

Communications to the Editor

Could 2.2.2-Propellatriene Exist?

Ernest R. Davidson

Department of Chemistry
Indiana University
Bloomington, Indiana 47405

Received October 23, 1996

Revised Manuscript Received December 23, 1996

In response to a lecture by Prof. Sheridan,¹ we recently raised the question of the possible existence of 2.2.2-propellatriene (Figure 1). We have now verified that this propellene molecule has at least a theoretical existence.

Calculations have been done using a 6-31G* basis set² and a 2 electron/2 orbital CASSCF wave function.³ This gives a two-configuration description of a singlet biradical and a ROHF description of a triplet state. Geometry optimization with this wave function and D_{3h} symmetry constraints was followed by single point MRMP2 calculations and CASSCF frequency calculations. The active orbitals had a_1' and a_2'' symmetry so the lowest energy states were of $^1A_1'$ and $^3A_2''$ symmetry.

The calculations showed that this propellene should have a singlet ground state. The computed singlet energy is below the triplet energy by 0.7 kcal/mol at the CASSCF level⁴ of theory and 1.6 kcal/mol with MRMP2.⁵ The MRMP2 wave function had much less biradical and more ionic character than the CASSCF. The inter-bridgehead distance is 2.324 Å for the singlet state and 2.390 Å for the triplet. These results indicate a weak inter-bridgehead bonding interaction. The molecule is fairly rigid with the lowest vibrational frequency about 439 cm^{-1} for the singlet and 456 cm^{-1} for the triplet. The rigidity indicates that there may be an appreciable barrier to rearrangement.

Our original interest in this molecule was caused by the observation that it could, in principle, be reached by folding

(1) Sheridan, R. Personal communication.

(2) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1973**, *54*, 724.

(3) Dupuis, M.; Marquez, A.; Davidson, E. R. *HONDO 95.3 from CHEM-Station*; IBM Corporation: Neighborhood Road, Kingston, NY, 12401, 1995.

(4) The actual CASSCF energy for the $^1A_1'$ state was -306.223874 . The unscaled zero point correction was 0.1162 hartrees. For the triplet, the ROHF energy was -306.222682 and the zero point energy was 0.1164 hartrees. This difference of 0.1 kcal/mol in zero point energy is not included in the numbers quoted in the text.

(5) The MRMP2 energy was computed using the MROPT2 method at the CASSCF optimized geometry. This method was employed for the Cope rearrangement in: Kozłowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 774.

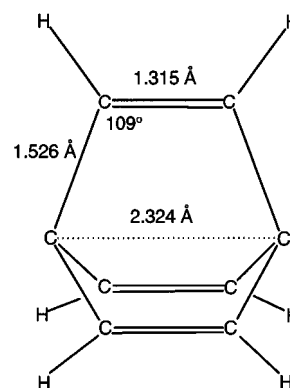


Figure 1. CASSCF computed structure of singlet 2.2.2-propellatriene.

the tetradical $:\text{HC}-\text{C}_6\text{H}_4-\text{CH}:$ and joining the terminal carbons with a double bond. This latter molecule is computed to have a high-spin (quintet) character associated with two carbenes attached to a phenyl ring. The high-spin form is lower in energy than singlet propellene, but the singlet dicarbene (whose structure is more like a quinone $\cdot\text{HC}=\text{C}_6\text{H}_4=\text{CH}\cdot$) is higher in energy than propellene. Another possible product of ring opening is singlet $\cdot\text{C}_6\text{H}_4-\text{CH}=\text{CH}\cdot$, which is computed to be 3.7 kcal/mol lower in energy than this propellene. Complete fragmentation to C_2H_2 and $\cdot\text{C}_6\text{H}_4\cdot$ is uphill in energy by only 5.0 kcal/mol.

For comparison, 2.2.2-propellane was computed at this same CASSCF level of theory. This gave two minimum energy structures for the singlet state: one with an inter-bridgehead bond length of 1.542 Å and one with a bond length of 2.514 Å. By comparison, the triplet gave a single minimum with a bond length of 2.436 Å. The longer bond singlet minima was computed to be 5.1 kcal/mol below the shorter bond form and 2.3 kcal/mol below the triplet. The lowest vibrational frequency was only 123 cm^{-1} , indicative of a much more flexible molecule. These results are quite similar to those we reported earlier.⁶ In the previous publication, we were unable to find a stable 2.2.2-propellane molecule with any higher level of theory because the calculation found no barrier to ring opening to $\text{CH}_2=\text{C}_6\text{H}_8=\text{CH}_2$. This ring-opening mechanism seems less likely for 2.2.2-propellatriene because it requires breaking a double bond rather than a single bond.

Acknowledgment. This work was supported by Grant No. CHE 90-07393 from the National Science Foundation. We also thank Jerry Berson for several stimulating questions.

JA963652P

(6) Feller, D.; Davidson, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 4133.