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Quantitative EPR Measurement of Long-Distance Electronic Interactions in Two Geometric Isomers of an Unsaturated Biradical

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Weak electronic interactions are often responsible for radiationless transitions occurring in nature, e.g., electron and energy transfer,[1] and their measurement is therefore an area of active research.[2] Organic biradicals are excellent model compounds for this purpose because they are easy to generate and detect by EPR spectroscopy and analysis of their spectra is usually not complicated. Furthermore, they are typically observed in or very close to their ground states, and they are most often neutral species, negating large solvent effects on their structure. Recently we demonstrated that flexible polymethylene biradicals containing one or more unsaturated bonds show average electronic couplings very different from those of their saturated analogs.[3] However, in that study it was not possible to perform experiments on isomerically pure samples, and therefore the measured coupling could not be related to a single molecular structure. In this paper we report the first measurements of scalar exchange interactions in unsaturated biradicals which differ only in that they are pure geometric isomers, and we compare both isomers to their saturated analog.

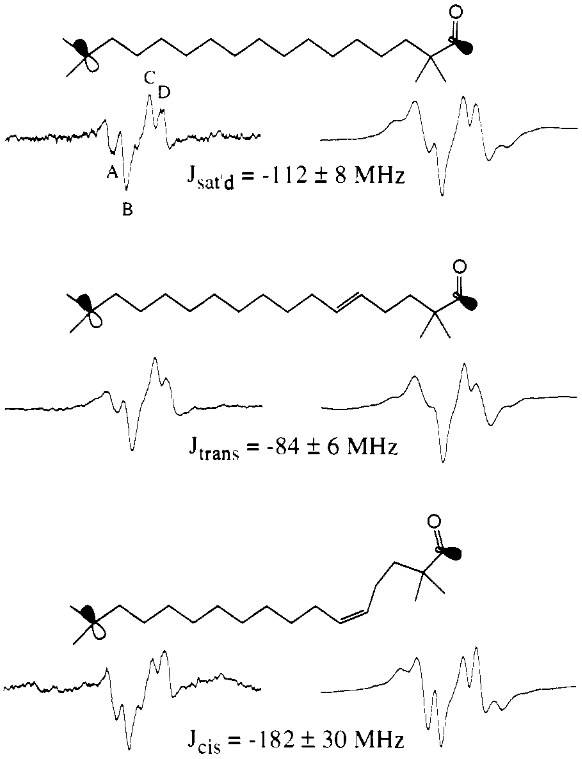
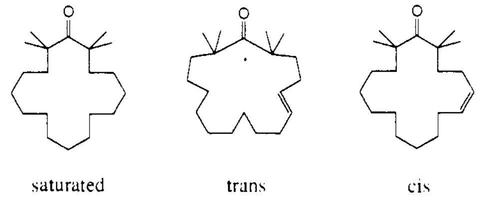


Figure 1. Time-resolved EPR spectra of the biradicals shown with their precursors in Scheme I. Experimental data are shown on the left and simulations on the right. The sweep width of each spectrum is 200 G, centered at 3375 G. Lines above the base line are in enhanced absorption, and those below are in emission. The spectra were obtained using a boxcar integrator with two gates of 100 ns, the second of which was opened 100 ns after the laser flash hit the sample. Intensity ratios A/B and C/D used in determining best fits for the saturated biradical (top) were A/B = 0.27 ± 0.03, C/D = 1.5 ± 0.1 (experimental), A/B = 0.29 ± 0.03, C/D = 1.3 ± 0.1 (simulated). For the trans unsaturated biradical (middle) A/B = 0.12 ± 0.04, C/D = 1.75 ± 0.15 (experimental), A/B = 0.08 ± 0.04, C/D = 2.0 ± 0.2 (simulated), and finally for the cis unsaturated species (bottom) A/B = 0.51 ± 0.04, C/D = 0.77 ± 0.07 (experimental), A/B = 0.68 ± 0.04, C/D = 0.79 ± 0.06 (simulated).

Scheme I



In our previous work, one of the compounds studied was a mixture of *cis-* and *trans*-2,2,16,16-tetramethyl-8-cyclohexadecen-1-one. We have discovered that if the double bond is in the 5 position instead of the 8 position, complete separation of the two isomers is possible by standard column chromatography. The three compounds shown in Scheme I were purified in this way, after which time-resolved EPR spectra were obtained in solution at room temperature.[4] The experimental results are shown in Figure 1, where for simplicity we have drawn only the most extended conformer of each biradical. Also shown are simulated spectra based on a well-established model for biradicals in solution[5] which contains a Zeeman energy term, nuclear hyperfine interaction for both ends of the chain, and an isotropic exchange interaction *J*. Dipolar interaction is not included due to the long chain length and rapid tumbling of the molecules. The fits in Figure 1 are visually satisfactory, although in all three cases the simulations show more intensity (absorption at low field, emission at high field) at the edges of the spectra than is observed experimentally. It should be noted that the simulation program calculates spin polarization from the correlated radical pair theory[6] (CRP) only and ignores any of the more routine chemically induced dynamic electron polarization (CIDEP) which is also produced. The CIDEP pattern will be emissive (E) at low field and absorptive (A) at high field, with the full hyperfine splitting present. In contrast, the biradical CRP polarization spectrum has half the hyperfine splittings of the corresponding monoradicals and has an AEAE intensity pattern. The CIDEP spectrum will therefore be out of phase with the CRP spectrum at the perimeters, leading to weaker intensities in these regions. The simultaneous solution of both CRP and CIDEP spectra is presently not possible

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[4] The samples were flash photolyzed under bubbling nitrogen in the microwave cavity of an X-band JEOL, USA, Inc. JES-RE1X EPR spectrometer equipped for direct detection. The solvent was benzene, and the concentration of ketone was approximately 0.1 M. Because of the low absorbance at the excitation wavelength ($\epsilon = 17$ at 308 nm), the concentration of biradicals was low enough to ensure only intramolecular interactions on the time scale of observation (100 ns). For a complete description of the apparatus, see: (a) Forbes, M. D. E.; Peterson, J.; Breivogel, C. S. *Rev. Sci. Instrum.* **1991**, *62*, 2662. (b) Forbes, M. D. E. *J. Phys. Chem.* **1993**, *97*, 3396.

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for more than one hyperfine term[7] and therefore is not performed here. In our analysis, we concentrate on obtaining the best fit of the four centermost lines in the spectrum, denoted A, B, C, and D in the figure. Intensity ratios A/B and C/D were found to be extremely sensitive to the value used for J in the simulations, and in fact the values of these ratios moved in opposite directions for the two isomers compared to the saturated species. The ratios quoted in the figure caption were those used to determine the best fit to each experimental spectrum.

The J couplings obtained from the final simulations are also displayed in Figure 1, and they differ by quantities well outside experimental error. The question of the mechanism of the coupling arises, i.e., through-bond (TB) or through-solvent (TS). Both mechanisms depend on the conformation of the biradical but in opposite ways. A maximum TB coupling is achieved with a completely extended chain, while the maximum TS interaction results from coiled conformers with short end-to-end distances. Since the chains are identical except at the 5 position (relative to the CO group), any differences in the measured J couplings must reflect either conformational restrictions by the more rigid bond (TS mechanism) or an increased exchange interaction via TB interactions. It is expected that a trans double bond will have a larger TB interaction than a cis bond (cf. ^{1}H NMR J couplings in cis vs trans olefins).[8] On the basis of our previous molecular orbital calculations,[3] the trans TB coupling is expected to be comparable to the saturated system. Conversely, the TS coupling, from consideration of the distribution of end-to-end distances, should be strongest for the cis and weakest for the trans isomer, with the saturated species in between. This is exactly what is observed experimentally, and therefore we conclude that while TB coupling in these three species may also be quite different, their EPR spectra at room temperature are dominated by the TS mechanism. This result is in line with previous observations that biradicals of long chain length (>14 carbon atoms) observed at high temperatures (>0 °C) are in what can be called the "through-solvent limit".[9] Given the chain length and the flexibility of these biradicals, the difference in J for the two isomers is remarkably large. Continued study of J couplings in unsaturated biradicals, including their solvent and temperature dependences, is presently underway in our laboratory.

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