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Low-Temperature Disappearance of Spin Correlation in Flexible 1,*n*-Biradicals (*n* = 22, 24, 26)

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Abstract: The direct detection electron paramagnetic resonance (EPR) spectra of three flexible polymethylene 1,*n*-biradicals (*n* = 22, 24, and 26) in tetrahydrofuran solution at low temperatures are reported. The acyl–alkyl biradicals, which show broad spin-polarized EPR transitions at room temperature and above, exhibit unusual structure at temperatures below 240 K. Simulations show that this additional fine structure is due to a collapse of emissive and absorptive transitions into each other, caused by a steady decrease in the spin exchange interaction (J) between the unpaired electrons. The effect is more pronounced at lower temperatures as the chains assume more extended conformations. For the C_{26} biradical the lowest temperature spectrum clearly shows the residual doublet state CIDEP (emissive/absorptive) indicative of uncorrelated radical centers. This transition from correlated to uncorrelated spins in a tethered chain is discussed in terms of through-bond and through-solvent spin–spin coupling mechanisms averaged over the equilibrium distribution of chain conformers.

Introduction

The single–triplet energy gap (ΔE_{ST}) in organic biradicals is an excellent probe of molecular structure.[1] Flexible 1,*n*-biradicals, which can be observed in liquid solution using direct detection electron paramagnetic resonance (EPR) spectroscopy,[2] have ΔE_{ST}'s that are accurately measurable over a wide range of values (10^{-5} to 1 cm^{-1}). If the motion of the flexible biradical is fast and the molecules are conformationally averaged on the EPR time scale, the interaction manifests itself as an additional splitting in the EPR spectrum and is usually referred to as the isotropic electron spin exchange interaction ($2J$). Long-range electronic interactions such as these can be difficult to quantify in processes involving donor–acceptor systems (e.g. electron and energy transfer) because of the presence of photoexcited states or excess charge which complicates the direct measurement of the electronic matrix element. Neutral biradicals at or near their electronic ground state do not suffer from these complications and are therefore good model compounds for the study of such matrix elements. We draw this comparision because, as for electronic matrix elements, biradical J couplings are proportional to the overlap of the orbitals involved. There are theoretical models for the magnitude of matrix elements driving electron and energy transfer processes over large distances,[3] especially in biological systems,[4] which have not been tested experimentally in simpler systems. Our laboratory has a long-term project aimed at measuring the sign and magnitude of J in biradicals at very long distances and as a function of simple systematic changes in molecular geometry.[5] To date is has not been possible to determine the chain length at which J couplings in biradicals go to zero, or more correctly, the chain length at which they become too small to be observable by EPR spectroscopy. In this paper we report time-resolved solution EPR spectra of 1,22-, 1,24-, and 1,26-polymethylene chain biradicals which show a large decrease in J with decreasing temperature, and we present evidence for the loss of spin correlation (i.e., when J approaches zero) in the C_{26} chain at the lowest temperatures accessable by our apparatus (ca. 230 K). These are the longest organic biradicals ever observed spectroscopically, and they have the smallest singlet–triplet energy gaps measured by any direct physical method.

In several recent publications from our laboratory, changes in J couplings with molecular structure for short and medium chain length biradicals were reported.[5,6] The spin correlated radical pair (SCRP) polarization typically observed in the EPR spectra of these species becomes very weak when the J couplings are large as in short (1,3- to 1,8-) biradicals, but can be useful in obtaining very accurate values for J by spectral simulation in longer chain structures (1,9- to 1,16-biradicals).[7] In this regard the time-resolved EPR method is superior to steady state EPR spectroscopy of stable biradicals, e.g. nitroxides, where a somewhat narrower range of J couplings is measurable.[8] In one of our previous studies we found that J is a strong function of temperature, especially at longer chain lengths.[9] This is due to contributions from two coupling mechanisms, through-bond and through-solvent, which have temperature coefficients of opposite sign. A decrease in temperature tends to favor extended conformations of the chains,[10] leading to a decrease in the through-solvent interaction. Since the longer chain biradicals are dominated by through-solvent coupling, even a small change in the distribution of end-to-end distances can produce a large change in the J coupling. This "temperature controlled" spin correlation

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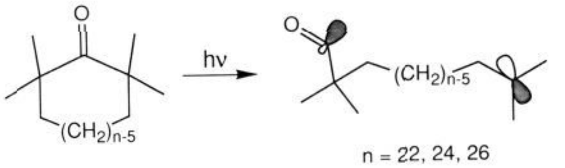
Scheme 1



should be enhanced in even longer chains, and this was the impetus for the present set of experiments.[11]

Results and Discussion

The systems under investigation are shown in Scheme 1. The main ring system of each precursor ketone was synthesized according to a previously published procedure.[12] Tetramethylation was carried out in order to speed up the rate of Norrish I cleavage from the excited triplet state of the ketone, ensuring the maximum yield of biradical per laser flash. The temperature dependence of the C_{22} biradical EPR spectrum is shown in Figure 1. The most unusual feature of this series is the apparent sharpening of several transitions as the temperature is lowered. The other chain lengths showed similar changes with decreasing temperature, which is particularly noticable in the centermost transition of each spectrum. The origin of this phenomenon, which the simulations shown below will support, is the gradual decrease of the through-solvent contributon to the J value as the conformational distribution shifts away from coiled geometries toward more extended ones. To understand this effect in more detail, it is useful to present the NMR analogy for the case of very small J couplings. Each hyperfine line in the spectrum represents a radical center with a chemical shift (from the center field) that is large compared with the J coupling to the other electron. The hyperfine line should appear as a normal $S = {}^1/_2$ transition, mildly perturbed by the exchange interaction, i.e., it should be split into two lines separated by $2J$. The only difference between this EPR spectrum and a first-order AX spin ${}^1/_2$ NMR spectrum is that the population differences, which arise in SCRP theory by singlet–triplet mixing, cause the low-field line of each doublet to be emissive (E) and the high-field line absorptive (A). It is then obvious that as the splitting ($2J$) decreases further, these E and A transitions will begin to overlap and cancel each other out. The additional fine structure observed in Figure 1 comes from the remaining transitions, of which there are many because of the large number of nuclear hyperfine couplings on the alkyl half of the biradical. It should be noted that the low-temperature spectra of these covalently linked systems show polarization patterns remarkably similar to those observed from unbound radical pairs confined to the interior of micelles.[13] In contrast to micellar radical pairs, however, these signals did not change shape with delay time, decaying instead uniformly to intensities below the sensitivity of the spectrometer by either chemical reaction or spin relaxation.

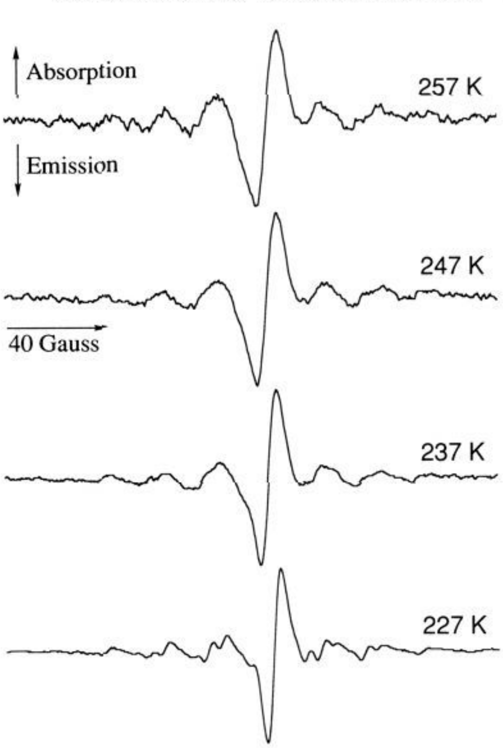


Figure 1. X-band time-ordered EPR spectra of the 1,22-biradical indicated in Scheme 1 as a function of temperature. All four spectra were obtained at a delay time of 0.1 μs after the laser flash with use of 100 ns boxcar gates.

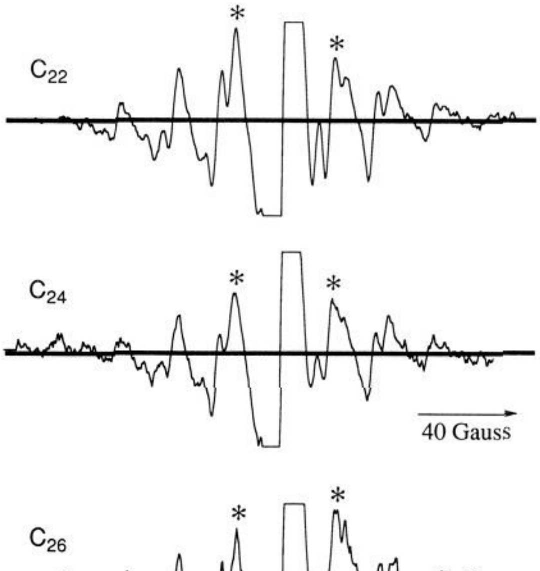


Figure 2. X-band time-resolved EPR spectra of the 1,22- (top), 1,24- (center), and 1,26- (bottom) biradicals, all taken at 227 K under the same conditions as described in the text and the caption to Figure 1. The vertical scale has been expanded to show all details except the center transition. A line has been drawn through the baseline to show the growth of the uncorrelated E/A CIDEP pattern with increasing chain length.

Spectra of the C_{22}, C_{24}, and C_{26} biradicals are shown on an expanded vertical scale in Figure 2. These spectra were taken at 227 K, the lowest temperature presently possible with our flow system. All three biradicals clearly show the additional fine structure described above, but an additional feature also presents

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(11) Effects of temperature and viscosity on the lifetimes of several flexible 1,*n* acyl–benzyl biradicals have been studied optically and related to chain dynamics by Zimmt et al.: (a) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1986**, *108*, 3618. (b) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 6726. (c) Zimmt, M. B.; Doubleday, C., Jr.; Turro, N. J.; Gould, I. R. *J. Am. Chem. Soc.* **1985**, *107*, 6724. Interpretation of their results is quite different from ours because they assume that spin–orbit coupling (SOC) is the dominant mechanism carrying triplets to singlets. Because SOC does not depend on the nuclear spin wave functions or the g factor differences, the SCRP and CIDEP polarization mechanisms are insensitive to this rate. In their model all singlet–triplet interconversion occurs at short end-to-end distances in orientations where SOC is maximized, and *chemical raction from the singlet is required to see a decay*. For the biradicals observed in our EPR spectra, Δg- or hyperfine-induced single–triplet mixing (which occurs at long distances where J is small or zero) is the necessary condition for an observable spectrum. Chemical reaction from the singlet state is *not* required. This is an interesting difference between the optical and EPR techniques and is the subject of present studies.

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(13) Closs, G. L.; Forbes, M. D. E.; Norris, J. R., Jr. *J. Phys. Chem.* **1987**, *91*, 3592.

itself in the chain length dependence. A line is drawn along the baseline of each spectrum to illustrate this. As the chain length increases, the low-field transitions acquire more emissive character while those at high field become more absorptive. Two representative transitions showing this phenomenon are indicated by asterisks in Figure 2. Such behavior is also observed in micellar radical pairs with increasing delay time and is attributed to polarization from uncorrelated radicals which have escaped the micelle and no longer experience an exchange interaction. In covalently linked biradicals there can be no such escape processes, but there can be contributions to the spectrum from the "normal" chemically induced dynamic electron spin polarization (CIDEP) transitions,[14] which is E/A for triplet precursors. The concentration of biradicals in our experiments is estimated at 10^{-6} M[8a], so on the time scale of our experiments (ca. 1 μs) it is not possible for this polarization to arise from intermolecular random encounters. It has been shown by Norris and co-workers[15] and by Wang et al.[16] that CIDEP is produced alongside SCRP polarization, since both mechanisms share single–triplet mixing as their origin. Most likely the intensity of the CIDEP is about the same for each biradical in Figure 2, but the SCRP is weaker in the C_{26} case due to a slightly smaller J coupling and further collapse of the E/A doublets. Further evidence for this comes from the fact that the overall signal intensities of the C_{22}, C_{24}, and C_{26} spectra decrease with chain length, as expected if the stronger SCRP polarization is disappearing. The intensities were compared by examining spectra obtained under identical conditions of light flux, concentration, solvent, temperature, and delay time.

The averaging of J over the conformational distribution is of interest. There may be a significant number of conformations of the C_{26} biradical for which $2J$ is much less than half of the line width of the transitions, which is the "solution EPR definition" of zero J for SCRP polarized biradicals. These biradicals will have completely collapsed their doublets, leaving only the residual CIDEP signals. If the biradicals undergo rapid motion, the "zero J" biradicals are averaged into the spectrum in a manner similar to a two-site NMR chemical exchange problem. Even if motional averaging is slow, the frequency differences between the SCRP and CIDEP transitions are small, so in that case we would see a spectrum that looks like a superpositon of the two mechanisms. However, even at these temperatures we believe that conformational jumps of the chains are fast enough to average these small interactions. With both mechanisms operative our SCRP simulation program can no longer be used to obtain an exact value for the J coupling, only an upper limit which we place at -1.5 MHz. This number was arrived at by conducting the simulations shown in Figure 3. Figure 3A shows the pure SCRP spectrum for the C_{26} biradical with $J = -1.5$ MHz. The essential features of the experimental spectrum are adequately reproduced except that there is too much absorption at low field and too much emission at high field. Figure 3B shows the pure CIDEP spectrum of the uncorrelated radical pair, and figure 3C is a superposition of the SCRP and CIDEP spectra in a ratio determined by approximate fit to Figure 3A. Clearly a much better fit of the C_{26} spectrum is obtained with the superposition and less CIDEP would be required to fit the C_{22} and C_{24} spectra in Figure 2. This is strong evidence in support of the loss of spin correlation due to the combined effects of lower temperatures and longer chain lengths. It is interesting to point out that in unbound radical pairs the effect of lowering the temperature is opposite to that observed here,[17] i.e. the magnitude of the SCRP polarization *increases* because the higher viscosity causes geminate pairs to remain in contact ($J \neq 0$) for times long enough to detect the fine structure.

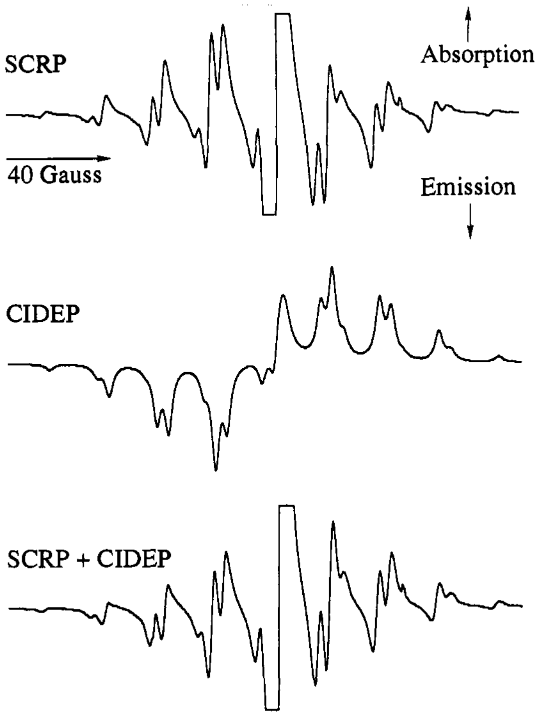

Figure 3. (A, top) Simulation of a biradical using pure SCRP theory with the hyperfine interactions and g factors for the monoradicals taken from ref 20, a line width of 5 G, and a J value of -1.5 MHz. (B, center) Simulation of the pure doublet state CIDEP spectrum of the uncorrelated biradical with a line width of 7 G for the acyl fragment and 3.5 G for the alkyl fragment. (C, bottom) Superposition of the SCRP and CIDEP described above which best fits the 1,26-biradical spectrum at the bottom of Figure 2.

By inspection of the central transitions in the spectra in Figure 1 it is clear that the line widths of the biradicals are also changing. It is well-known that acyl radicals have smaller line widths at lower temperatures,[18] most likely due to less mixing of the linear excited state from which decarbonylation takes place.[19] This narrowing could be responsible for the appearance of additional structure regardless of the magnitude of J. However, we observed spectra of pivaloyl radicals in THF[20] which showed normal acyl monoradical line widths of 7–8 G over this temperature range, and it is unlikely that a different line width exists in the biradicals. Although the line width of the alkyl fragment is believed to increase with decreasing temperature due to the presence of hyperfine anisotropy, this should be a fairly minor effect for the biradicals shown here because they have only β hyperfine interactions where the anisotropies are known to be quite small.[21] Interestingly, one of the manifestations of the loss of spin correlation is that the two ends of the biradical no longer share the same line width, as they do when the spins are strongly coupled. This may be interesting diagnostic tool for quantifying J values in the very long distance region.

These spectra have perhaps raised more questions then they have answered. The original issue of where J couplings "go to zero" in flexible polymethylene chain biradicals has been settled,

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(14) Molin, Yu, N., Ed. *Spin Polarization and Magnetic Effects in Radical Reactions*; Elsevier: New York, 1984.

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(16) Wang, Z.; Tang, J.; Norris, J. R., Jr. *J. Magn. Reson.* **1992**, *97*, 322.

(17) (a) Buckley, C. D.; Hunter, D. A.; Hore, P. J.; McLauchlan, K. A. *Chem. Phys. Lett.* **1987**, *135*, 307. (b) Kroll, G.; Plüschau, M.; Dinse, K.-P.; van Willigen, H. *J. Chem. Phys.* **1990**, *93*, 8709.

(18) Fischer, H.; Paul, H. *Helv. Chim. Acta* **1973**, *56*, 1575.

(19) The linear state is required for decarbonylation because it forces the carbonyl carbon to become sp hybridized as it is in CO. In the bent state this carbon is closer to sp^2 hybridized and it requires only a very small amount of mixing to broaden the transitions since the g factors for each hybridization are quite different. This explanation, and not g factor anisotropy, gives the correct temperature dependence.

(20) The pivaloyl radicals were produced by laser flash photolysis of di-*tert*-butyl ketone.

(21) Landolt-Börnstein, New Series, Group II, *Magnetic Properties of Free Radicals*, Vol. 9b.

at least to the extent that we now know where the transition to uncorrelated radical centers begins. The long chain length and low temperature required to observe this transition is somewhat surprising, but it should be noted that smaller and smaller J couplings could probably be measured if systems with narrower natural line widths could be synthesized. Another interesting question is whether or not any of the coupling mechanism is "indirect" through the biradical's excluded volume (26 methylene units occupy a large portion of the free volume between the radical centers).

Experimental Section

TREPR Methods. The tetramethyl ketones were photolyzed by a 308 nm eximer laser (Lambda Physik LPX 110i, 15 ns fwhm, 200 mJ, 60 Hz repetition rate) in THF (distilled from lithium aluminum hydride). Solutions were flowed through a 0.5 mm path length quartz flat cell within the microwave cavity of a JEOL, USA, Inc. X-band EPR spectrometer equipped for direct detection using a boxcar integrator as previously described.[5,7] The temperature of the flow system was controlled with acetone/dry ice cold baths in which both the sample reservoir and a heat exchange coil located just prior to entry into the microwave cavity were immersed. The flow lines, pump head, and microwave cavity were insulated with polyurethane foam and dry nitrogen was blown through the microwave cavity to eliminate frost buildup on the surface of the flat cell. All temperatures are accurate to ±2 K.

Characterization Methods. Low-resolution gas chromatography/mass spectrometry (GC/MS analyses were performed on a Hewlett-Packard 5890 GC automated with a 5971A MS instrument containing a 12 m HP-1 capillary column. High-resolution mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology Center, North Carolina State University. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-400 spectrometer. Infrared spectra were obtained neat with NaCl windows on a Bio-Rad FTS-7 spectrometer.

Solvents and Materials. Tetrahydrofuran was distilled from lithium aluminum hydride. Diisopropylamine was distilled from calcium hydride prior to use. Iodomethane and *n*-BuLi (Aldrich) were used as received. The synthesis of the parent cyclic ketones has been published previously.[12] Alkylations were performed using a previously described procedure[2b] in 75–82% yield. All products were purified by column chromatography on silica gel (200–400 mesh) with a 1% diethyl ether/petroleum ether eluent.

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