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.

(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.

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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 **2**$_{10}$, **2**$_{11}$, and **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, **2**$_{10}$ does not attain its asymptotic value. As the chain length of **2** decreases, H_{max} moves to higher field. For **2**$_{12}$, **2**$_{11}$, and **2**$_{10}$, H_{max} = 30 ± 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 **2**$_{11}$) and –16% (for **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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(5) Synthetic sequence starting with the parent cycloalkanone: (1) PhLi; (2) TsOH; (3) B$_2$H$_6$/H$_2$O$_2$/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.
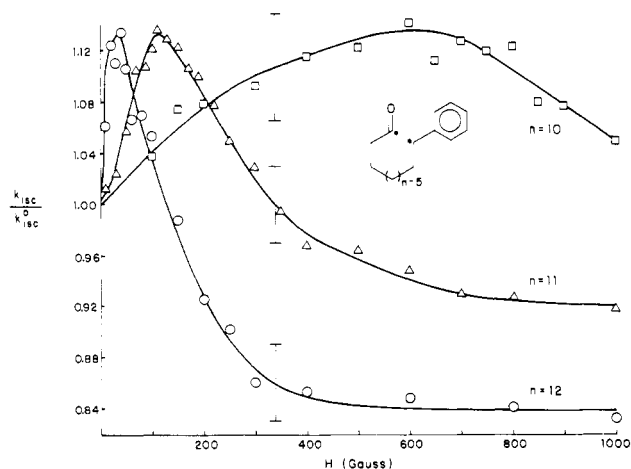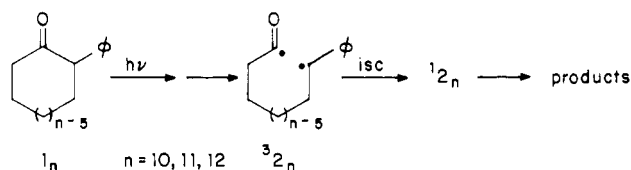
Figure 1. Ratio of the isc rate constant in a magnetic field H, k_{isc}, divided by the rate constant in the earth's field, k_{isc}^0. At 2100 G the ratios for 2_{10}, 2_{11}, and 2_{12} are 1.00, 0.91, and 0.84, repectively. Values of k_{isc}^0 are given in the text. Each point is an average of at least six measurements. Error bars are ±2 standard deviations.

Scheme I

$$1_n \qquad n = 10, 11, 12 \qquad {}^3 2_n$$

H increases beyond the T_{-1}–S degeneracy, the T_{+1} and T_{-1} energies are progressively removed from E_S, and k_{isc} decreases to its asymptotic value k_{isc}^{asympt} in which only T_0–S isc is important.[7] With $^2/_3$ of the T states removed, k_{isc}^{asympt} should be $^1/_3$ of k_{isc}^0.[8]

This model is qualitatively acceptable, but a 67% effect is much larger than we observe. Evidently most of the isc occurs in biradical conformers where k_{isc} is unaffected by the magnetic field. We offer a more general model for Figure 1 that draws on current knowledge of the S and T energy surfaces.[9]

Consider the limiting cases of long and short end-to-end distance R (Figure 2). At small R the radical centers interact appreciably to produce large variations in $E_S - E_T$. A typical variation might involve a torsional motion (θ) from a conformer with direct overlap (upper left) having $E_S < E_T$ to a conformer with zero resonance integral but a significant exchange integral, which favors $E_S > E_T$.[9] The resulting variation of $E_S - E_T$ with θ (bottom left) might be 1 or more kcal/mol.[9] At large R the end-to-end interaction is extremely small, so that $E_S \approx E_T$ in all conformers. In this regime the changes in both E_S and E_T are dominated by the torsional potentials appropriate to monoradicals.

In our experiments the maximum Zeeman splitting of the T levels is 0.2 cm⁻¹. Such a tiny splitting has no effect on isc at small
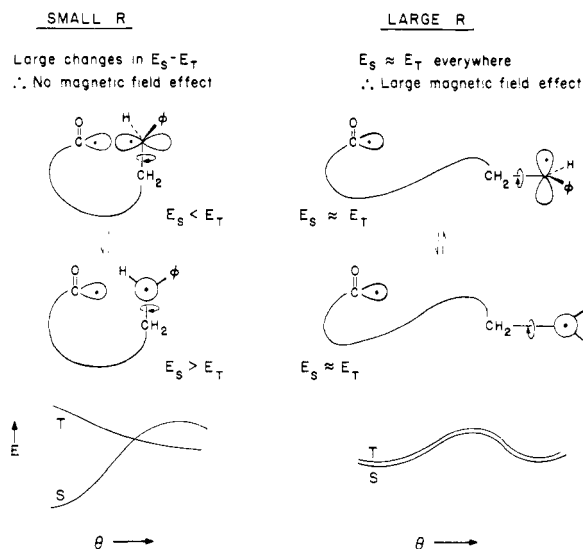

Figure 2. Effect of end-to-end distance R on conformationally induced changes in the S–T energy gap $E_S - E_T$. θ is the tortional angle. (Note: at large R, S–T intersections can occur but are not shown.)

R, where the variations in $E_S - E_T$ are orders of magnitude larger. However, at large enough R it is not unreasonable that the entire variation in $E_S - E_T$ lies within the range of our magnetic field. Therefore the magnetic field only affects k_{isc} in the conformers with large R. Of the two major isc mechanisms,[10] HFC and SOC, the dominant isc mechanism is expected to be SOC at small R and HFC at large R.[1] Consequently *the magnetic field affects only the HFC contribution to* k_{isc}.

This leads to a very simple measurement of the specific contributions of SOC and HFC to k_{isc} directly from Figure 1. Since $k_{isc}^0 - k_{isc}^{asympt}$ represents $^2/_3$ of the HFC contribution to k_{isc}^0, the full fractional contribution of HFC to k_{isc}^0 is equal to $^3/_2(k_{isc}^0 - k_{isc}^{asympt})/k_{isc}^0$, with the remainder of k_{isc}^0 due to SOC. At $H = 0$, the SOC/HFC ratio is 86/14 for 2_{11} and 76/24 for 2_{12}. At high field the HFC contribution drops by a factor of 3, and SOC/HFC becomes 95/5 for 2_{11} and 92/8 for 2_{12}.[11,12]

It is now clear that H_{max} in Figure 1 and in biradical-derived CIDNP does not measure the S–T gap averaged over the biradical lifetime, as assumed in the CIDNP literature.[2–4] Both Figure 1 and the CIDNP results derive nearly all their effect from biradical conformers with large R, but most of the isc occurs at small R where the S–T gap may be orders of magnitude larger. The *mean value* of the S–T gap is probably much larger than H_{max}, even though the biradical spends most of its time at large R. H_{max} should be interpreted as an approximate measure of the average S–T gap *in the regime of large R*.

(7) At higher fields than we can produce, the $\Delta g \beta H$ term would tend to increase k_{isc}.

(8) This is true if relaxation among the triplet levels is faster than k_{isc}, in which case the observed k_{isc} is the mean of the k_{isc} values for the three triplet levels, two of which are negligible. If this were not the case, we should (but in fact do not) observe a multiexponential decay resulting from independent decays of the triplet levels. Since dipolar relaxation decreases as R^{-6}, rapid triplet relaxation is expected for **2** if short end-to-end distances can be accessed rapidly relative to k_{isc}. Current data on chain dynamics support this hypothesis; see the following references. (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.

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(10) A third isc mechanism, ca. 10⁵–10⁶ s⁻¹ and hence slower than HFC or SOC, is electronic spin–lattice relaxation of the separate radical centers.

(11) Using time-resolved CIDNP, Closs and Redwine have recently estimated SOC/HFC by comparison of measured to theoretical enhancement factors. For the biradical derived from 2,2-dimethylcyclooctanone they obtin SOC/HFC ≈ 98/2 at high field. Closs, G. L.; Redwine, O. D. *J. Am. Chem. Soc.* **1985**, *107*, 4543.

(12) The separation of isc into SOC and HFC contributions is rigorous only when there are two distinct sets of biradical conformers, those with SOC as the only isc mechanism and those with only HFC. This ideal is never attained, but seems to be approximately true for **2**. For conformers in which the isc matrix element has a significant contribution from both HFC and SOC, the squared modulus of the matrix element produces cross terms which make a separation impossible.