J. Org. Chem. **2001,** *66,* 7951−7954

A Computational Study of Tetrahedrene: Strained Alkene or Dicarbene?

Ronald R. Sauers* and Jonathan S. Harris

Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

sauers@rutchem.rutgers.edu

Received June 21, 2000

A computational study of tetrahedrene at the RCCD/cc-pVDZ level led to a singlet-state structure with a lowest energy vibrational mode of 660 cm^{-1}. The corresponding triplet state was found to be ca. 37 kcal/mol lower in energy than the singlet state. The heat of formation of the singlet state was estimated to be 270 kcal/mol. An isomeric singlet bicyclic dicarbene bis-bicyclo[1.1.0]-cyclobutylidene was found to be ~94 kcal/mol lower in energy than tetrahedrene.

Introduction

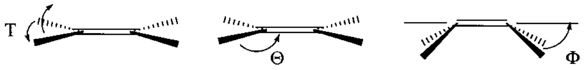


Figure 1. Alkene strain: torsion (*T*); bond angle (θ); pyramidalization (Φ).

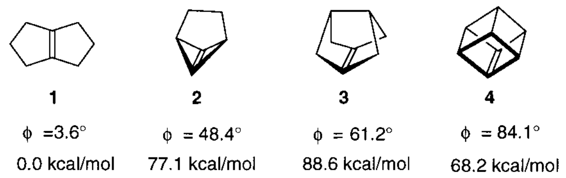


Figure 2. Pyramidalization angles and olefin strain energy for alkenes.

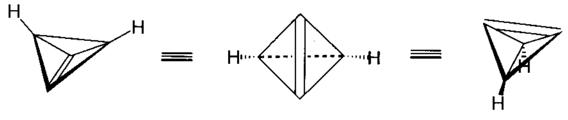


Figure 3. Tetrahedrene.

Strained alkenes have attracted special attention among synthetic and computational chemists owing to their high reactivity and the unusual bonding in comparison with unstrained analogues. In 1989, a special issue[1] of *Chemical Reviews* devoted five chapters to the description of strained organic molecules in which strain is due to the coexistence of small rings and unsaturation.[1−4] Alkene strain typically results from structural changes that involve twisting of end groups, compression or expansion of $C{=}C{-}R$ bond angles, and/or pyramidalization (Figure 1).[2,5a] Each of these distortions disrupts the normal sp^2/p hybridization with a corresponding reduction in π bonding. Twisting the end groups to a 90° conformation, for example, totally destroys the overlap between the p orbitals and leads to a diradical state. Cyclopropene and many of its derivatives represent extremes of systems with $C{=}C{-}C$ bond angle compression ($\Theta \ll 120°$) and are highly reactive but isolable molecules. As early as l975, it was recognized that certain bicyclic alkenes, for example, bicyclo[3.3.0]oct-1(5)-ene (**1**), prefer the syn-pyramidal geometry.[6] Theoretical studies provided insight into the importance of stereoelectronic factors and indicated that beyond a certain point, pyramidalization can lead to stabilizing interactions as a consequence of mixing of occupied π orbitals and vacant molecular orbitals.[5a,7] More recent examples of highly syn-pyramidalized alkenes include the extraordinarily strained systems: tricyclo[3.1.0.$0^{2,6}$]hex-1(6)-ene (**2**),[8] tricyclo[3.3.0.$0^{3,7}$]oct-1(5)-ene (**3**),[5,9] cubene (**4**)[10] (Figure 2), and others.[11] Computed out-of-plane angles and heats of hydrogenation relative to bicyclo[3.3.0]oct-1(5)-ene (**1**) here defined as olefin strain energies (OSE) are also shown.[5b]

With a view of probing the limits of strain in alkenes, we initiated a computational study of tetrahedrene **5** (Figure 3). Although tetrahedrene has not yet been synthesized, it was expected that with syn-pyramidalization angles on the order of $\Phi = 124°$ and $C{=}C{-}C$ bond angles ~62°, it would embody considerable internal strain. Ultimately, it was of interest to speculate that excessive strain might promote cleavage of the π bond and/or the σ bond. The objective of this work was to

---

[1] *Chem. Rev.* **1989**, *89*, No. 5.

[2] Borden, W. T. *Chem. Rev.* **1989**, *89*, 1067−1093.

[3] Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

[4] Dodziuk, H. *Modern Conformational Analysis*; VCH: New York, 1995; Chapter 8.

[5] (a) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 4710−4718. (b) A value of 26.7 kcal/mol was used for the heat of hydrogenation of **1**.

[6] (a) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941−6955. (b) Chou, P. K.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 697−698. (c) Nguyen, T. L.; Le, T. N.; Mebel, A. M.; Lin, S. H. *Chem. Phys. Lett.* **2000**, *326*, 468−476.

[7] Wagner, H.-U.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P. v. R.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 1210−1213.

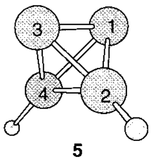
[8] Ströter, T.; Jarosch, O.; Szeimies, G. *Chem.-Eur. J.* **1999**, *5*, 1422−1431.

[9] Branan, B. M.; Paquette, L. A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 774−776.

[10] Staneke, P. O.; Ingemann, S.; Eaton, P.; Nibbering, N. M. M.; Kass, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 6445−6446.

[11] (a) Williams, R. V.; Colvin, M. E.; Tran, N.; Warrener, R. N.; Margetic, D. *J. Org. Chem.* **2000**, *65*, 562−567. (b) Marchand, A. P.; Namboothiri, I. N. N.; Ganguly, B.; Watson, W. H.; Bodige, S. G.; *Tetrahedron Lett.* **1999**, *40*, 5105−5109. (c) Chenier, P. J.; Southard, D. A., Jr. *J. Org. Chem.* **1990**, *55*, 4333−4337. (d) Jonas, V.; Frenking, G. *J. Org. Chem.* **1992**, *57*, 6085−6088.

10.1021/jo000941u CCC: $20.00



5

	Distances (Å):				Angles:		
	i.	ii.	iii.		i.	ii.	iii.
1-2:	1.489;	1.478;	1.458	1-3-2:	62.0°;	62.4°,	60.1°
1-3:	1.400;	1.369;	1.453	1-2-3:	56.1°;	55.2°,	59.8°
2-4:	1.615;	1.618;	1.591	1-2-4:	57.1°;	56.8°,	57.9°
				2-1-4:	65.7°;	66.4°,	65.1°

Figure 4. Geometric data for tetrahedrene (C2v). (i) RCCD/cc-pVDZ; (ii) RB3LYP/6-311+G(d); (iii) CASSCF(4,4)cc-pVDZ.

compute structural and thermochemical information for this molecule as a basis for evaluating its properties and potential existence.

Computational Methods

All structures were fully optimized by an analytical gradient using the Gaussian94 and Gaussian98 suites.[12] Density functional (DFT) calculations used the exchange potentials of Becke[13a] and the correlation functional of Lee, Yang, and Parr.[13b] Electron correlation was included via optimizations utilizing second-order Møller–Plesset perturbation theory methods (MP2).[14] Coupled cluster theory[15] with double substitutions (CCD) in combination with Dunning's double-ξ correlation consistent basis set[16] was used for higher-level optimizations. CASSCF methods[17] were used as incorporated in Gaussian98. Frequencies were computed by analytical and numerical methods (CCD results). Reported enthalpies were corrected for zero-point energy differences (ZPVE) (unscaled[18]) and thermal effects at 298.150 K.

Results and Discussion

Full geometry optimization of C_{2v} tetrahedrene **5** at the RHF/6-311++G(d,p) level gave rise to a structure with a C=C bond length of 1.348 Å that displayed one negative frequency -644.7 cm^{-1} after normal coordinate analysis. Although this result characterized **5** as a first-order saddle point, inclusion of electron correlation via Møller–Plesset and DFT methods gave rise to "true" minimum energy structures shown in Figure 4, that is, no negative frequencies after vibrational analysis. Others have shown that correlation energy plays an unusually important role in small ring systems.[19] In this regard, insight into the unusual nature of the bonding in **5** is evident from examination of the molecular orbital plot[20] (Figure 5) of the highest occupied molecular orbital (HOMO) of **5.** Clearly, the "double bond" of tetrahedrene is unique in its orbital structure in that electron density is delocalized over the entire framework as a result of mixing interactions between the π orbitals of the double bond and the Walsh orbitals of the cyclopropane rings.

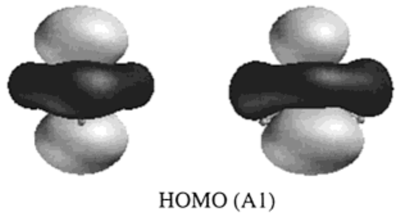


Figure 5. HOMO [RB3LYP/6-311+G(d)]: tetrahedrene **5.** Viewed along HC–CH axis (L); C=C axis (R).

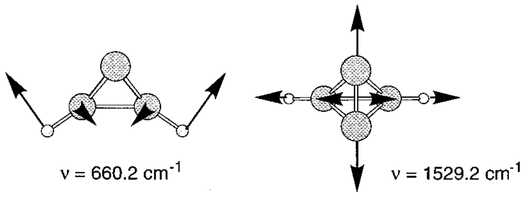


Figure 6. Select vibrational modes for tetrahedrene **5**: RCCD/cc-pVDZ.

Full geometry optimization at the RCCD/cc-pVDZ level led to structure **5** shown in Figure 4. At this level, the lowest energy vibrational mode for **5** appeared at 660 cm^{-1} (A1) and involves stretching of the HC–CH bond via scissoring motions (Figure 6). A higher energy frequency at 1529.2 cm^{-1} (A1) is a complex mode involving C=C stretching and other motion. These results indicate that **5** exists in a potential well that may be deep enough to permit isolation.

Olefin strain energy for tetrahedrene was estimated from the computed heat of hydrogenation to form tetrahedrane, 144.5 kcal/mol (RCCD/cc-pVDZ). By the method of Hrovat and Borden,[5] we calculated an OSE of ~117.8 kcal/mol for **5**, the highest value to date (cf. Figure 2). An alternative diagnostic for strain is the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (LUMO).[5] Unstrained tetrasubstituted alkenes have relatively large computed gaps ~5.8 eV for bicyclo[3.3.0]oct-1(5)-ene (**1**) (RB3LYP/6-311+G*), but strained alkenes have significantly smaller gaps due to a lowering of the LUMO energy, for example, **3** is ~4.1 eV (RB3LYP/6-311+G*). Our computed value for tetrahedrene, ~2.1 eV, at the same level is consistent with this trend.

Although all indications favor a stable ground-state singlet configuration for tetrahedrene, stability tests[21] on the optimized wave functions (e.g., RMP2/6-31G*, B3LYP/6-31G*, RB3LYP/6-311+G*) revealed RHF → UHF instability problems. These results indicate that a lower

---

[12] (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

[13] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B*: *Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.

[14] Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618–622.

[15] (a) Scuseria, G. E.; Schaefer, H. F. *J. Chem. Phys.* **1989**, *90*, 3700–3703. (b) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968–5975.

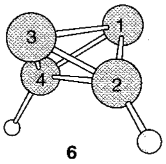
[16] Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

[17] Hegarty, D.; Robb, M. A. *Mol. Phys.* **1979**, *38*, 1795. Eade, R. H. E.; Robb, M. A. *Chem. Phys. Lett.* **1981**, *83*, 362.

[18] Scaling factors for these DFT and MP2 methods are small, 1–3%. Scott, A. P.; Radom, L. *J. Chem. Phys.* **1996**, *100*, 16502–16513.

[19] (a) Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 7325–7328. (b) Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652–7659.

[20] MO plots were prepared from cube files derived from RB3LYP/6-311+G(d) calculations and viewed with CS Chem3D 5.0 from CambridgeSoft Corp., Cambridge, MA.



6

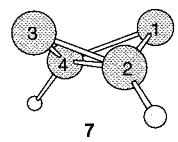
Distances (Å): i.; ii.; iii.	Angles: i.; ii.; iii.
1-2: 1.452; 1.438; 1.476	1-3-2: 51.3°; 52.0°; 61.7°
1-3: 1.815; 1.746; 1.397	1-2-3: 77.3°; 74.8°; 56.5°
2-4: 1.731; 1.770; 1.591	1-2-4: 53.4°; 52.6°; 57.4°

Figure 7. Geometric data for tetrahedrene triplet state (C_{2v}). (i) UCCD/cc-pVDZ; (ii) UB3LYP/6-311+G(d); (iii) CASSCF-(4,4)cc-pVDZ.

energy wave function exists for **5** and that the ground state of the structure is more correctly described as a triplet state or a diradical.[21] Re-optimization of **5** as a triplet state at the UB3LYP/6-311+G* level led to a stationary point **6** with a stable wave function with essentially no spin contamination from higher states (found, $S^2 = 2.007$; for a pure triplet, $S^2 = 2.000$) and an energy 36.6 kcal/mol lower than that of the singlet state. Similarly, we found a singlet−triplet gap at the R(U)-CCD/cc-pVDZ level of −37.0 kcal/mol ($S^2 = 2.027$) with a lowest energy vibrational mode = 418 cm^{-1}. Since these methods may overemphasize the importance of charged separated states,[22] we also computed the $\Delta(E_s - E_t)$ gap using CASSCF(4,4)/cc-pVDZ methodology[17] and found a value of 28.0 kcal/mol. The computed triplet state geometries are shown in Figure 7. The abnormally long bonds[23]found for the triplet state (1.82−1.75 Å) as compared to the singlet state (1.40 Å) are noteworthy, and this factor may contribute to the reduced singlet−triplet gaps. Electron repulsion would be expected to be greatly reduced in the triplet state relative to the singlet state as a consequence.

The singlet diradical state was also investigated by re-optimizing the unstable wave function generated from the RB3LYP/6-31G* experiment above at the singlet UB3LYP/6-31G* level. The new wave function was 6.4 kcal/mol lower in energy and led to an isomer ~94 kcal/mol lower in energy with a C1- - -C2 separation of 2.14 Å.[24] The resulting wave function proved to be stable, and the resulting structure is best described as 1,3-dicarbene **7** (Figure 8).

Re-optimization of **7** at higher levels (RB3LYP/6-311+G*, RMP2/6-311++G**, and RCCD/cc-pVDZ) led to stationary states with no negative frequencies, stable wave functions, and little change in structure. Efforts were made to locate an energy barrier between **5** and **7** using synchronous transit-guided quasi-Newton methodology.[25] This method attempts to find a transition structure starting from initial coordinates that lie midway between the two structures in question. In the event, the method did not lead to a converged structure.



7

Distances (Å): i.; ii.; iii.	Angles: i.; ii.; iii.
1-2: 1.454; 1.438; 1.463	2-1-4: 68.7°; 69.7°; 69.3°
1-3: 2.165; 2.126; 2.172	1-2-3: 96.2°; 95.4°; 95.2°
2-4: 1.641; 1.664; 1.668	1-2-4: 55.6°;55.2°; 55.4°

Figure 8. Geometric data for bis-bicyclo[1.1.0]cyclobutylidene (C_{2v}). (i) RCCD/cc-pVDZ; (ii) RB3LYP/6-311+G(d); (iii) MP2/cc-pVDZ.

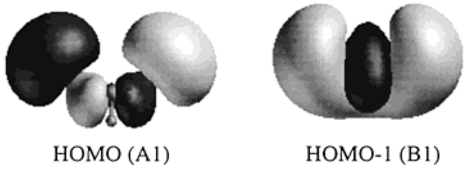


Figure 9. HOMO (L) and HOMO-1 (R) [RB3LYP/6-311+G-(d)]: bis-bicyclo[1.1.0]cyclobutylidene **7**. Viewed along HC−CH axis.

More details on the electronic structure of **7** were obtained from a population analysis and NBO methods.[26] The HOMO (Figure 9) showed a degenerate pair of $sp^{0.69}$ orbitals localized on the two carbenic centers. The HOMO-1 (Figure 9) proved to be highly delocalized over the entire framework as a consequence of the high degree of p character (~93%) in the orbitals associated with the strained HC−CH bond (vide infra). Consistent with this, we found that the energy of the HOMO of **7** was ca. 18.4 kcal/mol lower in energy than that for the monocarbene analogue bicyclo[1.1.0]butylidene **10** (RCCD/cc-pVDZ). The energy of the HOMO-1 of **7** was 41 kcal/mol lower in energy than the HOMO of **10**.

The unique proximity of the carbene centers in **7** prompted us to undertake computations to evaluate its thermochemical properties. The computed reaction heat for hydrogenation of the bis-carbene was compared to those for cyclopropylidene **8** and bicyclo[1.1.0]butylidene **10**. The bicyclic carbenes were found to be stabilized relative to cyclopropylidene but were of comparable stability (Figure 10).

These data can be used to make a homodesmotic comparison between dicarbene **7** and monocarbene **10** in which case the ΔH for eq 1 is equal to 4.8 kcal/mol. This

7 11 10 (1)

result suggests that despite the stabilization that might be attributable to delocalization of the HOMO and the HOMO-1, the presence of the two closely spaced carbene centers in **7** does not lead to appreciable stabilization of the system relative to the monocarbene.

A second criterion for singlet carbene stabilization involves comparison of singlet−triplet gaps for carbenes **8**, **10**, and **7** (Table 1).[27] The large singlet−triplet gap for cyclopropylidene **8**[28] is a result of the destabilizing effect of angular distortion on the triplet-state energy and a

---

[21] (a) Schlegel, H. B.; McDouall, J. J. W. In *Computational Advances in Organic Chemistry*; Ögretir, C., Csizmadia, I. G., Eds.; NATO-ASI Series C 330; Kluwer Academic Pubs: The Netherlands, 1991; pp 167−185. (b) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed; Gaussian: Pittsburgh, 1996; pp 34−37.

[22] For a discussion, see: Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; pp 1−72. We know of no alkenes with triplet state energy below the singlet level. The computed $\Delta(E_s - E_t)$ gap for the highly strained homocub-1(9)-ene has been reported to be 1.2 kcal/mol. Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2719−2720. Holthausen, M. C.; Koch, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 668−670. The computed $\Delta(E_s - E_t)$ gap for tricyclo-[3.3.0.0^{3,7}]oct-1(5)-ene (**3**), −13.7 kcal/mol, is consistent with this idea: (C=C)S_1 = 1.379 Å; (C=C)T_1 = 1.619 Å.

[23] The longest single bond measured experimentally is 1.72 Å in benzcyclobutadiene derivatives: Toda, F.; Tanaka, K.; Stein, Z.; Goldberg, I. *Acta Crystallogr., Sect. C* **1996**, *52*, 177−180. See also: Kaupp, G.; Boy, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 48−49 and Isea, R. *J. Mol. Struct.* **2001**, *540*, 131−138 for discussions of long bonds. The CASSCF results may not be accurate given the limited active space that we could handle.

[24] Single point energy calculations at the RCCSD(T)/cc-pVDZ//RCCD/cc-pVDZ level gave a **5**−**7** energy difference of 84.8 kcal/mol (uncorrected for ZPVE).

Table 1. Triplet−Singlet Gaps for Carbenes[28]

	CCD/cc-pVDZ			B3LYP/6-311+G(d)		
carbene	*E* singlet^a	*E* triplet^a	$\Delta\ T - S^b$	*E* singlet^a	*E* triplet^a	$\Delta\ T - S^b$
8^c	−116.136618	−116.113709	14.4	−116.519268	−116.497469	13.7
10^d	−154.120550	−154.047630	45.8	−154.624051	−154.550110	46.4
7	−152.870669	−152.805041	41.2	−153.365563	−153.309365	35.3

^{a} ZPE corrected enthalpy at 298.150 K (hartrees). ^{b} kcal/mol. ^{c} C_{2v}. ^{d} C_s.

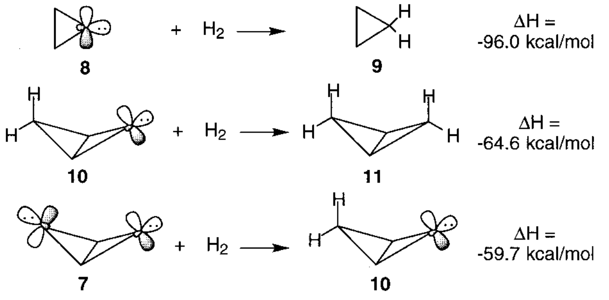


Figure 10. Enthalpy changes for hydrogenation reactions at 298.150 K [RB3LYP//6-311+G(d)].

stabilizing effect on the singlet state due to changes in the degree of s character of the extra-ring orbital. Ring strain is believed to destabilize triplet states relative to singlet states; the C−C−C angle in dimethylcarbene is on the order of 130° as compared to 110° for the singlet state.[28−30] Singlet−triplet gaps for bicyclo[1.1.0]cyclobutylidene **10** and bis-carbene **7** are much larger, as a result of additional singlet-state stabilization resulting from delocalization of electron density from the p-like orbitals of the highly strained "bond" between the two CH centers into the "vacant" p orbitals at the carbene centers. In agreement with this, NBO formalism (RB3LYP/6-31G*) revealed significant electron density (0.444 e) in each of the carbenic p orbitals (cf. Figure 8).

Estimates of the heats of formation of **5** and **7** were made by means of thermochemical comparisons at the RCCD/cc-pVDZ levels with the known heat of formation of diacetylene (111 kcal/mol): **5** → 270 kcal/mol; **7** → 179 kcal/mol.[31]

Summary

Calculations indicate that tetrahedrene **5** is a metastable molecule at best,[32] and experimental efforts to synthesize it must take cognizance of potential rearrangements to the bis-carbene **7** and/or other isomers. The greater stability of the bis-carbene **7** relative to tetrahedrene is unprecedented and has stimulated a search for related systems. Future investigations will explore a variety of energy-lowering paths for the unique bis-carbene **7**, for example, hydrogen shifts, alkyl migration, ring opening, and electrocyclic rearrangements. The computed structure of the triplet state of tetrahedrene has unique bond lengths and may be more accessible experimentally than the singlet state because concerted energy-lowering rearrangements are less probable.

Acknowledgment. Helpful discussions and comments from the following are gratefully acknowledged: W. T. Borden, J. K. Lee, K. Krogh-Jespersen, D. Hrovat, and O. Wiest. We are also grateful to R. Siegel and the Center for Computational Neuroscience at Rutgers University (Newark) for computational resources.

Supporting Information Available: Tables giving Cartesian coordinates, zero-point energies (ZPVE), select eigenvalues, harmonic vibrational frequencies and intensities for ^{1}**5**, ^{3}**5**, ^{1}**6**, ^{3}**6**, ^{1}**7**, ^{3}**7**, ^{1}**8**, ^{1}**10**, and diacetylene at the RB3LYP/6-311+G(D) and RCCD/cc-pVDZ levels of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

JO000941U

---

(25) Peng, C.; Schlegel, H. B. *Isr. J. Chem.* **1993**, *33*, 449−454. We also carried out a relaxed potential energy scan search for a transition state in which the distance between the two alkene carbons was varied incrementally by 0.04 Å units. Twenty increments sufficed to span the gap between these carbons in tetrahedrene vs the bis-carbene. Two energy maxima were produced, neither of which led to stationary states when the corresponding geometries were subjected to normal transition state optimizations.

(26) Glendening, J. K.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 4.0.* Theoretical Chemistry Institute, University of Wisconsin: Madison, 1996.

(27) Nicolaides, A.; Matsushita, T.; Tomioka, H. *J. Org. Chem.* **1999**, *64*, 3299−3305.

(28) (a) Cramer, C. J.; Worthington, S. E. *J. Phys. Chem.* **1995**, *99*, 1462−1465 calculated an T−S gap of 13.8 kcal/mol. (b) Bettinger, H. F.; Schreiner, P. R.; Schleyer, P. v. R.; Schaeffer, H. F., III. *J. Phys. Chem.* **1996**, *100*, 16147−16154 report a range of computed T−S values for cyclopropylidene from 11.1 to 14.9 kcal/mol.

(29) For a discussion of the influence of structural features on carbene T−S gaps, see: Stracener, L. L.; Halter, R. J.; McMahon, R. J.; Castro, C.; Karney, W. L. *J. Org. Chem.* **2000**, *65*, 199−204.

(30) (a) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034−7041. (b) Matzinger, S.; Fülscher, M. P. *J. Phys. Chem.* **1995**, *99*, 10747−10751. (c) Ford, F.; Yuzawa, T.; Platz, M. S.; Matzinger, S.; Fülscher, M. *J. Am. Chem. Soc.* **1998**, *120*, 4430−4438.

(31) Kiefer, J. H.; Sidhu, S. S.; Kern, R. D.; Xie, K.; Chen, H.; Harding, L. B. *Combust. Sci. Technol.* **1992**, *82*, 101−130. Calculated enthalpy for diacetylene (ZPVE corrected) at 298.150 K (RCCD/cc-pVDZ): −152.978269 hartrees.

(32) An earlier, computational study at the HF/4-31G level reported that tetrahedrene was a saddle point. Simkin, B. Y.; Glukhovtsev, M. N. *Zh. Org. Khim.* **1982**, *18*, 1337−1345.