

1.971 Å. At the TCSCF level of theory this latter structure was computed with the 3-21G basis set to be 12.0 kcal/mol above the one in Figure 1a with $r = 1.609$ Å. However, with the six-electron, six-orbital MCSCF wave function the relative energies were reversed, indicating that the MCSCF wavefunction gives an optimal value of r that is considerably larger than that given by the TCSCF wave function.

Since the minimum energy C_{2h} geometry for the 3-21G MCSCF wave function appeared to have an optimal value of r close to that of the SCF wave function ($r = 2.023$ Å), several geometries with fixed values of r in this neighborhood were optimized at the SCF level of theory. Energies were then calculated using the MCSCF wave function; and the minimum MCSCF energy was found to occur at $r = 2.062$ Å. The structure thus optimized is shown in Figure 1b. Its MCSCF energy of -231.6997 hartrees is 14.1 kcal/mol below that of the structure in Figure 1a.

Both the geometry of the MCSCF optimized structure and the fact that the second largest coefficient in the MCSCF wave function is only 0.18 show that this structure is not a diradical. That the structure is, indeed, the transition state in a concerted pericyclic reaction is indicated by the fact that upon simultaneously lengthening one of the two equivalent C-C bonds and shortening the other in 0.01-Å increments, the energy falls smoothly with both SCF and MCSCF wave functions. The MCSCF energy of the transition state is 29.4 kcal/mol above that of 1,5-hexadiene, whose geometry in the all-transoid conformation was optimized at the SCF level. This energy difference is in reasonable agreement with the activation energy of 34 kcal/mol that is measured for the Cope rearrangement.⁵

Our 3-21G MCSCF results provide strong computational evidence that the preferred pathway for the Cope rearrangement of the parent 1,5-hexadiene is via a concerted pericyclic reaction. The reason that a diradical structure is found at lower levels of theory is that the STO-3G basis set and a TCSCF wave function each prejudice the calculations by selectively stabilizing cyclohexane-1,4-diyl relative to two allyl radicals. The single p function used for both σ and π bonds in STO-3G biases this basis set toward the former type of bond, and a TCSCF wave function that correlates the nonbonding pair of electrons in cyclohexane-1,4-diyl provides no correlation for the nonbonding pair in two allyls.

Since cyclohexane-1,4-diyl and two allyl radicals may be viewed as contributors to the resonance hybrid that represents the concerted pericyclic transition state,¹⁴ the correct determination of the lowest energy C_{2h} structure depends critically on the ability of a calculation to describe both these contributors equally well. Otherwise, the result obtained will be biased toward the non-concerted alternative that is favored by the computational method employed.¹⁵

Our 3-21G MCSCF finding that the Cope rearrangement proceeds via a concerted pericyclic transition state of C_{2h} symmetry is in disagreement with the previous MINDO results, which found the lowest energy C_{2h} species to be a metastable diradical intermediate.⁷ Our 3-21G MCSCF results indicate that in the Cope rearrangement bond making and bond breaking occur in unison, thus also contradicting Dewar's general assertion that multibond reactions cannot normally be synchronous.⁸

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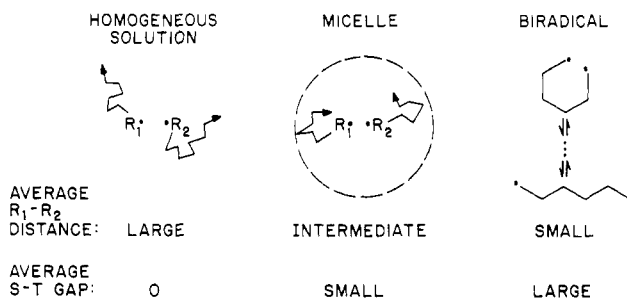
Energetics and Dynamics of Radical Pairs in Micelles. Measurement of the Average Singlet-Triplet Energy Gap by means of the Magnetic Field Dependence of ¹³C CIDNP

Matthew B. Zimmt, Charles Doubleday, Jr.,* and Nicholas J. Turro*

Department of Chemistry, Columbia University
New York, New York 10027

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Among species with homolytically broken bonds, radical pairs and biradicals occupy opposite structural and dynamical extremes, as illustrated below.



The radical fragments of a geminate pair are free to diffuse independently in solution, but the two ends of a biradical are severely constrained. Intuitively one expects that radical pairs generated within a micelle occupy a position intermediate between these two extremes. Several aspects of the chemistry of radical pairs in micelles have in fact been found to be unique to the micellar medium.¹ What is lacking is a structural/dynamical scale that allows a quantitative measure of the position occupied by radical pairs in micelles. We wish to report the first such measurements.

A reasonable definition for such a scale is the singlet-triplet energy gap E_{ST} , and the easiest way to measure it is by the magnetic field dependence of CIDNP.²⁻⁴ For radical pairs in homogeneous solution E_{ST} is typically zero.^{2b} For biradicals E_{ST} is nonzero and can be either positive (triplet ground state) or negative (singlet ground state).³ The above diagram illustrates the approximate inverse relation between E_{ST} and the spatial separation of the radical centers. In biradicals there is experimental^{3b-d} and theoretical⁵ evidence that other factors, such as through-bond coupling and the mutual orientation of the two ends, strongly affect E_{ST} .

Consider a biradical with $E_{ST} < 0$. In an external magnetic field the triplet sublevels T_{+1} , T_0 , T_{-1} are split by the Zeeman energy while E_{ST} , the energy difference between the S and T_0 states, is unaffected. If we adjust the magnetic field to produce a T_{-1} -S degeneracy the intersystem crossing rate—and hence the CIDNP intensity—will exhibit a local maximum²⁻⁴ at this field

(14) Borden, W. T. "Modern Molecular Orbital Theory for Organic Chemists"; Prentice-Hall: Englewood Cliffs, NJ, 1975; pp 129-131.

(15) Similarly, an SCF calculation would be biased toward finding a concerted pericyclic pathway, since diradicals cannot be adequately described with a single-determinantal wave function. Because both diradical contributors to the resonance hybrid for the concerted transition state are described equally poorly with an SCF wave function, the optimal C_{2h} geometry at the SCF level is similar to that found at the MCSCF level, where both contributors are described equally well. Nevertheless, the poor description at the SCF level of the diradical contributors to the transition state results in the calculated energy of activation being 12.3 kcal/mol higher at the SCF than at the MCSCF level of theory.

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(2) (a) Closs, G. L.; Doubleday, C. *J. Am. Chem. Soc.* **1973**, *95*, 2735. (b) Closs, G. L. In "Chemically Induced Magnetic Polarization"; Muus, L. P., Atkins, P. W., Pedersen, J. B., Eds.; Reidel: Dordrecht-Holland, 1977; p 225.

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

(4) DeKanter, F.; Kaptein, R. *J. Am. Chem. Soc.* **1982**, *104*, 4759.

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

