwhelmingly covalent (dot–dot configuration) upon donor–acceptor substitution (MeO/NO₂). This is true even when the substituents are directly attached to the radical centers, as in the planar model system **4** (Table 2, supporting information). Hence, no significant triplet lifetime shortening is to be expected for donor–acceptor substitution!

We tentatively propose the following general guidelines for the effects of electron-donating and -accepting substituents on triplet lifetimes of carbon-centered 1,*n*-biradicals ($3 \leq n \leq 7$, e.g., structures **1**–**4**) whose ISC rates are governed by SOC. (i) The lowest singlet state wave function is insensitive to moderate polarizing perturbations, δ_{AB} . Substituent effects on triplet lifetimes are dominated by the effect of the covalent perturbation (resonance integral), γ_{AB} , which is approximately additive for both symmetrical and unsymmetrical substitution for a given biradical structure. Similarly, γ_{AB} , and hence the rate of ISC, are expected to increase by developing covalent bonding in flexible biradicals.¹⁵ (ii) If the polarizing perturbation increases beyond S_0 – S_1 crossing ($\delta_{AB} > \delta_{crit}$), the singlet state will rapidly fall below the triplet state; hence, rule (i) should hold for localized biradicals whenever the triplet state is known to be the ground state.

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Supporting Information Available: Table 2 (relative contributions of the covalent and zwitterionic configurations in the S_0 wave function calculated by AM1 for model systems **3** and **4**) (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(13) Time-dependent perturbation theory predicts that k_{ISC} is proportional to the square of the SOC matrix element; see either Fermi's Golden Rule (Robinson, G. W. In *Excited States*; Lim, E., Ed.; New York: Academic Press, 1974; p 1) or the Landau–Zener model (Landau, L. *Phys. Z. Sowjet.* **1932**, *2*, 46. Zener, C. *Proc. R. Soc. London A* **1932**, *139*, 696).

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