standard) δ −0.31 (s, 9 H, $(CH_3)_3Ge$), −2.83 (s, 6 H, $(CH_3)_2N$), −6.48 and −7.11 (d, 4 H, aromatic protons, J = 8 Hz).

Anal. Calcd for $C_{11}H_{19}NGe$: C, 55.54; H, 8.05; N, 5.83. Found: C, 55.37; H, 8.29; N, 6.16.

The other anilines were all obtained from commercial sources.

Charge-transfer spectra were recorded on a Cary-14 spectrophotometer. The low-temperature apparatus consisted of a jacketed cell mounting through which a stream of cooled nitrogen gas was passed. The temperature was controlled by varying the rate of nitrogen flow and was constant to ±5°. These slight variations in temperature had negligible effects on the charge-transfer spectra below −50°. The entire cell compartment was purged with dry nitrogen to prevent water condensation at the low temperatures.

For the room temperature spectra, 5–10 μl of the aniline were added to 3 ml of a solution 10^{-3} M in acceptor in 10-mm quartz sample cells and the spectra determined immediately. Using this technique, spectra could be recorded before significant decomposition occurred. For the low-temperature work, because of increased complex formation and slower decomposition, about 0.1 μl of the aniline was sufficient to obtain satisfactory spectra. The results are tabulated in Table I.

Oxidation potentials were determined by cyclic voltammetry using a standard three-electrode cell consisting of a platinum button working electrode (Beckman, 39273), a saturated calomel reference electrode, and a platinum coil as the counter electrode. The potential sweep was provided by a Chemtrix 300 polarographic amplifier with type 205 polarographic time–base plug-in units. A Keithley 602 electrometer was used to calibrate the starting potentials and the measurements were recorded using a Tektronix 564 storage oscilloscope equipped with a Polaroid camera.

In a typical run a solution 10^{-4} M in sample and 0.1 M in tetrabutylammonium perchlorate was maintained under an atmosphere of dry argon throughout the measurement. A rate of 0.100 V/sec was employed scanning a 1.00-V range. The average deviation of $E_{P/2}$ values measured in separate runs was ±0.01 V.

Estimation of pK_a Values. The basicities of the anilines reported by Benkeser[21] were determined in 50% aqueous ethanol. In order to compare these values with those obtained for aqueous solutions[22] the equation, $pK_{a(EtOH-H_2O)} = pK_{a(aq)} + C$, was used. For anilines studied by both workers the constant, C, had a value of approximately −1.0 pK unit.

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Chemistry of Diradicals. III. Calculation of Spin Correlation Effects on the Rotational Barriers in 1,4 Diradicals

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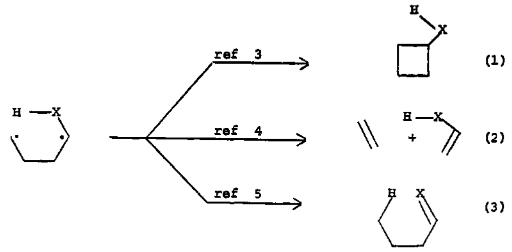
Abstract: The C_1–C_2 or C_3–C_4 bond rotational barriers are calculated for the singlet and triplet 1,4 diradical species. Substantially higher barriers are found for the singlet diradical as compared to the triplet diradical or other model systems. These trends are discussed in terms of simple molecular orbital and valence bond concepts. It is postulated that variable bond rotational barriers are capable of rationalizing the quantitative features of 1,4 diradical chemistry.

In this paper, molecular orbital concepts will be used in an attempt to understand the influence of the nonbonded radical centers on rotational barriers in diradical species. As we have previously pointed out,[1] reasonably accurate estimates of bond rotational barriers are critically important to a quantitative description of diradical systems; variations in estimated thermochemical quantities lead to startlingly different theoretical descriptions of the 1,3 and 1,4 diradical systems.[1–3]

Experimental studies of diradicals, and, in particular, reports of spin correlation effects in the reactions of these systems, have been frequent in recent years. Common features have been noted in nearly all contributions. Thus, in the 1,4 diradical species, high stereospecificity is noted in singlet manifolds while triplet diradicals show little or no selectivity in typical reactions,[3–5] such as eq 1–3. These differences in stereoselectivity have been attributed to the longer lifetimes of the triplet species, which are required to intersystem cross (to singlet species) before bond forming events can occur.[3] Despite the attractiveness of this explanation, comparison of these results with older work on cyclobutane pyrolyses[6,7] has led us to point out several apparent inconsistencies and to propose an alternative explanation.[1] Briefly, the following points from this treatment may be summarized. The pyrolysis of 1,2-dimethylcyclobutane is consistent with the intermediacy of 1,4 diradicals which encounter activation barriers to closure or cleavage reactions of 6–8 kcal/mol leading to generalized potential energy surfaces such as that shown in Figure 1. This description then requires bond rotational barriers approaching the



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[1] Paper II in this series is L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93**, 1988 (1971).

[2] R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *ibid.*, **92**, 7091 (1970).

[3] P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968).

[4] L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *ibid.*, **93**, 1984 (1971).

[5] N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969).

[6] H. R. Gerberich and W. D. Walters, *ibid.*, **83**, 4884 (1961).

[7] E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

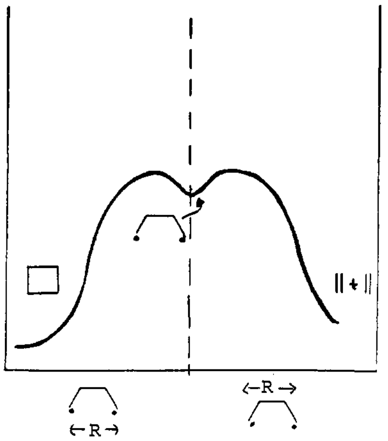


Figure 1. Potential energy surface for the 1,4 diradical.

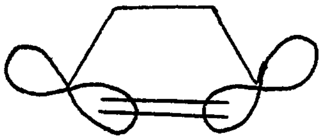
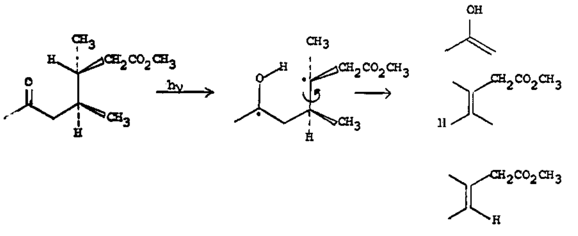


Figure 2. Through-space 1,4 diradical interaction.

unusually large values of $\sim$10 kcal/mol in tertiary diradical systems such as shown in Scheme I to account for the high stereoselectivity in the singlet reactions of the diradical intermediate.[4]

Scheme I. System for Determining Stereoselectivity of Diradical Cleavage Reaction



Additionally, accounting for the extremely low stereoselectivity in the triplet-derived reactions required unreasonably slow spin inversion rates, $\sim 10^4$ sec^{-1}. Thus, our analysis[1] required that one either abandon the quantitative features of the thermochemical analysis of cyclobutane reactions, accept large barriers to internal rotation in these diradical systems and subsequently long-spin inversion lifetimes, or develop alternative rationalizations. In paper II in this series we chose the third course. In this paper use of SCF–MO methods will be made to examine the assumption implicit in our earlier work, namely that rotational barriers are similar in the singlet and triplet diradical states, and that barriers estimated from more classically bonded structures (saturated and olefinic hydrocarbons) are useful models for these systems. The balance of this paper will be devoted to a discussion of the 1,4 diradical system, both because a greater variety of spin correlation effects have been documented here than in other systems, and because this was the primary focus of our earlier analyses.

Qualitative Molecular Orbital Picture. Little is known concerning the electronic structure of 1,4 diradicals since no such species has ever been observed directly. Nevertheless, it is useful to consider, from several points of view, the bonding in this very reactive intermediate. From the simplest point of view it can be recognized that the 1,4 diradical possesses only small activation barriers[8] associated with its cleavage reactions to ethylenes, and to a substantial extent might strongly resemble two rather weakly coupled ethylenes. This situation may be described in valence bond symbolism with the two canonical structures **1** ↔ **2**. To

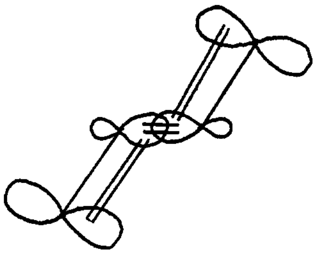
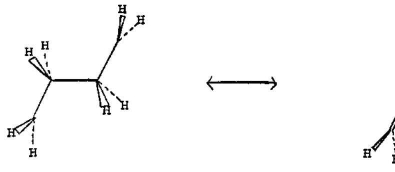


Figure 3. Through-bond 1,4 diradical interaction.



1 2

the extent that resonance form **2** is important, the terminal methylene groups would be expected to mimic the behavior of their ethylene counterparts with resulting large rotational barriers in the singlet state. In the diradical triplet state, once again with reference to ethylene as a model, much lower barriers would be anticipated, and in fact the geometry shown above might be destabilized relative to that in which terminal methylene hydrogens are rotated into the plane of the carbons.

A more detailed description of this proposed property may be obtained by examining the basis for the interaction between the terminal carbons in a molecular orbital framework. Two mechanisms for 1,4 interaction are commonly considered as an approximation to the electronic structure. The first of these involves a *through-space* overlap of the two radical centers, depicted in Figure 2 for the cis-like structure. Clearly, as the internuclear distance C_1–C_4 is shortened, such an overlap interaction leads to an adequate description of cyclobutane, where C_1–C_2 and C_3–C_4 bond rotational barriers are very high indeed. To the extent then that such interactions are strong in the 1,4 diradical, the associated bond rotational barriers might be expected to be high.

Through-bond interactions may also be considered, creating effective 1,4 interaction as illustrated in Figure 3, for the trans-like structure.

Now in a diradical of cis-like structure both through-space and through-bond interactions are important, and it is difficult to say with certainty which dominates at model equilibrium bond lengths and angles.[9] The behavior of 1,4 diradicals in this region has been the

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(8) The calculations of Hoffmann and coworkers[2] show no barrier to cleavage while the thermochemical analysis of Benson and O'Neal[7] gives a barrier height of about 7 kcal/mol.

(9) However, later argument and ref 10–12 suggest strongly that through-bond coupling dominates through-space interaction even in cisoid geometries for the 1,4 diradical.

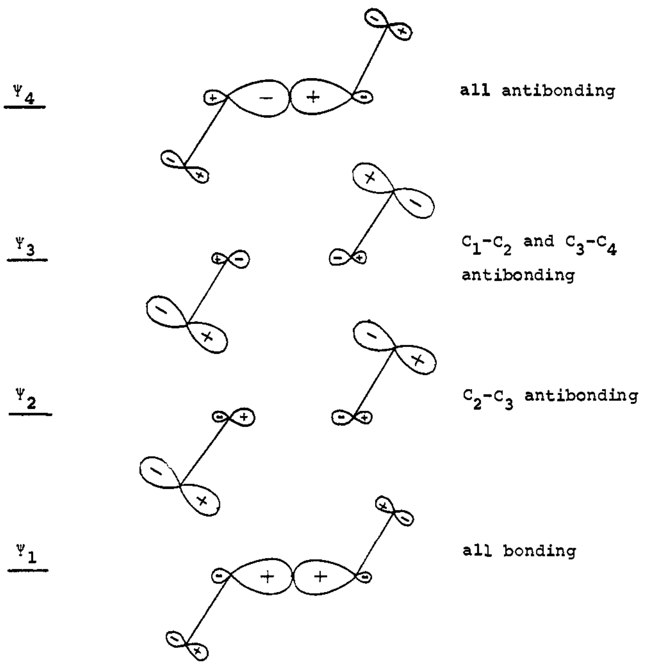


Figure 4. Molecular orbitals showing through-bond interaction in the 1,4 diradical. The size of the orbital is roughly scaled to orbital coefficient magnitude.

subject of extended Hückel calculations by Hoffmann and coworkers[2] and will be discussed by us in a future publication, but at this point there seems to be no need to postulate inhibition of rotation about the C_2–C_3 bond which leads to trans-like configurations. Since trans-like structures are likely to possess fewer steric barriers to rotation, and since we wished to evaluate the through-bond contribution to C_1–C_2 and C_3–C_4 bond rotation barrier separately, we have in the main assumed such conformations in our calculations.

In the extended trans-like 1,4 diradical it is easy to describe the molecular orbitals which appear to be important in assessing the influence of the through-bond interaction on bond rotation barriers. Using the two p type radical centers and the two sp^3 hybridized carbon orbitals which make up the C_2–C_3 bond as a basis, four molecular orbitals may be derived. The form is precisely that of butadiene projected onto the plane with orbital coefficients adjusted to account for differing bond energies (see Figure 4). Note that rotations about the C_2–C_3 axis will not influence the picture to be developed here, at least until significant through-space C_1–C_4 bonding occurs.

Rotation of a terminal methylene group would tend to destabilize both orbitals Ψ_1 and Ψ_2, but would stabilize orbitals Ψ_3 and Ψ_4. Thus, in a singlet configuration $\Psi_1^2\Psi_2^2$, an appreciable barrier to rotation might exist, a barrier which would at least partially be removed in the triplet, $\Psi_1^2\Psi_2\Psi_3$.

The magnitude of these rotational barriers depends to a considerable extent on the magnitude of this through-bond coupling interaction. Experimental evidence that such interactions are indeed significant has been dramatically illustrated by the photoelectron spectroscopy performed by Bischof, *et al.*,[10] on 1,4-diazabicyclo[2.2.2]octane (Dabco, **3**). Following an earlier development of through-bond and through-space interaction pictures by Hoffmann[11] the extremely large nonbonding orbital splitting (2.1 eV!) was attributed by Heilbronner and Muszkat[12] largely, if not entirely, to through-bond coupling. In an attempt to gain further insight into the accuracy of this simple picture, more complete molecular orbtial calculations have been performed using the INDO method of Pople, Beveridge, and Dobosh[13] with an available program.[14]

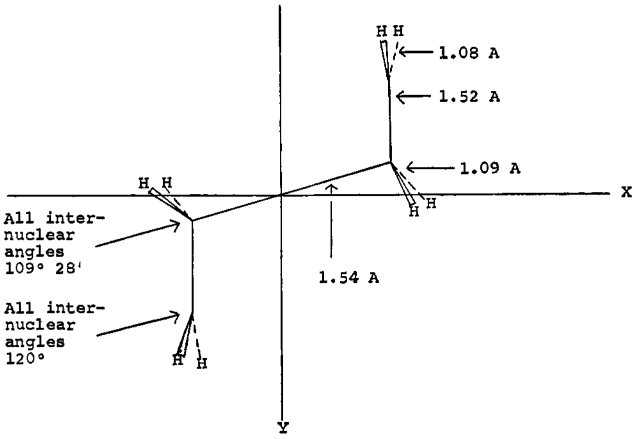
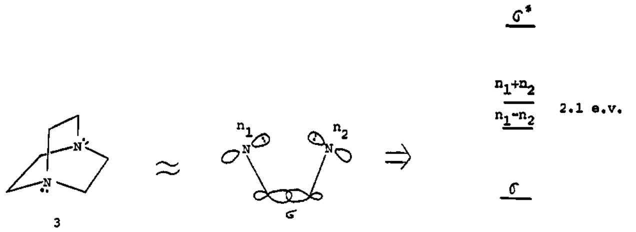


Figure 5. 0,0° conformation of 1,4 diradical showing bond lengths and angles employed in all calculations.



3

INDO Calculations. The CNDO and INDO methods have been described previously in the literature by the originators and those who have applied the methods to various problems.[15] The INDO calculations on the extended trans 1,4 diradical show good agreement with the qualitative arguments presented in the last section. Using the model geometry shown in Figure 5 and thereafter varying only the angle of tilt of the terminal CH_2 group, the energy changes as a function of twist angle shown in Figure 6 were obtained. As can be seen, the singlet diradical steeply increases in energy while the triplet potential energy surface is essentially flat. As a check on the procedures used, calculation of the analogous barrier in a butyl radical of similar geometry gave barrier values an order of magnitude lower than that of the singlet diradical at comparable geometries. The energy differences as a function of angle for the butyl radical are also plotted in Figure 6. Unfor-

(10) P. Bischof, J. A. Hashmal, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, 4025 (1969).

(11) R. Hoffmann, A. Imamura, and J. W. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968); also R. Hoffmann, *Accounts Chem. Res.*, **3**, 1 (1971).

(12) E. Heilbronner and K. A. Muszkat, *J. Amer. Chem. Soc.*, **92**, 3818 (1970).

(13) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 47, 2026 (1967).

(14) A CN INDO program is available from Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind.

(15) An excellent and readable textbook covers the theory and development of these methods together with a critical evaluation of its usefulness; see J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

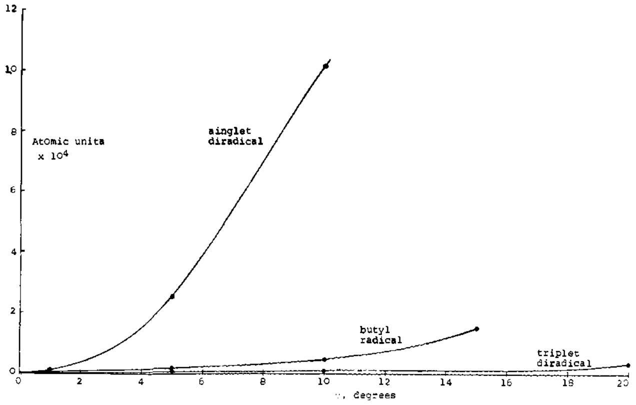


Figure 6. The change in binding energy as a function of rotation angle, θ, of a terminal methylene in the singlet diradical, the triplet diradical, and the butyl radical. See Figure 5 for model geometry.

tunately, the singlet diradical energy failed to converge at large twist angles; the trend, however, is quite obvious even at low angles. At 10° for example, the singlet diradical has increased in energy nearly 0.7 kcal/mol, the triplet 0.05 kcal/mol, and the butyl radical 0.07 kcal/mol.

Rotation of the methylene group 90° produced barriers of 0.5 kcal/mol for the triplet diradical and 1.7 kcal/mol for the butyl radical. Although the singlet diradical calculations failed to converge at large angles of twist, we were able to approximate this value by rotating both ends through 90°.[16] We reasoned that, after one methylene had been rotated fully, all through-bond coupling would be removed, and the second rotation could be accurately accounted for by the "model" butyl radical calculation.[17] Thus the calculated singlet barrier is $\Delta E(90°, 90 - 0°, 0°;$ singlet diradical$) - \Delta E(90 - 0°;$ butyl radical$) \cong \Delta E(0°, 90 - 0°;$ singlet diradical$) = 0.067$ au = 45 kcal/mol.

The *numerical values* extrapolated and calculated for the barrier heights in the diradical system are of dubious reliability, particularly in view of the common finding that CN INDO calculations frequently lead to overestimated bond energies and energy spacings.[18] We make the usual assumption, however, that semiempirical calculations of this sort give *generally reliable qualitative results* even in the absence of precise quantitative predictions. We conclude, therefore, that some substantial additional barrier to rotation exists in the singlet diradical as a result of through-bond interactions which cannot be found in the triplet species or the butyl radical.

Implications in the Interpretation of Diradical Spin Correlation Effects. Current difficulties in the interpretation of 1,4 diradical spin correlation effects result from attempts to correlate data resulting from *all* methods of generation of these species. As was indicated in the introductory statement, the high stereospecificity noted in the singlet state manifolds of the diradicals generated by Bartlett,[3] Stephenson,[4] and Yang[5] required rather high barriers to C_1–C_2 (or C_3–C_4) rotation, while application of these same barriers led to unreasonably long lifetimes in the nonstereospecific triplet diradical reactions. Application of the molecular orbital concepts in this paper allows these inconsistencies to be removed. The high barriers to rotation calculated in the singlet diradical, as compared to the butyl radical, for example, give support to the notion that rotational barriers *might well* be abnormally high for these species. In addition, the application of rotational barriers derived from singlet diradical behavior to the analysis of triplet diradical properties finds little support in the present work. Using this analysis it would thus be impossible to determine the triplet–singlet spin interconversion time by comparing the stereoselectivities of typical singlet and triplet diradical reactions. It appears then that a combination of factors may be responsible for the low stereoselectivity of the triplet diradical reactions, only one of which is the longer lifetime of the triplet-derived species relative to its singlet counterpart, and that neither our recent hypothesis[1] nor the older rationalization of Bartlett and Porter[3] may be completely correct. Experiments are in progress designed to test the various possibilities.

Acknowledgment. The generous support of the Camille and Henry Dreyfus Foundation through a Teacher–Scholar grant is gratefully acknowledged.

(16) The lack of symmetry in these highly twisted species appears to cause the program to search highly ionic solutions. For example the 0–25° singlet diradical had a computed dipole moment of 20.1 D.

(17) This is borne out by examination of the triplet manifold where $\Delta E(90°, 90 - 0°, 0°;$ triplet diradical$) = 0.0035$ au $= \Delta E(90 - 0°;$ butyl radical$) + \Delta E(0°, 90 - 0°, 0°;$ triplet diradical$)$. The extended Hückel theory (EHT) calculations of Hoffmann and coworkers[2] on the 1,4 diradical system offer strong support for this assumption. These workers were able to compute ΔE for both single and double rotation of the terminal methylene groups through 90° (geometries similar to that shown in Figure 5 were employed); values of 0.53 and 0.58 eV, respectively, were found. EHT methods, of course, do not distinguish singlet and triplet configurations, and calculate an "average" over the spin states. Our results indicate that the major part of the barrier calculated by EHT is due to a singlet configuration. It is comforting that rotation of the second methylene requires very little energy, in the EHT calculations.

(18) See, for example, the calculations of the ethylene and benzene electronic spectra by P. A. Clark and J. L. Ragle, *J. Chem. Phys.*, **46**, 4235 (1967).