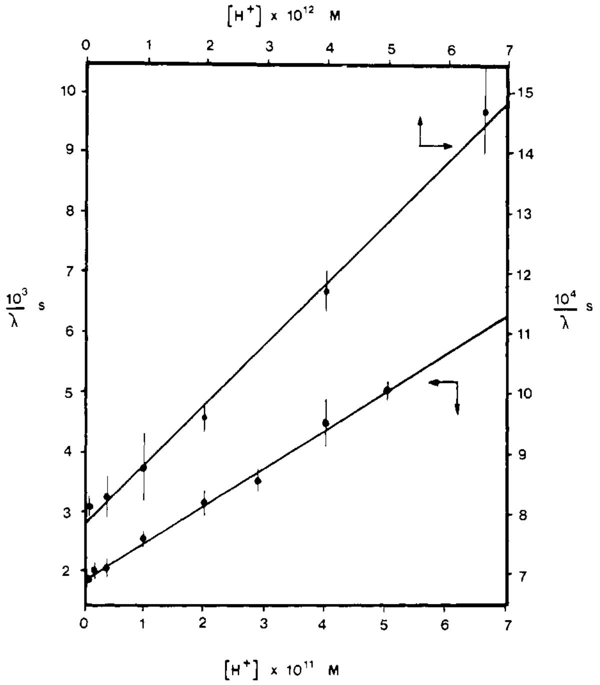


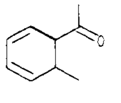
Figure 1. Plot of reciprocal of first-order decay rate constants for the dienolates **3a** and **3b** in water against proton concentration. Upper line **3b**; lower line **3a**.

Fitting values of λ measured at low $[H^+]$ to eq 3 for both **1a** and **1b** (Figure 1) yields values of K and k_β of $(3.80 \pm 0.17) \times 10^{-11}$ and 539 ± 17 s^{-1} for **1a** and $(1.07 \pm 0.5) \times 10^{-11}$ and 1184 ± 21 s^{-1} for **1b**, respectively. The values of the constants corresponding to K and k_β for acetophenone enolate are 4.6×10^{-11} and 7×10^3, respectively.[8]

By use of the values of K obtained, the values of d were calculated and plotted against λ according to eq 4 (Figure 2) to yield k_σ and a further estimate of k_β. For **1a**, k_σ obtained from the intercept is indistinguishable from zero within error, corresponding to an upper limit of ca. 5 s^{-1}, while for **1b** k_σ is 40 ± 13 s^{-1}. The gradients of the lines yield values of k_β identical with those determined at high pH from eq 3.

The magnitude of k_σ for **1b** indicates a dienol lifetime in water at room temperature of ca. 0.02 s, while the value for **1a** is at least an order of magnitude greater.[10] The lifetime of **1b** is in contrast to the lifetimes of simple enols which are stable, observable species in the absence of catalysts.[11] This difference supports the proposition that dienols can reketonize by a noncatalyzed pathway (the proposed 1,5-sigmatropic hydrogen shift) whereas for simple enols no noncatalyzed pathway is available (the necessary antarafacial transition state for a 1,3-hydrogen shift is unattainable for first-row elements).

The values of k_σ for **2a** and **2b** are much slower than those for the analogous process of the dienols produced photochemically from o-alkyl aromatic ketones. In the case of **6a** this process occurs at a rate of 10^6 s^{-1} in water.[5] The large difference presumably reflects two factors: in **2a** and **2b** the dienol is free to adopt a transoid conformation unfavorable for the 1,5-hydrogen shift, whereas in the aromatic system the dienol is held in a cisoid orientation; also, in the aromatic system the reketonization reaction of the dienol is much more exothermic than is the case with **2** as the system is also rearomatizing. Application of Hammond postulate arguments predict that **6a** should therefore reketonize faster than **2**.



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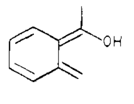
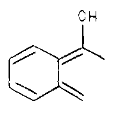


6a



6b

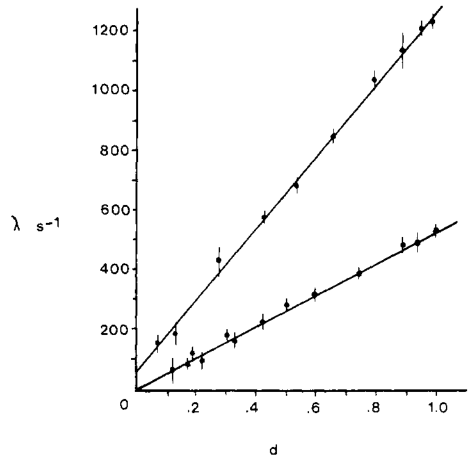


Figure 2. Plot of first-order decay rate constants for the dienolates **3a** and **3b** in water against fraction of dienolate present in the dienol-dienolate equilibrium. Upper line **3b**; lower line **3a**.

The larger value of k_σ for **1b** as compared with **1a** suggests that the sterically hindering methyl groups in **1b** encourage the adoption of a cisoid conformation of the dienol and implies that the dienol **1a** is more stable in the transoid orientation. This is supported by the observed effects of substitution upon the efficiency of photochemical deconjugation of unsaturated esters[6] and by the experimentally observed preferential adoption of transoid conformations[12] by dienes.

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(10) It could be argued that k_σ for **2a** is infinite—i.e., there is no 1,5-shift mechanism for this dienol; however, **1a** photodeconjugates only if base is present, confirming that an uncatalyzed reketonization pathway exists.

(11) Capon, B.; Siddhanta, A. K. *Tetrahedron Lett.* **1982**, *23*, 3199. Henne, A.; Fischer, H. *Helv. Chim. Acta* **1975**, *58*, 1598.

(12) "Electronic Absorption Spectra and Geometry of Organic Molecules"; Suzuki, H., Ed.; Academic Press: New York, 1967. Mui, P. W.; Grunwald, E. *J. Am. Chem. Soc.* **1982**, *104*, 6562.

Nanosecond Flash Photolysis Studies of Intersystem Crossing Rate Constants in Biradicals: Structural Effects Brought About by Spin-Orbit Coupling

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This paper concerns the structural effects of spin-orbit coupling (SOC) as a mechanism of intersystem crossing (isc) in triplet-derived biradicals. First we show that SOC is strongly enhanced in biradicals with an acyl terminus relative to biradicals with only hydrocarbon termini. Second, we present evidence that, even for long chains, biradicals containing an acyl terminus prefer to undergo isc in conformers with small end-to-end distances. This appears to be a direct result of the dominance of SOC over electron-nuclear hyperfine coupling (HFC) in the isc process.

We have measured lifetimes (τ) of the biradicals in eq 1-3 by monitoring their nanosecond transient UV absorption at 320 nm.[1] All biradicals were characterized by their transient UV absorption

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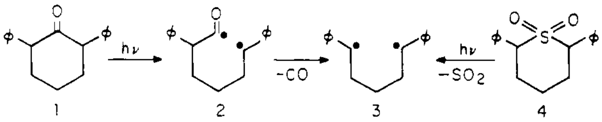
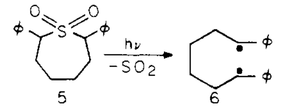
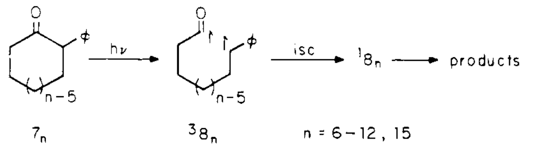
(1) Excitation sources were either a Lambda Physik excimer laser operating at 248 or 308 nm (base-line pulse width 20 ns) or a Quanta-Ray Nd-YAG laser, frequency-quadrupled to 266 nm (fwhm 6 ns). The transient absorption apparatus utilizing the excimer laser has been described: Turro, N. J.; Aikawa, M.; Butcher, J. *J. Quant. Electron.* **1980**, *QE-16*, 1218.



(1)



(2)



(3)

spectra in Ar-saturated MeOH or CH_3CN (λ_{max} 308 ± 2, 320 ± 2 nm,[2] identical with that of the 1-phenylethyl radical **9**[3]), and by the invariance of τ to addition of isoprene,[4] which, on our time scale, quenches the triplet precursor to the biradical but not the biradical itself.[5] Table I lists results for the biradicals in eq 1 and 2. At 25 °C in MeOH, **1**[6] produces a transient with τ = 900 ± 50 ns, assigned to **3**.[7] The Arrhenius parameters for decarbonylation of 2-phenylpropanoyl to **9**,[8] are E_a = 6.2 ± 0.5 kcal and log A = 12.2 ± 0.5, which implies that **2** decarbonylates within the laser pulse. The assignment of **3** was confirmed by independent generation from **4**[9a,10] in CH_3CN (Table I) to give a 920 ± 50 ns transient with λ_{max} = 308 ± 2, 320 ± 2 nm.

1 was examined from +60 to -83 °C in MeOH. Down to -40 °C the decay fits well to a single exponential and yields Arrhenius parameters E_a = 0.85 ± 0.15 kcal/mol and log (A/s^{-1}) = 6.7 ± 0.2. Below -40 °C a fast component appears in the decay trace, which becomes the dominant component around -70 °C. At -83 °C the new species has τ = 121 ± 10 ns with λ_{max} = 310 ± 2, 322 ± 2 nm, and τ does not decrease with added isoprene, up to 0.09 M. We attribute this signal to **2**. Indeed, the Arrhenius parameters for the decarbonylation of 2-phenylpropanoyl[8] predict that at -83 °C **2** should be the only biradical available for study on the timescale of our experiment. Caldwell[11] has recently reported τ = 50 ± 3 ns for $\mathbf{8}_6$ in MeOH at 25 °C, and we have measured 58 ± 6 ns. At -80 °C in MeOH the lifetime of $\mathbf{8}_6$ becomes 112 ns, close to the 121-ns lifetime of **2** (Table I).

To compare acyl-benzyl vs. benzyl-benzyl biradicals of the same chain length we synthesized **5**,[9b] a precursor to the 1,6-biradical **6**. Table I shows that the lifetime of **6** is 1080 ± 50 ns, even slightly longer than that of **3**.

Taken together, the above results suggest a large intrinsic difference in the lifetimes of acyl-benzyl vs. benzyl-benzyl biradicals, at least for 1,5- and 1,6-biradicals. Evidence has accumulated[5,12-18] that the lifetimes of triplet biradicals at 25 °C are governed by isc to the singlet biradical, rather than by subsequent product formation on the singlet potential energy surface. Thus, at 25 °C τ^{-1} is the isc rate constant, k_{isc}, and our data imply that k_{isc} is greatly enhanced by the presence of an acyl terminus. Although HFC and SOC both contribute to isc, replacement of a benzylic by an acyl terminus *decreases* the total HFC in the

Table I. Biradical Lifetimes and Experimental Conditions

precursor	λ, nm[a]	solvent	T, °C	biradical	τ, ns
1	248	CH_3OH	25	**3**	900 ± 50
1	248	CH_3CN	25	**3**	874 ± 50
4	266	CH_3CN	25	**3**	920 ± 50
4	308[b,c]	CH_3CN	25	**3**	920 ± 50
5	308[b,c]	CH_3CN	25	**6**	1080 ± 50
1	248	CH_3OH	-83	**2**	121 ± 10
$\mathbf{7}_6$	308	CH_3OH	-80	$\mathbf{8}_6$	112 ± 10
$\mathbf{7}_6$	248	CH_3OH	25	$\mathbf{8}_6$	58 ± 6
$\mathbf{7}_6$[d]	266	CH_3OH	25	$\mathbf{8}_6$	50 ± 3[d]

[a] Wavelength used to excite the precursor. [b] Triplet-sensitized with 0.35 M acetone using 0.03 M sulfone. Transient absorption spectra had λ_{max} = 320 ± 2 nm (see ref 2). [c] Acetone sensitization of acyclic dibenzylic sulfones produces triplet radical pairs: Givens, R.; Hrinczenko, B.; Liu, J.; Matuszewski, B.; Tholen-Collison, J. *J. Am. Chem. Soc.* **1984**, *106*, 1779. [d] From ref 11.

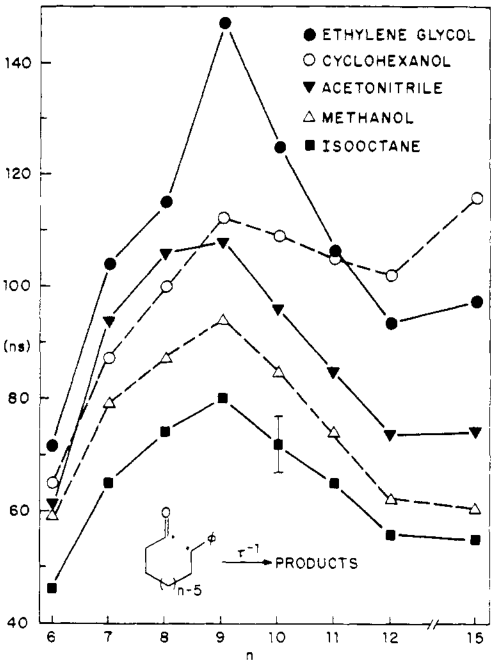


Figure 1. Lifetimes of the biradicals **8** as a function of chain length and solvent at 20 °C. Each point is an average of 7-10 measurements and is good to ±5 ns (±2 standard deviations, 95% confidence level). A representative error bar is shown.

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(2) With 308-nm excitation the λ_{max} at 308 nm was obscured by the laser light.

(3) Gould, I.; Zimmt, M.; Turro, N. J.; Baretz, B.; Lehr, G. *J. Am. Chem. Soc.* **1985**, *107*, 4607.

(4) On addition of up to 0.03 M isoprene, τ remained constant to within 5%.

(5) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252.

(6) Synthesized by refluxing dibenzyl ketone and 1,3-dibromopropane with *t*-BuOK in *t*-BuOH.

(7) 1,1,5,5-Tetraphenylpentane-1,5-diyl in benzene has recently been reported to have τ = 900 + 200 ns. Barton, D. H. R.; Charpiot, B.; Ingond, K. U.; Johnston, L. J.; Motherwell, W. B.; Scaiano, J. C.; Stanforth, S. *J. Am. Chem. Soc.* **1985**, *107*, 3607.

(8) Turro, N. J.; Gould, I.; Baretz, B. *J. Phys. Chem.* **1983**, *87*, 531.

(9) (a) Synthesized from glutaryl dichloride as follows: (1) $AlCl_3$, benzene; (2) $NaBH_4$; (3) concentrated HCl; (4) Na_2S, DMF; (5) MCPBA. (b) Same sequence, starting with adipoyl dichloride.

(10) Previous time-resolved work on acyclic dibenzylic sulfones shows that both benzylic racicals are created within the laser pulse (<20 ns). See: Gould, I.; Tung, C.-H.; Turro, N. J.; Givens, R.; Matuszewski, B. *J. Am. Chem. Soc.* **1984**, *106*, 1789.

(11) Caldwell, R. A.; Sakuragi, H.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 2471.

(12) (a) Closs, G.; Doubleday, C. *J. Am. Chem. Soc.* **1973**, *95*, 2735. (b) Closs, G. *Adv. Magn. Reson.* **1975**, *7*, 1.

(13) (a) Doubleday, C. *Chem. Phys. Lett.* **1979**, *64*, 67. (b) Doubleday, C. *Ibid.* **1981**, *77*, 131. (c) Doubleday, C. *Ibid.* **1981**, *79*, 375. (d) Doubleday, C. *Ibid.* **1981**, *81*, 164. (e) Doubleday, C. *Ibid.* **1982**, *85*, 65.

(14) (a) DeKanter, F.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759. (b) DeKanter, F.; den Hollander, J.; Huizer, A.; Kaptein, R. *Mol. Phys.* **1977**, *34*, 857.

(15) (a) Bartlett, P.; Porter, N. *J. Am. Chem. Soc.* **1968**, *90*, 5317. (b) Schultz, P.; Dervan, P. *J. Am. Chem. Soc.* **1982**, *104*, 6660. (c) Wagner, P. J. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 381.

(16) (a) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629. (b) Caldwell, R. A.; Creed, D. *J. Phys. Chem.* **1978**, *82*, 2644. (c) Caldwell, R. A.; Sakuragi, H.; Majima, T. *J. Am. Chem. Soc.* **1984**, *106*, 2471.

(17) (a) Scaiano, J. C. *Tetrahedron* **1982**, *38*, 819. (b) Scaiano, J. C.; Lee, C.; Chow, Y.; Maciniak, B. *J. Phys. Chem.* **1982**, *86*, 2452.

(18) (a) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 3586. (b) Closs, G. L.; Redwine, O. D. *J. Am. Chem. Soc.* **1985**, *107*, 4543.

biradical by about 50% while greatly *increasing* k_{isc}. We infer that the presence of an acyl terminus increases SOC in the biradical (presumably because of spin density on oxygen) and that SOC is the dominant isc mechanism in acyl–benzyl biradicals.[19]

To investigate this further, we measured τ for the biradicals **8** in a variety of solvents at 20 °C (Figure 1). The solvents cover a range of properties, but there is no monotonic dependence of τ on $E_T(30)$,[20] dielectric constant, or viscosity. The important feature of Figure 1 is that the qualitative pattern of τ vs. n is essentially independent of solvent,[21] which indicates an intrinsic molecular effect rather than a medium effect.

The pattern of isc lifetimes in Figure 1 is strikingly similar to the published data on cyclization reactions.[22c] Evidence on strain energies of cycloalkanes and the rates and equilibria of cyclization processes show that cyclization is favorable for $n = 6$, becomes most unfavorable for $n = 8$–10, and then more favorable for larger rings.[22c,d] The quantitative features of the curve depend on the process being studied and on the nature of the termini, but they are all qualitatively similar. Figure 1 clearly resembles a cyclization process and *suggests that isc in acyl–benzyl biradicals* **8** *requires a nearly cyclic conformation with small end-to-end distance.*

The physical basis for this hypothesis is as follows. For efficient isc to occur, ^{3}**8** must adopt a structure where the singlet (S) and triplet (T) surfaces intersect and where a large isc matrix element couples the S and T states. CIDNP studies[13] and ab initio calculations on tri-[23] and tetramethylene[24] suggest that S–T interactions are induced by internal rotations and are so numerous and ubiquitous that they cannot be avoided. Thus it is reasonable to assume that every biradical conformer is in the vicinity of an S–T intersection. However, the isc matrix element depends strongly on the biradical conformation. The isotropic HFC contribution to the isc matrix element is ca. 0.01 cm^{-1} in all conformers, but SOC decreases approximately exponentially with increasing end-to-end distance R[25] and can be on the order of 1 cm^{-1} for specific geometries at short R.[26] This gives rise to a simple model in which isc is efficient only if the biradical adopts a nearly cyclic conformer with small R where SOC can be very large. Data on chain dynamics[22] applied to **8** imply that ^{3}**8** equilibrates among chain conformers prior to isc. Therefore k_{isc} should depend on the *equilibrium fraction* of triplet conformers with small R. This fraction should to some degree reflect the strain energy of the appropriate cyclic compound. *We propose that the pattern of isc lifetimes in Figure 1 qualitatively parallels the fraction of* ^{3}**8** *conformers with small R.* There may be several such conformers that contribute. In the classification scheme discussed by Winnik,[22c] isc in ^{3}**8** at 25 °C resembles a cyclization process which is conformationally rather than kinetically controlled.

Acknowledgment. We thank the National Science Foundation and the Air Force Office of Scientific Research for support of this research. C.D. acknowledges NSF Grant CHE8421140 for partial support. We also thank Janice Hicks for useful discussions and Richard A. Caldwell, Gerhard L. Closs, and J. C. Scaiano for communicating their results prior to publication.

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(19) The π-acyl radical lies ca. 1 eV above the bent form and is probably not involved: (a) Johns, J.; Priddle, S.; Ramsay, D. *Discuss. Faraday Soc.* **1963**, *35*, 90. (b) Brown, J.; Ramsay, D. *Can. J. Phys.* **1975**, *53*, 2232. (c) Baird, N. C.; Kathpal, H. *Can. J. Chem.* **1977**, *55*, 863. (d) Yamashita, K.; Kaminayama, M.; Yamabe, T.; Fukui, K. *Chem. Phys. Lett.* **1981**, *83*, 78.

(20) Reichardt, C. In "Molecular Interactions"; Ratajczak, H., Orville-Thomas, W., Eds.; Wiley: New York, 1982; Vol. 3, p 241.

(21) Cyclohexanol is highly viscous (49 cP, compared to 13.6 cP for ethylene glycol) and shows a different τ vs. n pattern at large n. The effect of viscosity and temperature on τ will be examined in a separate publication.

(22) (a) Nairn, J.; Braun, C.; Caluwe, P.; Szwarc, M. *Chem. Phys. Lett.* **1978**, *54*, 469. (b) Nairn, J.; Braun, C. *J. Chem. Phys.* **1981**, *74*, 2441. (c) Winnik, M. A. *Chem. Rev.* **1981**, *81*, 491. (d) Winnik, M. A. *Acc. Chem. Res.* **1985**, *18*, 73.

(23) (a) Doubleday, C.; McIver, J.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533. (b) Goldberg, A.; Dougherty, D. *J. Am. Chem. Soc.* **1983**, *105*, 284.

(24) Doubleday, C.; McIver, J.; Page, M. *J. Am. Chem. Soc.*, in press.

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

(26) (a) Furlani, T.; King, H. F. *J. Chem. Phys.* **1985**, *82*, 5577. (b) Furlani, T. Ph.D. Thesis, State University of New York at Buffalo, 1984.

Magnetic Field Effect on the Intersystem Crossing Rate Constants of Biradicals Measured by Nanosecond Transient UV Absorption

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We report the first observation of a magnetic field effect on the total intersystem crossing (isc) rate constants of biradicals. This allows a simple measurement of the *separate contributions of spin–orbit coupling (SOC) and electron–nuclear hyperfine coupling (HFC) to the isc rate constant.* Our quantitative results affirm the conclusion of the accompanying paper[1] that SOC is the dominant isc mechanism in biradicals with an acyl terminus. The results suggest a revision of the accepted interpretation of biradical CIDNP.[2-4]

Excitation of **1**[5] at 308 nm with an excimer laser produces transient absorption signals which show single-exponential decay and are assigned to ^{3}**2**[1] (Scheme I). At 25 °C in Ar-saturated MeOH the isc rate constants, k_{isc}, (±3%) are 1.06×10^7, 1.23×10^7, and 1.49×10^7 s^{-1} for $\mathbf{2}_{10}$, $\mathbf{2}_{11}$, and $\mathbf{2}_{12}$, respectively.[1]

When a magnetic field H is applied to the sample with a pair of Helmholtz coils, k_{isc} varies significantly (Figure 1).[6] As H increases, k_{isc} increases from its value in the earth's field, $k_{isc}{}^0$, to a maximum, $k_{isc}{}^{max}$, at $H = H_{max}$. It then decreases to an apparently asymptotic value, $k_{isc}{}^{asympt}$, with $k_{isc}{}^{asympt} < k_{isc}{}^0$. At our maximum field of 2100 G, $\mathbf{2}_{10}$ does not attain its asymptotic value. As the chain length of **2** decreases, H_{max} moves to higher field. For $\mathbf{2}_{12}$, $\mathbf{2}_{11}$, and $\mathbf{2}_{10}$, $H_{max} = 30 \pm 10$, 120 ± 20, and 600 ± 100 G, respectively. Relative to $k_{isc}{}^0$, the overall variations in k_{isc} are +13% at H_{max} for all biradicals, and −9% (for $\mathbf{2}_{11}$) and −16% (for $\mathbf{2}_{12}$) in the asymptotic region.

Figure 1 bears a strong resemblance to the CIDNP field dependence curves obtained from cycloalkanones,[2a] and both results are expected to arise from the same phenomenon. The field H splits ^{3}**2** into T_{+1}, T_0, and T_1 levels. The accepted interpretation of CIDNP is that the singlet state S lies below T, and the CIDNP intensity is maximized when H is adjusted to produce a T_{-1}–S degeneracy.[2-4] This value of H ($=H_{max}$) then corresponds to the S–T energy gap, $E_S - E_T$, averaged over the biradical lifetime.[2-4] The increase in H_{max} with decreasing biradical chain length reflects the decrease in mean end-to-end distance and hence an increase in the S–T gap.[2-4] The T_{-1}–S degeneracy produces a *local maximum in* k_{isc}, which is monitored by CIDNP indirectly as the *difference* of k_{isc} for the α and β nuclear spin states *and which we have now observed directly via transient UV absorption.* As

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(1) Zimmt, M.; Doubleday, C.; Gould, I.; Turro, N. J. *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) (a) Closs, G.; Doubleday, C. *J. Am. Chem. Soc.* **1973**, *95*, 2735. (b) Closs, G. *Adv. Magn. Reson.* **1975**, *7*, 1.

(3) (a) Doubleday, C. *Chem. Phys. Lett.* **1979**, *64*, 67. (b) Doubleday, C. *Ibid.* **1981**, *77*, 131. (c) Doubleday, C. *Ibid.* **1981**, *79*, 375. (d) Doubleday, C. *Ibid.* **1981**, *81*, 164. (e) Doubleday, C. *Ibid.* **1982**, *85*, 65.

(4) DeKanter, F.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759. (b) DeKanter, F.; den Hollander, J.; Huizer, A.; Kaptein, R. *Mol. Phys.* **1977**, *34*, 857.

(5) Synthetic sequence starting with the parent cycloalkanone: (1) PhLi; (2) TsOH; (3) $B_2H_6/H_2O_2/NaOH$; (4) pyridinium chlorochromate.

(6) Weller has obtained magnetic field effects similar to Figure 1 for zwitterionic biradicals by monitoring triplet yield or fluorescence intensity. (a) Weller, A.; Staerk, H.; Treichel, R. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 271. (b) Staerk, H.; Kuhnle, W.; Treichel, R.; Weller, A. *Chem. Phys. Lett.* **1985**, *118*, 19.

0002-7863/85/1507-6726$01.50/0