J. Am. Chem. Soc. **1996,** *118,* 249−250

New Approaches to Singlet−Triplet Spin−Orbit Coupling in Photochemistry and Diradical Chemistry. Mechanistic and Exploratory Organic Photochemistry[1,2]

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Received September 5, 1995

There is a widespread belief that excited state reactivity is controlled by the probability of excited state to ground state transitions, either at points where there is a conical intersection,[3] in the case of singlet reactions, or where there is enhanced intersystem crossing to ground state, in the case of triplets. A contrary view[3a,4] has noted that, for complex organic reactions, an equally important factor is the nature of the reaction hypersurface and the tendency for an excited state to traverse minimum energy pathways to seek out such points of radiationless decay. Where energy minima do occur and can be reached by reacting triplets, it is important to assess the rate of intersystem crossing. Most commonly, this is controlled by spin−orbit coupling (SOC), the interaction of electron spin with the angular orbital momentum in a transition between triplet and singlet states.

Recently we have turned to quantitative assessment of SOC factors. A limitation has been the lack of availability of requisite computational methodology. Specifically, one was faced with the choice of using a one-electron (1e) SOC operator with a satisfactory set of "active MOs",[5a,b] or a complete one- and two-electron (2e) operator with a restricted HOMO−LUMO active space.[6] Often it is suggested that addition of the 2e component of the operator leads to a diminution of the SOC.[6]

We now report (a) the ability to utilize the best of both SOC approaches using a 1e + 2e SOC operator in conjunction with the choice of a variable active space composed of MCSCF MOs; (b) the relative importance of the approximations of using just a 1e SOC operator with an extended active space versus using a full 1e + 2e operator and just HOMO−LUMO MOs; (c) the extension, using the full 1e + 2e operator, of our concept of dissecting SOC into contributions between orbital pairs, showing how the total SOC develops; (d) the application of our treatment to 1,*n*-alkanediyls, where a unique alternation of SOC with the parity of the number of intervening bonds between the odd-electron centers is found; (e) definition and consideration of the direct through-space versus through-bond source of SOC; (f) the finding that even with the 1e + 2e operator, SOC derives mainly from interaction between geminal orbitals rather than the formal odd-electron ones.

Table 1. Dependence of SOC on Active Space and Dependence on Inclusion of the Two-Electron Operator (RMS Values, (cm^{-1}))

			SOC RMS[c]			
		scaled	1e operator		1e + 2e operator	
compound	active space[a]	value, 3-21G[b]	STO-3G	3-21G	STO-3G	3-21G
oxyallyl	[2,2]		0.10708		0.06129	
	[4,4]	0.2778	0.82986	0.44012	0.42738	0.24354
propanediyl	[2,2]		2.43000		1.29110	
	[4,4]	1.8783	2.46750	3.09920 (3.25310)[d]	1.31170	1.66620 (1.80730)[d]
butanediyl	[2,2]		0.00001		0.00001	
	[4,4]	0.00001	0.00009	0.00002	0.00004	0.00001
pentanediyl	[2,2]		0.10459		0.05447	
	[4,4]	0.24760	0.23802	0.40739	0.12689	0.20966
hexanediyl	[2,2]		0.00149		0.00076	
	[4,4]	0.00000	0.00001	0.00000	0.00000	0.00000
heptanediyl	[2,2]		0.10633		0.05514	
	[4,4]	0.02152	0.01064	0.03541	0.00748	0.01837
octanediyl	[2,2]		0.00001		0.00000	
	[4,4]		0.00002		0.00001	

[a] Number of electrons in number of MOs. [b] Scaled 1e method of Gordon et al.[5d] [c] 1e or 1e + 2e operator spin−orbit coupling values. [d] 6-31G*.

Previously we have reported on the concept of dissection of SOC contributions due to interaction of orbital pairs. At the time, we were restricted to use of a 1e operator. Our basic idea was to dissect the SOC components into hybrid orbital pairs around the molecule of interest.[2,7]

In our present work, we developed computational ability using the full 1e + 2e SOC operator. Again, we have made use of the Weinhold hybrid orbitals,[8] which are useful in organic chemistry since these are directed along traditional bonds. Also, as spin−orbit contributions are computed, we accumulate localized contributions; in this we segregate the 1e and 2e components as well as the $M_s = +1, 0, -1$ and Lx, Ly, Lz components. For convenience, we incorporated our programming into the GAMESS package, making considerable use of code obtained from Prof. T. Furlani.[6]

In determining the success of the methodology, we applied our attention to oxyallyl and a series of 1,*n*-alkanediyls. The results are listed in Table 1. We note that the dominant contributors to SOC are geminal pairs of hybrid orbitals which have an inter-orbital angle close to 90°.

Turning to the matter of the two common approximations, namely use of a 1e operator versus use of a limited HOMO−LUMO active space, one sees that a limited active space may afford only a minor fraction of the SOC, while the 2e operator modifies the overall SOC only fractionally. Thus, omission of the 2e operator leads to a more minor error,[5e] contrasted with the orders of magnitude error possible[2] when a two-MO (e.g., HOMO−LUMO) approximation is made. This is especially true for oxygen-containing molecules having a nonbonding p_y orbital. A major contribution then comes from the $p\pi - p_y$ SOC interaction, but appearance of the p_y orbital often occurs only in MOs much below the HOMO. The oxyallyl moiety is of particular interest, since it is the penultimate excited species postulated for the "type A" (Lumi) cyclohexadienone rearrangement[4] and is known[9] experimentally to intersystem cross to a ground state S_0 oxyallyl zwitterion, which then undergoes a

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(1) Publication 179 of our photochemical series and 238 of the general sequence.

(2) For our previous publication, see: Zimmerman, H. E.; Kutateladze, A. G. *J. Org. Chem.* **1995**, *60*, 6008−6009.

(3) (a) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1564−1565. (b) Bernardi, F.; Robb, M. *J. Am. Chem. Soc.* **1995**, *117*, 6944−6953. (c) Bernardi, F.; Robb, M. *J. Am. Chem. Soc.* **1990**, *112*, 1737−1745.

(4) (a) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* **1962**, *84*, 4527−4540. (b) Zimmerman, H. E. A New Approach to Mechanistic Organic Photochemistry. In *Advances in Photochemistry*; Noyes, A., Jr., Hammond, G. S., Pitts, J. N., Jr., Eds.; Interscience: New York, 1963; Vol. 1, pp 183−208. (c) Zimmerman, H. E. *Seventeenth National Organic Symposium of the American Chemical Society*; Bloomington, IN; ACS: Washington, DC, 1961; 1961; pp 31−41.

(5) (a) Koseki, S.; Schmidt, M.; Gordon, M. S. *J. Phys. Chem.* **1992**, *96*, 10768−10772. (b) The GAMESS program[6b] contains such a spin−orbit coupling module.[5c] (c) Schmidt, M. W.; et al. *J. Comput. Chem.* **1993**, *14*, 1347−1363. (d) However, note the elegant technique of Gordon et al.[5e] for scaling the 1e operator to approximate the 2e results (see Table 1). (e) Koseki, S.; Gordon, M. S.; Schmidt, M. W.; Matsunaga, N. *J. Phys. Chem.* **1995**, *99*, 12764−12772.

(6) (a) Furlani, T. R.; King, H. F. *J. Chem. Phys.* **1985**, *82*, 5577−5583. (b) Furlani, T. R. Ph.D. Thesis, University of Buffalo, NY, 1984.

(7) Zimmerman, H. E.; Kutateladze, A. G.; Maekawa, Y.; Mangette, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 9795−9796.

(8) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926. (b) Here we employed Pre-NHO's with orthogonalized coefficient vectors. These have the advantage of being completely localized without the usual NBO tails. See supporting information.

(9) (a) Zimmerman, H. E.; Lynch, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 7745−7756. (b) Zimmerman, H. E.; Lamers, P. H. *J. Org. Chem.* **1989**, *54*, 5788−5804. (c) Zimmerman, H. E.; Crumrine, D. S.; Döpp, D.; Huyffer, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 434−445. (e) Schultz, A. G.; Plummer, M. *J. Org. Chem.* **1989**, *54*, 2112−2117.

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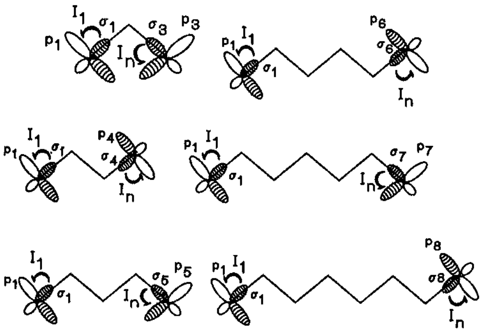

Figure 1. Alkanediyls basis set terminal geminals for the diyls defined. The local SOC integrals I_1 and I_n, with counter clockwise sp^2 → p rotation, are negative with changing signs and positive with no sign change.

ground state rearrangement to the bicyclo[3.1.0] photoproduct. We see in Table 1 that use of two bonding and two antibonding MOs for oxyallyl affords a SOC contribution which is considerably larger than that resulting from use of only HOMO−LUMO. Using a limited (i.e., HOMO−LUMO) active space thus omits inclusion of the dominant $p\pi-p_y$ geminal contribution. For 1,n-alkanediyl diradicals, the smaller active space is reasonably adequate.

A particularly striking result comes from the 1,n-diyls, all in an *s-trans* conformation (see Figure 1). Thus, the diyls with an even number of C−C bonds and C_s symmetry (namely, 1,3-propanediyl, 1,5-pentanediyl, and 1,7-heptanediyl) exhibit large SOC, which diminishes as the separation between the odd-electron centers increases. However, the diyls with an odd number of C−C bonds and C_2 symmetry (namely, 1,4-butanediyl, 1,6-hexanediyl, and 1,8-octanediyl) have negligible SOC values, which also vanish with increasing chain length. Both the 1e and 2e contributions follow this pattern, as can be seen in Table 1.

For an understanding of this behavior, we turn to eq 1, which gives the SOC contribution resulting from SOC interaction at each of two centers, 1 and n, and two localized hybrid orbitals at each center. In the diyls, the terminal hybrid orbitals are σ and close to p in nature. The C's are coefficients weighting these hybrid orbitals in MOs k and l. I_1 and I_n are integrals for centers 1 and n, giving the SOC contributions for the two hybrids at a carbon. Each of these integrals is maximized at a 90° inter-orbital angle and is null at 0°. In the full computation, these contributions are summed over all hybrid pairs at all molecular centers and for all pairs of MOs K and L. Additionally, the terms are weighted by coefficients M, giving the weight of the Slater determinants in each configuration and the weight of each configuration in the states of interest. The MOs span the entire molecular chain (i.e., through-bond). But since the 1,n-diyls have most of the SOC contributed by HOMO and LUMO, we can use just K for HOMO and L for LUMO to illustrate the dependence of the total SOC on the even or odd number of carbons in the diyl.

$$\mathrm{SOC} = M\left[\begin{vmatrix} C_{\mathrm{p}1L} & C_{\sigma 1L} \\ C_{\mathrm{p}1K} & C_{\sigma 1K} \end{vmatrix} I_1 + \begin{vmatrix} C_{\mathrm{p}nL} & C_{\sigma nL} \\ C_{\mathrm{p}nK} & C_{\sigma nK} \end{vmatrix} I_n\right] \qquad (1a)$$

$$\mathrm{SOC} = M[D_1 I_1 + D_n I_n] \qquad (1b)$$

It is readily shown that the determinants D_1 and D_n have opposite signs, independent of the length of the diyls, while $I_1 = I_n$ for an even number of carbons, and $I_1 = -I_n$ for an odd number of carbons. The net result is that for an even number of carbons, the two terms cancel and afford zero SOC, while for an odd number of carbons, the two terms have like signs and add, providing net SOC.

Table 2. SOC Dissections (Active Space of 4)

1,n-alkanediyl	hybrid pair (3-21G)[a]	angle between hybrids	1e SOC		1e + 2e SOC	
			z[b]	RMS	z[b]	RMS
1,3-propanediyl	$p_3-\sigma_{32}$	95.49	−1.464	1.464	−1.214	1.214
	$p_1-\sigma_{12}$	95.49	−1.464	1.464	−1.214	1.214
	p_1-p_3	81.21	0.083	0.083	0.030	0.030
1,4-butanediyl	$p_4-\sigma_{43}$	95.62	−0.282	0.282	−0.230	0.230
	$p_1-\sigma_{12}$	95.62	0.282	0.282	0.230	0.230
	p_1-p_4	0.0	*c*	*c*	*c*	*c*
1,5-pentanediyl	$p_5-\sigma_{54}$	95.63	−0.105	0.105	−0.087	0.087
	$p_1-\sigma_{12}$	95.63	−0.105	0.105	−0.087	0.087
	$\sigma_{34}-\sigma_{32}$	109.40	−0.083	0.083	−0.075	0.075
1,6-hexanediyl	$\sigma_{45}-\sigma_{43}$	109.85	0.024	0.024	0.022	0.022
	$\sigma_{34}-\sigma_{32}$	109.85	−0.024	0.024	−0.022	0.022
	$p_1-\sigma_{12}$	94.11	0.015	0.015	0.010	0.010
	$p_6-\sigma_{65}$	94.11	−0.015	0.015	−0.010	0.010
1,7-heptanediyl	$\sigma_{34}-\sigma_{32}$	109.47	−0.018	0.018	−0.017	0.017
	$\sigma_{56}-\sigma_{54}$	109.47	−0.018	0.018	−0.017	0.017
	$\sigma_{45}-\sigma_{43}$	109.53	−0.004	0.004	−0.003	0.003
	... some C−H ...					
	$p_1-\sigma_{12}$	95.62	*c*	0.0018	*c*	0.0022
	$p_7-\sigma_{76}$	95.62	*c*	0.0018	*c*	0.0022
1,8-octanediyl	$p_1-\sigma_{12}$	95.62	*c*	0.0015	*c*	0.0012
	$p_1-\sigma_{12}$	95.62	*c*	0.0015	*c*	0.0012
	$\sigma_{56}-\sigma_{54}$	109.53	*c*	0.0014	*c*	0.0012
	$\sigma_{45}-\sigma_{43}$	109.53	*c*	0.0014	*c*	0.0012

[a] The subscript numbering refers to atoms in the chain. [b] Only the z-components since the molecules were $x-y$ oriented. [c] Neglible values.

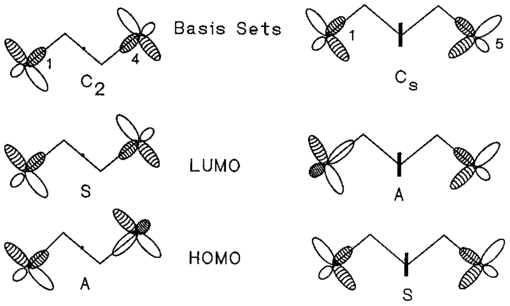

Figure 2. Largest contributors to the spin−orbit coupling of two diyls. C_2 symmetry for butanediyl and C_s symmetry for pentanediyl.

The useful empirical relation of the SOC on the sine of the angle between two odd-electron p-orbitals[10] derives from the fact that each MO extends through the entire molecule, with the consequence that the relative orientation of terminal p-orbitals is controlled by the relative geminal orientation at the individual centers, leading to a maximum SOC at a 90° orientation between the p-components of each geminal. Note the dissection in Table 2. Figure 2 gives the basis (definitional) set of terminal hybrid orbitals and HOMO and LUMO pictorially for the examples of butanediyl and pentanediyl.[11]

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged. We thank Prof. T. Furlani of the University of Buffalo for supplying source code.

Supporting Information Available: Outline of NBO dissection programming (7 pages). 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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[10] (a) Doubleday, D.; McIver, J. W.; Page, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 6533. (b) Carlacci, L.; Doubleday, D.; Furlani, T.; King, H. *J. Am. Chem. Soc.* **1987**, *109*, 5323.

[11] Also, the odd-membered diyls have more appreciable singly promoted singlet configurations, while these are vanishing for the even members.