

Conformation of a Geminal Dicyclopropyl-Substituted Trimethylenemethane Triplet [2-(Dicyclopropylmethylidene)cyclopentane-1,3-diyl][†]

Gitendra C. Paul* and Joseph J. Gajewski*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Paul A. Kestyn, Sadaf Khorasanizadeh, and Paul M. Lahti*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003

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Triplet 2-(dicyclopropylmethylidene)cyclopentane-1,3-diyl, CP2TMM, has a $\Delta m_s = 2$ ESR transition revealing hyperfine splitting consistent with coupling to two equivalent α hydrogens and five equivalent β hydrogens and one other hydrogen with a small hyperfine coupling constant. This is consistent only with a conformation in which one cyclopropane ring conjugates with the π triplet so that the other cyclopropane is twisted allowing the tertiary cyclopropyl hydrogen to hyperconjugate. Geometry optimization of the triplet state of CP2TMM was carried out using the 3-21G basis set with a UHF wave function and while the singlet state was optimized using a GVB perfect pairing wave function. The most stable conformation of each spin state is a C_2 -symmetric structure providing a 10 kcal/mol singlet–triplet energy gap favoring the triplet. This gap is reproduced at the 6-31G* level using the 3-21G geometries. However, this structure cannot reproduce the hyperfine splitting observed; 1 kcal/mol higher in energy is an asymmetrical conformation of triplet CP2TMM which can account for the hyperfine interactions.

Introduction

Trimethylenemethane, TMM, is an important biradical species since it is one of the simplest of the non-Kekule hydrocarbons; it is a species in which two π electrons cannot be paired to make a π bond.¹ The cross-conjugated nature of the π framework is responsible for this, and the results of simple Huckel calculations give two degenerate nonbonding MOs into which two electrons must be placed.² Hund's rule requires that these nonbonding MOs should be singly occupied in the form of a triplet state. Indeed, the triplet state appears to be the lowest energy species since Dowd showed that the ESR spectrum increases in intensity as the temperature is lowered.³ The question of the geometry of the triplet state was also answered by Dowd who found only four $\Delta m_s = 1$ ESR transitions which are due to zero-field splitting, and this requires a symmetry equal to or greater than D_{3h} barring an accidental degeneracy; in addition he found that a $\Delta m_s = 2$ transition in an oriented crystal derived from photolysis of 3-methylenecyclobutanone was split into seven lines with intensities following the binomial expansion, suggesting that all six hydrogens were equivalent ($a_H = 8.9$ G). Yoshida prepared the TMM triplet by γ irradiation of methylenecyclopropane and found that the $\Delta m_s = 2$ transition was split into seven lines like Dowd's spectrum.⁴ Thus a planar triplet is consistent with the facts.

Recently two of us reported on the reactions of a

dicyclopropyl-substituted trimethylenemethane biradical ensconced in a five-membered ring, 2-(dicyclopropylmethylidene)cyclopentane-1,3-diyl (CP2TMM).⁵ These types of trimethylenemethane species were first prepared by Berson starting with the Diels–Alder adduct of 6,6-dimethylfulvene and diethyl azodicarboxylate.⁶ After reduction with hydrogen gas, which only reduces the endocyclic double bond, hydrolysis of the ester, and decarboxylation, oxidation of the diamine gave the azo compound precursor to the TMM species. Berson found that thermolysis and photolysis of the dimethyl dimethylene TMM precursor led to dimeric products and adducts with added olefins. Photolysis of this precursor at low temperatures led to an ESR spectrum characteristic of a randomly oriented triplet state with less than D_{3h} symmetry. Further, the temperature dependence of the signals is characteristic of a ground state triplet.

We have reported an ESR spectrum of the CP2TMM species resulting from the azo compound precursor derived initially from 6,6-dicyclopropylfulvene that closely resembles that obtained by Berson for the 6,6-dimethyl species.⁵ However, unlike the Berson ESR spectrum ours provided a $\Delta m_s = 2$ region with hyperfine splitting which we can now interpret in terms of specific rotamers about the bonds to the cyclopropane rings.

Results

The $\Delta m_s = 2$ region of the ESR spectrum of CP2TMM is given in Figure 1. Initial simulations of the spectrum suggested that there were two hyperfine couplings of 10 G each, which were probably due to the α sp^2 C–H protons, and five equivalent hyperfine couplings of 14 G

[†] Dedicated to the memory of Paul Dowd.

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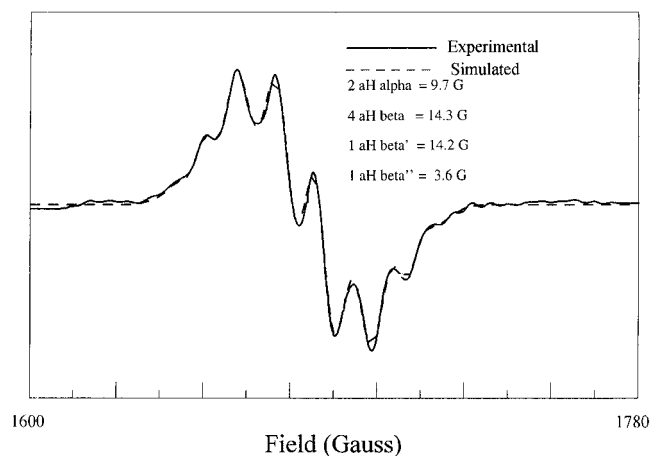


Figure 1.

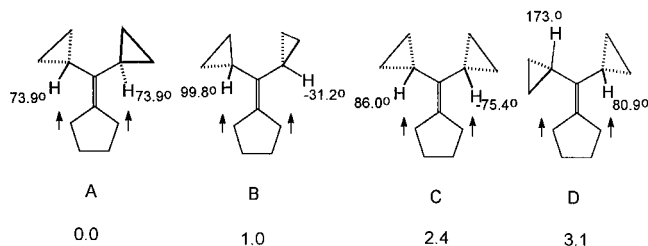
each, which were associated with sp^3 C–H β hydrogens. However, subsequent simulations, see below, provided greater reproducibility, and this is included in Figure 1.

Coupling to only five β hydrogens is only possible if the two cyclopropane rings are not equivalent. This might be possible if one cyclopropane ring is oriented to conjugate with the π system of the triplet which would prevent the β hydrogen on that ring from hyperconjugating with the π system, and the other cyclopropane ring then must be oriented so that the hydrogen on it can hyperconjugate.

To examine the conformational possibilities, *ab initio* calculations were carried out using the GAUSSIAN94⁷ and GAMESS⁸ computational programs implemented on a Silicon Graphics Indigo UNIX workstation. Optimization of the triplet state of CP2TMM was carried out using the 3-21G basis set with a UHF wave function, while the singlet state was optimized using a GVB perfect pairing wave function to allow for the expected diradical nature of this state. No symmetry constraints were imposed in the calculations. Optimization was initiated from multiple starting points using the molecular mechanics-estimated structures in order to sample the conformer space of CP2TMM. A number of computational studies on TMMs have employed higher level wave functions⁹ but have suggested that this modest level of theory should suffice to give reasonable qualitative results for so large a molecule without symmetry assumptions.

Overall, the 3-21G optimization calculations indicated that the lowest energy triplet conformer is similar to **A**, the C_2 -symmetrical species with 73.9° cyclopropyl–/cyclopropyl–C=C dihedral angles (Chart 1), but only 1 kcal/mol higher in energy is an asymmetrical triplet conformer, **B**, with 99.8° and -31.2° dihedrals. The latter

Chart 1



is more consistent with the hyperfine splitting since it has nonequivalent cyclopropyl hydrogens. Two other conformations are higher in energy than **A** and **B**. One corresponds to conformer **C** and is 2.3 kcal/mol higher in energy than **A** and has nearly C_s -symmetry with 86.0° and -75.4° dihedrals as defined above with some pyramidalization at the exocyclic carbon. Another, conformer **D**, is 3 kcal/mol above **A** and has 173° and 80.9° dihedral angles as defined above.

Interestingly, conformations **A** and **B** are also obtained as the low-energy conformers with relative energies of 0.0 and 2.7 kcal/mol, respectively, in a molecular mechanics calculation that assumes strong torsion barriers between sp^2 carbons but no torsion barrier for cyclopropyl group rotation. In the cyclopropylcarbinyl radical itself, the most stable conformation is a bisected form,¹⁰ and this appears to be the case for the dicyclopropylcarbinyl radical as well,¹¹ but the barrier to rotation in the cyclopropylcarbinyl radical is only 2.75 kcal/mol.¹² Using this value for the cyclopropane–H/cyclopropane–C–C=C 2-fold barrier term results in three conformations for the bicyclopropyl TMM triplet with the most stable being the C_2 structure described above. The next higher energy species (3.1 kcal/mol higher) is one resembling **B** above with the cyclopropane–H–C–C=C dihedrals of 101° and -48° . Finally, 4.8 kcal/mol higher in energy is a structure resembling **D** above with dihedrals of 173.6° and 83.9° .

The GVB optimization of the planar singlet state of CP2TMM found conformer **A** to be the minimum energy structure. The singlet geometry shows considerable bond localization with the exocyclic $C(sp^2)$ – $C(sp^2)$ bond being only 1.33 Å, while the endocyclic TMM bonds are 1.47 Å long. By comparison, all the $C(sp^2)$ – $C(sp^2)$ bonds in the triplet computations of CP2TMM are about 1.41 Å long, even in the asymmetric cyclopropane rotamers. These trends in bond length are completely analogous to computational findings⁹ for the two-configuration singlet state and 3E state of parent TMM, which have a Jahn–Teller distorted, planar structure geometry and a delocalized D_{3h} geometry, respectively.

After evaluating the relative conformational energies of the triplet state of CP2TMM, we computed the 3-21G ROHF energies of conformers **A** and **B** of CP2TMM using geometries optimized at the 3-21G UHF level, to avoid problems of energetic lowering of the UHF state by spin contamination (e.g., $\langle S^2 \rangle_{UHF} = 2.208$ for **A** at the 3-21G/UHF level). These results are summarized in Table 1. The triplet 3-21G ROHF//3-21G UHF to singlet 3-21G GVB energy gap $\Delta E(T-S)$ is 10.5 kcal/mol, which is not as large as the more recent computed triplet–singlet energy gaps for planar TMM which are in the neighbor-

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Table 1. State Energies for CP2TMM

	triplet state ^a energy	singlet state ^b energy	$\Delta E(T-S)^c$
3-21G//3-21G (conformer A) ^d	-460.986567 (-461.020262) ^d	-460.969770	10.5
6-31G*/3-21G (conformer A) ^d	-463.579572 (0.0) ^e	-463.562892	10.5
6-31G*/3-21G (conformer B) ^d	-463.577947 (1.0) ^e		
6-31G*/3-21G (conformer C) ^d	-463.575876 (2.3) ^e		
6-31G*/3-21G (conformer D) ^d	-463.574791 (3.0) ^e		

^a 3-21G UHF optimization, energy in hartrees. ^b 3-21G GVB optimization, energy in hartrees. ^c Energy in kcal/mol. ^d ROHF energy (UHF energy) at this geometry. ^e ROHF energy in kcal/mol relative to the 6-31G*(ROHF)//3-21G(UHF) energy of conformer A.

hood of 17.5 kcal/mol.⁹ Using the frozen geometries at the 3-21G UHF and GVB levels, we also computed the 6-31G* ROHF and 6-31G* GVB energies and found $\Delta E(T-S)$ to be virtually unchanged from the lower level results. The effects of basis set on the energy gap thus appear to be small, so we have high confidence in these computational findings. The singlet state GVB wave functions for **A** were both consistent with the expected diradical nature, having GVB pairing coefficients of 0.785 (-0.619) and 0.795 (-0.606) at the 3-21G and 6-31G* levels, respectively. We do not expect the effects of cyclopropyl ring torsion on the singlet state of CP2TMM to have large effects on $\Delta E(T-S)$ relative to the numbers computed for the energy minimum conformer **A** structures. Qualitatively, therefore, we feel that $\Delta E(T-S)$ is approximately 10 kcal/mol for CP2TMM and that multiple conformers about the cyclopropyl rings are energetically accessible without greatly altering this situation. Open-shell singlet state computations gave energies that were considerably higher and were not further explored.

As additional support for our structural assignment, we investigated the density distribution and Fermi contact populations in triplet conformer **B** of CP2TMM using the GAUSSIAN94 formulation of Becke's density functional method incorporating the nonlocal correlation formulation of Lee, Yang, and Parr, using a 6-31G(d) basis set [BLYP/6-31G(d)].^{13,14} The Fermi contact results were converted into predicted hyperfine coupling constants using the method detailed in Foresman and Frisch, following eq 1:¹⁵

$$\text{hfc (MHz)} = 22.80 \times \text{hfc (G)} = (16\pi/3)(g_e/2)(\gamma_H)(47.705336 \text{ MHz})B_F \quad (1)$$

In the equation, γ_H = the magnetogyric ratio of hydrogen (2.792 670), $g_e = 2.0032$ for a free electron, and B_F is the Fermi contact integral value from the computation. The results are in excellent accord with the experimental results in that the two hydrogens bonded to C(sp²) atoms are predicted to have hfc values of -8.5 G, while the four cyclopentane ring hydrogens plus the cyclopropylcarbonyl hydrogen of near-perpendicular orientation to the TMM fragment all have hfc values of 13.3 ± 1.0 G. The cyclopropylcarbonyl hydrogen that is oriented at -31° relative to the TMM fragment has a predicted hfc of about 4 G, only one-third of the hfc for the hydrogen

having the perpendicular C-H orientation which allows it to overlap well with the TMM π space. This hfc for the pseudoparallel cyclopropyl C-H bond decreases rapidly as the cyclopropylcarbonyl C-H bond approaches coplanarity with the TMM fragment. All the other cyclopropyl hydrogens have negligible hfc values (0.1–0.8 G) when calculated by this approach.

Having the computational results in hand as a comparison to the initial estimate of Figure 1, we refined the line shape fit to the experimental spectra using the program EPRVARLW by B. Kirste.¹⁶ This program provides the best fit to a spectrum with up to 12 different hfc values and having varying line widths for each line. This algorithm provides considerable flexibility in fitting a glassy spectrum such as the one examined here. The initial guesses for hyperfines were (a) assuming conformer **A** of CP2TMM, $a(1) = 8$ G (two sp² C-H), $a(2) = 14$ G (four cyclopentyl C-H), $a(3) = 13$ G (two cyclopropyl C-H); (b) assuming a 90°,30° conformer of CP2TMM (**B**), $a(1) = 8$ G (two sp² C-H), $a(2) = 14$ G (four cyclopentyl C-H), $a(3) = 13$ G (pseudoperpendicular cyclopropyl C-H), $a(4) = 4$ G (pseudoparallel cyclopropyl C-H). Variability of 4 G was allowed in the hyperfine constants $a(n)$. Using a combination of Monte Carlo and Simplex fitting algorithms, we found that the best fit statistically and visually was given by model b with final parameters: $a(1) = 9.7 \pm 2$ G, $a(2) = 14.3 \pm 1$ G, $a(3) = 14.2 \pm 3$ G, $a(4) = 3.6 \pm 2$ G, all with line width = 10 G for a GAUSSIAN line shape. The concordance between the DFT-computed hfc values and EPRVARLW-simulated model assignments is excellent (figure 1).

Discussion

The hyperfine splitting observed for the $\Delta m_s = 2$ ESR transition for triplet CP2TMM is consistent with conformation **B** and not the C_s conformation, **A**. Further, a near 1:1 ratio of the two conformations should provide only a broad singlet with many more inflection points than those observed, so either the equilibrium in the triplet must favor **B** or in the event that equilibration is slow in the glassy matrix, **B** results from a favorable conformation of the azo precursor. If the former explanation is correct, then conjugation by one cyclopropane ring in the triplet is stronger than conjugation by both in the form of **A** and may even provide for greater stability of conformation **D**. However, this suggestion is contrary to the calculations for reasons that are unclear unless zero-point energy corrections and the higher symmetry number of **A** conspire to provide this difference. The symmetry number difference contributes an $R \ln 2$ factor to the entropy which results in only a 0.14 kcal/mol destabilization of **A** relative to **B** at 100 K. Therefore, other factors must be important, although perhaps a 2 kcal/mol differential error in energies may not be unreasonable at this level of theory.

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