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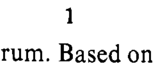
Geometrical Structure and Energetics of Closs's Diradical: 1,3-Cyclopentadiyl

Sir:

As the physical techniques (such as matrix isolation) available to organic chemists have become increasingly sophisticated, the study of diradicals has become a central focus of contemporary physical organic chemistry.[1-3] Whereas in the past diradicals have been readily postulated as reaction intermediates, the direct detection and characterization of such species is a much more recent development.[4,5]

Perhaps the most dramatic illustration of this trend concerns the diradical of bicyclo[2.1.0]pentane. The existence of this transient species has been suspected since the early 1960s, when Chesick[6] determined an activation energy of 39 kcal/mol for the reversible cis–trans isomerization of 2-methyl[2.1.0]-bicyclopentane. However, not until 1975 was there reported the first detection by physical methods of *any* 1,3 or 1,4 diradical. In this light the significance of the characterization of the 1,3-cyclopentadiyl radical[7] by Buchwalter and Closs becomes particularly apparent.

Buchwalter and Closs found that ultraviolet irradiation of matrix-isolated **1** at 5.5 K yielded a well-defined electron spin resonance (ESR) spectrum. Based on the fact that this spectrum persists down to 1.3 K (and on preliminary CIDNP results), they concluded that the 1,3-cyclopentadiyl diradical has a triplet ground state. Further analysis of the decay kinetics of this species suggested to Closs the schematic potential energy surface reproduced in Figure 1. This figure indicates that the triplet state of Closs's diradical is a minimum on its potential energy surface, while the lowest singlet state represents a transition state between the cis and trans bicyclopentanes. In this regard it is interesting to note that Benson-type thermochemical calculations[8] suggest a potential well of depth of 13 kcal for the singlet diradical.



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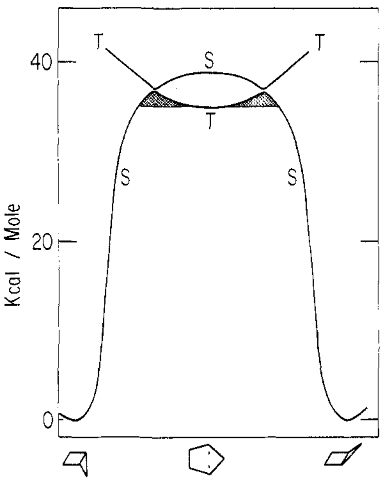

Figure 1. Schematic energetic view[7] of the isomerization between bicyclo[2.1.0]pentane and 1,3-cyclopentadiyl.

It seems fair to say that very little is known about the quantitative molecular structures of triplet diradicals. Since theoretical methods have proved consistently reliable[9] in predicting the structures of the more conventional closed-shell hydrocarbons, we decided to carry out a detailed study of triplet 1,3-cyclopentadiyl. Self-consistent-field (SCF) theory was used in conjunction with a double-ζ (DZ) basis set[10] designated C(9s 5p/4s 2p) H(4s/2s). Some idea of the reliability of this may be gauged by the extensive calibrations[11] of Hehre, Pople, Radom, and Schleyer. For a sample set of 19 hydrocarbons, they find the slightly smaller but essentially comparable 4-31G basis set to predict C–C single- and double-bond distances to within an average of 0.006 and 0.020 Å of the appropriate experimental equilibrium internuclear separations. The restricted Hartree–Fock methods of Pitzer[12] were used in conjunction with the HONDO integral routines.[13] The complete theoretical treatment of a point on the C$_5$H$_8$ potential energy surface (68 contracted gaussian functions) required 3.4 h of Harris Corporation Slash Four minicomputer time.

The electron configuration for triplet 1,3-cyclopentadiyl in C_{2v} symmetry is

$$1a_1^2 2a_1^2 1b_2^2 2b_2^2 3a_1^2 4a_1^2 5a_1^2 3b_2^2 4b_2^2 6a_1^2 7a_1^2 1b_1^2 5b_2^2 8a_1^2 6b_2^2 9a_1^2 2b_1^2 - 1a_2^2 2a_2 3b_1$$

The triplet equilibrium structure was determined at the DZ SCF level of theory subject to several assumptions. All C–H distances were assumed to be 1.09 Å and each of the three methylene angles θ (HCH) was constrained to be 109°. These are certainly the least interesting aspects of the structure of Closs's diradical and are uncontroversial parameters which have relatively little effect on the predicted total energies.

Figure 2 gives the present theoretical structure of 1,3-cyclopentadiyl, and for comparison the experimentally known[14] structure of bicyclo[2.1.0]pentane. Since this is the first experimentally known cyclic diradical whose structure has been predicted theoretically, it is important to ask whether the predicted structure agrees with classical organic chemistry concepts.[15] The answer for Closs's diradical is a convincing "yes". First, the three unique C–C single-bond distances lie in the same order as that observed for bicyclo[2.1.0]pentane.[14]

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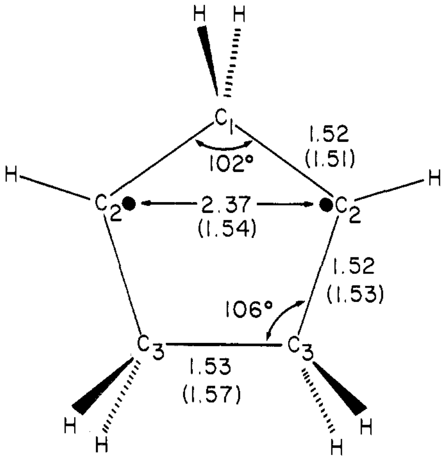


Figure 2. Predicted equilibrium geometry of Closs's diradical, 1,3-cyclopentadiyl. In parentheses is given the experimental (r_s) structure of the related closed-shell singlet molecule bicyclo[2.1.0]pentane. Bond distances are given in ångstroms. Omitted for clarity is the 113° $C_1C_2C_3$ angle.

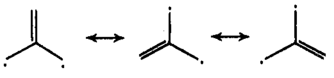
Table I. Relative Energies of Several Electron Configurations of 1,3-cyclopentadiyl. The Triplet-State Total Energy Was −193.84905 Hartrees

electronic confign and state	rel energy, kcal
$2a_2 3b_1$ $^1B_2$	142.2
$2a_2^2$ $^1A_1$	90.9
$3b_1^2$ $^1A_1$	85.6
$c_1 2a_2^2 + c_2 3b_1^2$ $^1A_1$	0.9
$2a_2 3b_1$ $^3B_2$	0.0

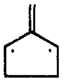
Perhaps more important, the C_2–C_2 distance is a full 0.83 Å longer than in the bicyclo species. This C_2–C_2 distance of 2.37 Å is in fact only slightly less than the separation of ~2.48 Å expected[16] for cyclopentane. Thus we see that triplet 1,3-cyclopentadiyl has a structure consistent with features classically anticipated on the basis of the known structures of these two closed-shell singlet molecules.

At the predicted triplet equilibrium geometry, an examination of the other diradical states[17] was carried out. It was found (see Table I) that the two closed-shell singlet configurations are nearly degenerate and rather high lying, at 85.6 and 90.9 kcal, respectively, above the $^3B_2$ state. However the relative energy of the lowest $^1A_1$ state is radically lowered by the more appropriate[18] two-configuration SCF treatment. There the coefficients of the $\ldots 2a_2^2$ and $\ldots 3b_1^2$ configurations are nearly equal, −0.70 and 0.71. By this criterion, Closs's singlet diradical at this geometry is almost perfectly diradical-like in character. The theoretical value of 0.9 kcal for the singlet-triplet separation $\Delta E(^3B_2-^1A_1)$ is at best reliable to ±3 kcal. Nevertheless it is impossible to deny the fact that our prediction is in remarkably close agreement with the experimental deduction (seen in Figure 1) of Buchwalter and Closs.[7]

After completing this research, it occurred to us that Closs's diradical is structurally related to the unsubstituted trimethylenemethane (TMM) (eq 1). In fact this analogy is nearly as


(1)

close as that between the primitive TMM and Berson's TMM[19] (**2**). The small singlet-triplet separation for 1,3-cyclopentadiyl suggests that ΔE(S–T) for Berson's TMM might be significantly less than that for the primitive TMM. This would nicely resolve a smoldering discrepancy between theory[20] and experiment.[19]



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Nickel-Induced Conversion of Carbon–Oxygen into Carbon–Carbon Bonds. One-Step Transformations of Enol Ethers into Olefins and Aryl Ethers into Biaryls

Sir:

In connection with a general study of the Felkin reaction—the replacement of the hydroxy group of allyl alcohols by hydrogen or an alkyl function in the reaction of Grignard reagents with such alcohols in the presence of phosphine-ligated nickel dichloride[1]—a new reaction was encountered, involving the substitution of alkoxy groups bound to carbon-carbon double bonds by alkyl and aryl units.[1a,2] Hence there was undertaken an investigation of the reactions of phenylmagnesium and methylmagnesium bromides with enol and aryl ethers induced by bis(triphenylphosphine)nickel dichloride, the results of which are presented herewith.

As Table I indicates,[3] various types of enol ethers are susceptible to cleavage and arylation or alkylation, leading to olefins in high yield. The replacement of the alkoxy or aryloxy group of the aldehyde enol ethers yields mainly olefins with

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