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# $C_5H_4$: Pyramidane and Its Low-Lying Isomers

**Joseph P. Kenny, Karl M. Krueger, Jonathan C. Rienstra-Kiracofe, and Henry F. Schaefer III***

*Center for Computational Quantum Chemistry, Department of Chemistry, University of Georgia, Athens, Georgia 30602*

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The chemistry of the $C_5H_4$ singlet potential energy surface was investigated at sophisticated levels of theory with a focus on the stability of pyramidane (tetracyclo[2.1.0.0$^{1,3}$0$^{2,5}$]pentane or [3.3.3.3]fenestrane), a structure featuring a carbon atom at the apex of a square pyramid. Zero-point corrected relative energetics were predicted with both coupled cluster and density functional methodologies. Computations with both methodologies agree qualitatively with previous theoretical results, demonstrating that the pyramidane structure is a true minimum with substantial barriers to isomerization. At the CCSD(T)/TZ2P level a relative energy of 24 kcal/mol was predicted for the transition state to tricyclo[2.1.0.0$^{2,5}$]pent-3-ylidene, the lowest barrier to isomerization of pyramidane. The transition state to bicyclo[2.1.0]pent-2-ene-5-ylidene, the other transition state known to lead directly to the pyramidane structure, was found to lie 33 kcal/mol above pyramidane. Relative energies are also provided for several lower-lying $C_5H_4$ isomers, including isomers incorporating linear carbon chains.

## Introduction

Structures in which a carbon atom possesses pyramidal coordination have been described as the bridge between organic and organometallic chemistry.[1] Following the prediction of a stable pyramidal structure for the $(CH)_5^+$ ion by Stohrer and Hoffman,[2] experimental evidence[1,3,4] and theoretical results[1,5−7] for pyramidal bonding environments were presented by several researchers. Minkin[8] and Schwarz[9] have provided reviews of this subject.

Tetracyclo [2.1.0.0$^{1,3}$0$^{2,5}$]pentane or [3.3.3.3]fenestrane (**1**), henceforth referred to as pyramidane, is attractive as a simple neutral structure with pyramidally coordinated carbon. The first suggestion that this was a stable structure was given by Minkin, Minyaev, Zakharov, and Avdeev in 1978.[10] Their semiempirical MINDO/3 calculations predicted pyramidane to be a true minimum on the $C_5H_4$ potential surface. This work was soon followed by suggestions for a synthetic approach.[11]

The final contribution from Minkin and co-workers incorporated more reliable *ab initio* results providing important insight into possible synthetic routes.[12] The computations at the HF/STO-3G//HF/4-31G level confirmed their earlier semiempirical results predicting pyramidane stability and suggested tricyclo[2.1.0.0$^{2,5}$]pentylidene (**5**), lying about 15 kcal/mol above pyramidane, as a suitable precursor. Their work included important results regarding the electronic states of pyramidane and cyclopentadienylidene. A singlet ground state was predicted for pyramidane with a singlet-triplet splitting of 47 kcal/mol. The lowest energy cyclopentadienylidene-type isomer was found to have a triplet ground state, eliminating these species as possible realistic synthetic precursors.

The HF/6-31G* and MP2 results provided by Balaji and Michl in 1988 again confirmed that pyramidane was indeed a local minimum.[13] The most recent works on pyramidane are the 1998 and 2000 contributions of Lewars.[14,15] His comprehensive study of the $C_5H_4$ surface demonstrated that the transition state to tricyclo[2.1.0.0$^{2,5}$]pent-3-ylidene (**3**) represents the lowest barrier to isomerization of pyramidane. At the QCISD(T)/6-31G*//MP2(FC)/6-31G* level a value of 23 kcal/mol was predicted for this barrier.

Despite the wealth of theoretical results predicting the stability of this fascinating molecule, to our knowledge it has never been synthesized. Therefore we have examined stationary points on the $C_5H_4$ singlet surface with the goal of determining whether the features predicted hold at the reliable coupled cluster level of theory. We have also utilized inexpensive density functional methodologies and comment on the agreement between density functional and coupled cluster methodologies for the unusual structures studied.

## Theoretical Methods

The primary basis set employed in this study, denoted DZP, was the standard double-ζ set of Huzinaga and Dunning[16,17] augmented with a set of *d* polarization functions on carbon [$\alpha_d(C) = 0.75$] and a set of *p* polarization functions on hydrogen [$\alpha_p(H) = 0.75$]. This basis set, designated [C(9s5p1d/4s2p1d) and H(4s1p/2s1p)], resulted in 95 contracted basis functions.

The larger TZ2P basis set consisted of the contracted triple-ζ functions of Dunning[18] augmented with two sets of *d* polarization functions on carbon [$\alpha_d(C) = 1.50$ and 0.375] and two sets of *p* polarization functions on hydrogen [$\alpha_p(H) = 1.50$ and 0.375]. This basis set, designated [C(10s6p2d/5s3p2d) and H(5s2p/3s2p)], resulted in 156 contracted basis functions.

Geometry optimizations for all structures were performed with the CCSD(T) method.[19−23] Computations were carried out for all structures with the smaller DZP basis set. The pyramidane minimum and the two transition states leading directly from it were also optimized with the TZ2P basis set to obtain more reliable energetics and gauge the validity of the DZP results. All CCSD(T) computations were carried out with the ACES II package.[24] The geometry optimization convergence criterion was $10^{-7}$ Hartree/bohr (Hartree/radian for angles) for the RMS gradient and the spin-restricted Hartree−Fock (RHF) reference was used.

All structures were also optimized using density functional methods (DFT) incorporating both the B3LYP[25,26] and the

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* Author to whom correspondence should be addressed.

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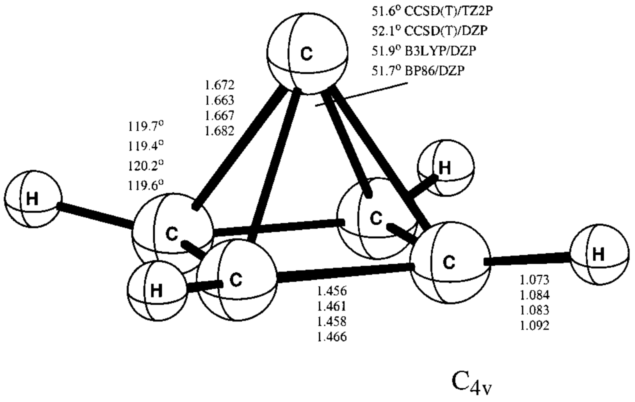

**Figure 1.** Structure of tetracyclo[2.2.0.0$^{1,3}$0$^{2,5}$]pentane, structure **1** (bond distances in angstroms).

BP86[27,28] functionals. The BP86 functional, a pure DFT exchange functional, was included mainly to allow comparison with the parametrized B3LYP functional. The DZP basis set was used for all DFT computations.

All DFT investigations were performed with the Gaussian 94 package.[29] Geometry optimizations were attempted with the default grid (75 302) and SCF convergence criterion (density converged to $10^{-8}$) for all structures. Using these defaults stationary points could not be converged upon for the linear carbon chain isomers. Convergence was achieved for these molecules by tightening the SCF convergence to $10^{-12}$ and using a more dense integration grid (99 434).

Harmonic vibrational frequencies were evaluated for all structures in order to compute zero-point energy corrections as well as to characterize the stationary points as minima or transition states. Frequencies computed numerically at the CCSD(T)/DZP level were used to correct both CCSD(T)/DZP and CCSD(T)/TZ2P energies. At the DFT level, frequencies were computed analytically for both functionals. All minima and transition states were found to have zero and one imaginary frequencies, respectively, at both the CCSD(T) and DFT levels. We have assumed that the characterization of transition states indicated by previous intrinsic reaction coordinate (IRC) studies[14] and supported by animation of the computed imaginary frequencies holds for our results.

## Results

All bond distances and (selected) bond angles for each structure are provided in Figures 1−10. Given the atypical bonding environments examined, some comment on the relative performance of each method is worthwhile. Taking the CCSD(T)/TZ2P geometries for structures **1**, **3**, and **6** as our superior theoretical results, we compared bond distances and bond angles for these three structures with those found at lower levels of theory. The average absolute difference between the CCSD(T)/TZ2P bond distances were 0.008 and 0.007 angstroms for CCSD(T)/DZP and B3LYP, respectively. The average absolute differences of bond lengths for the BP86 functional is somewhat larger at 0.014 Å. Bond angles found at all three lower levels of theory, with average absolute differences below 0.5°, compared quite well with the CCSD(T)/TZ2P results. For qualitative purposes, coupled cluster with the small DZP basis set and both DFT methodologies were thus found to give good agreement with our best theoretical geometries for these three structures. We found no evidence suggesting that this level of qualitative agreement would not be found for the other structures studied.

Zero-point vibrationally corrected relative energies found at coupled cluster and DFT levels of theory are given in Table 1.

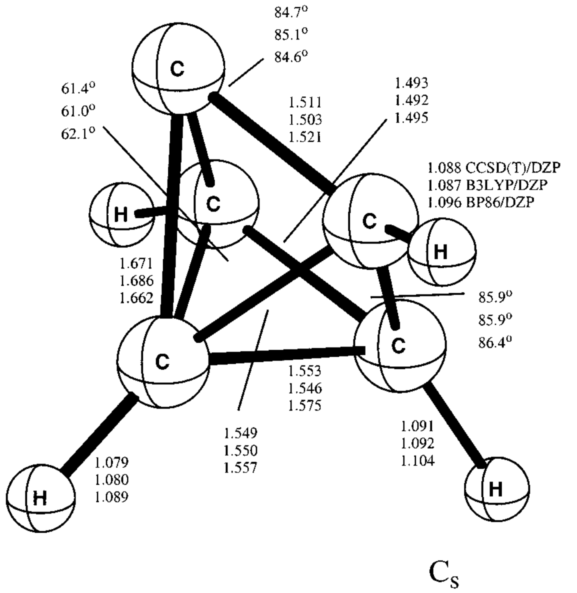

**Figure 2.** Structure of tricyclo[2.1.0.0$^{2,5}$]pent-3-ylidene, structure **2** (bond distances in angstroms).

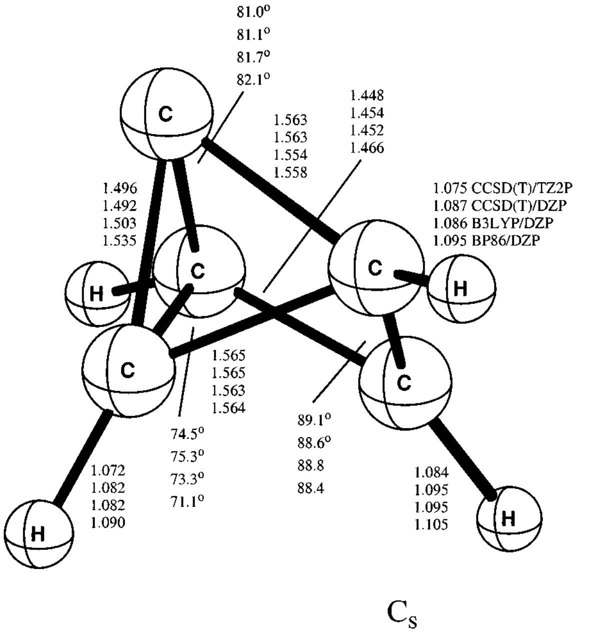

**Figure 3.** $C_s$ symmetry transition state, structure **3** (bond distances in angstroms). This transition state connects structure **1** with structure **2**.

The large number of structures for which coupled cluster frequencies were desired places some limits on the size of basis set which may be used. To assess the accuracy of the CCSD(T)/DZP total energies, we optimized pyramidane (**1**) and the transition states leading directly to it (**3**,**6**) at the CCSD(T)/TZ2P level. Differences between TZ2P and DZP relative energies were 0.8 and 1.9 kcal/mol for structures **3** and **6**, respectively. Given the substantial energy separations predicted for the studied systems, errors on the order of several kcal/mol will not change the qualitative features of the potential surface. We conclude that the CCSD(T)/DZP results do give a reliable qualitative prediction of the $C_5H_4$ singlet potential energy surface. A graphical representation of this surface, with CCSD(T)/TZ2P results given at critical points, is provided in Figure 11.

While both DFT functionals reproduced the coupled cluster geometrical parameters reasonably well, the BP86 relative energetics were in better agreement with the CCSD(T)/DZP

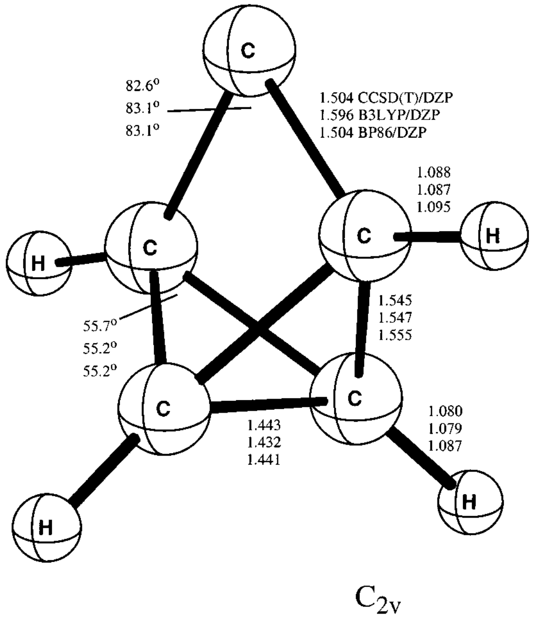

**Figure 4.** $C_{2v}$ symmetry transition state, structure **4** (bond distances in angstroms). This transition state connects mirror image forms of structure **2**.

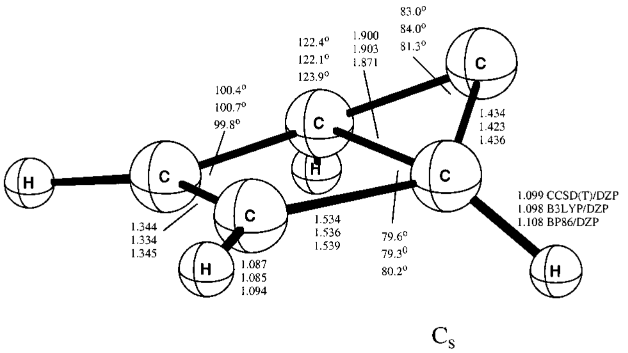

**Figure 5.** Structure of bicyclo[2.1.0]pent-2-ene-5-ylidene, structure **5** (bond distances in angstroms).

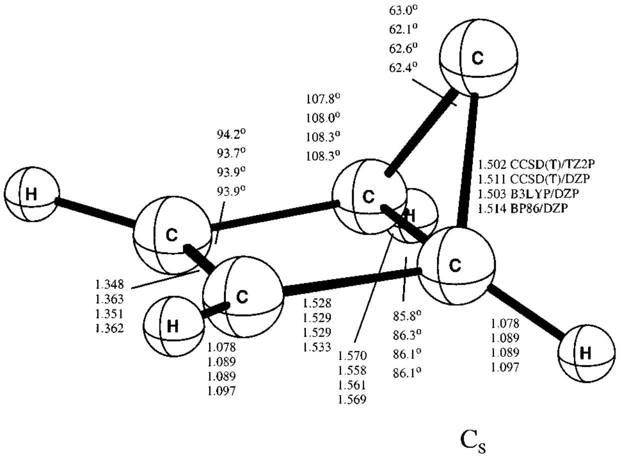

**Figure 6.** $C_s$ symmetry transition state, structure **6** (bond distances in angstroms). This transition state connects structure **1** with structure **5**.

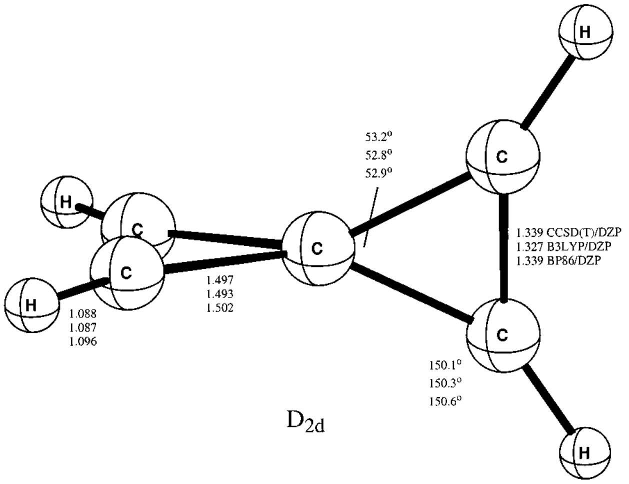

**Figure 7.** Structure of spiropentadiene, structure **7** (bond distances in angstroms).

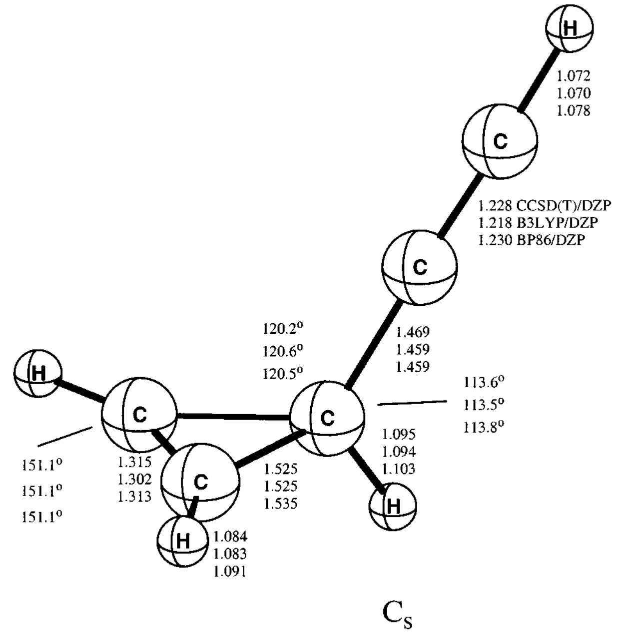

**Figure 8.** Structure of 3-ethynylcyclopropene, structure **8** (bond distances in angstroms).

results. For the structures studied, the average absolute differences between B3LYP and CCSD(T)/DZP relative energies was 5.5 kcal/mol. Excluding structures **7**−**10**, for which large discrepancies were found, improves this number to 3.9 kcal/mol. The BP86 functional yielded much better energetics, with average absolute differences of only 2.8 and 1.5 kcal/mol for structures **1**−**10** and **1**−**6**, respectively. While structures **1**−**6** appear to be adequately described by density functional methods, the lower-lying carbon chain isomers (**9**,**10**) discussed below may prove problematic.

Harmonic vibrational frequencies at both the coupled cluster and DFT levels were consistent with the characterization of each stationary point as either a minimum or a transition state. Harmonic frequencies are given in Table 2 for pyramidane (**1**) at both the coupled cluster and DFT levels. The absence of low or imaginary frequencies indicates that this structure is a true minimum on the $C_5H_4$ potential energy surface.

Our best predictions for relative energies were obtained at the CCSD(T)/TZ2P level for structures **3** and **6**, and the CCSD(T)/DZP level for all other structures. From the pyramidane minimum, the lowest barrier was found to lead to tricyclo-[2.1.0.0$^{2,5}$]pent-3-ylidene (**2**). This structure was found to lie 19.8 kcal/mol above pyramidane. Structure **3**, the transition state to structure **2**, was located 24.1 kcal/mol above pyramidane. Our CCSD(T)/TZ2P value for this barrier is somewhat larger than Lewars' QCISD(T)/6-31G*//MP2(FC)/6-31G* value of 23.0 kcal/mol[14] and his G2(MP2) value of 22.7 kcal/mol.[15] The

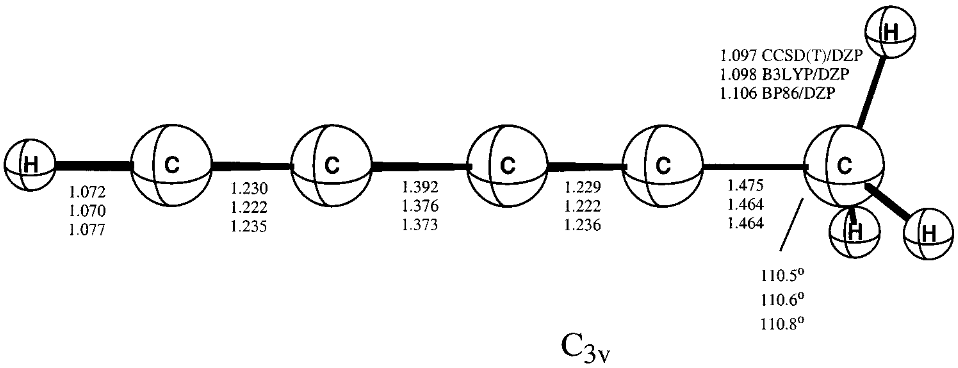

**Figure 9.** Structure of 1,3-pentadiyne, structure **9** (bond distances in angstroms).

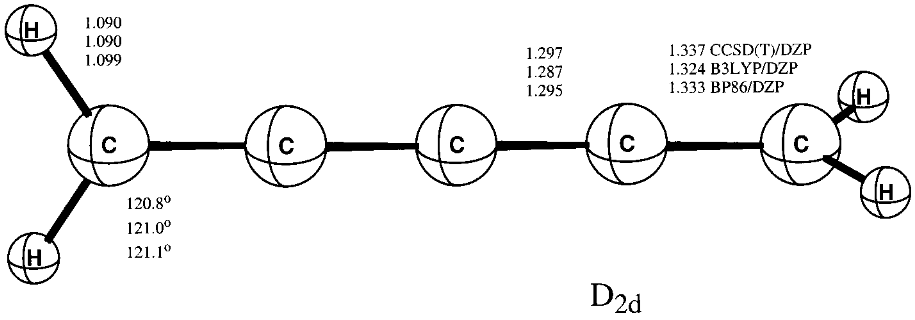

**Figure 10.** Structure of 1,2,3,4-pentatetraene, structure **10** (bond distances in angstroms).

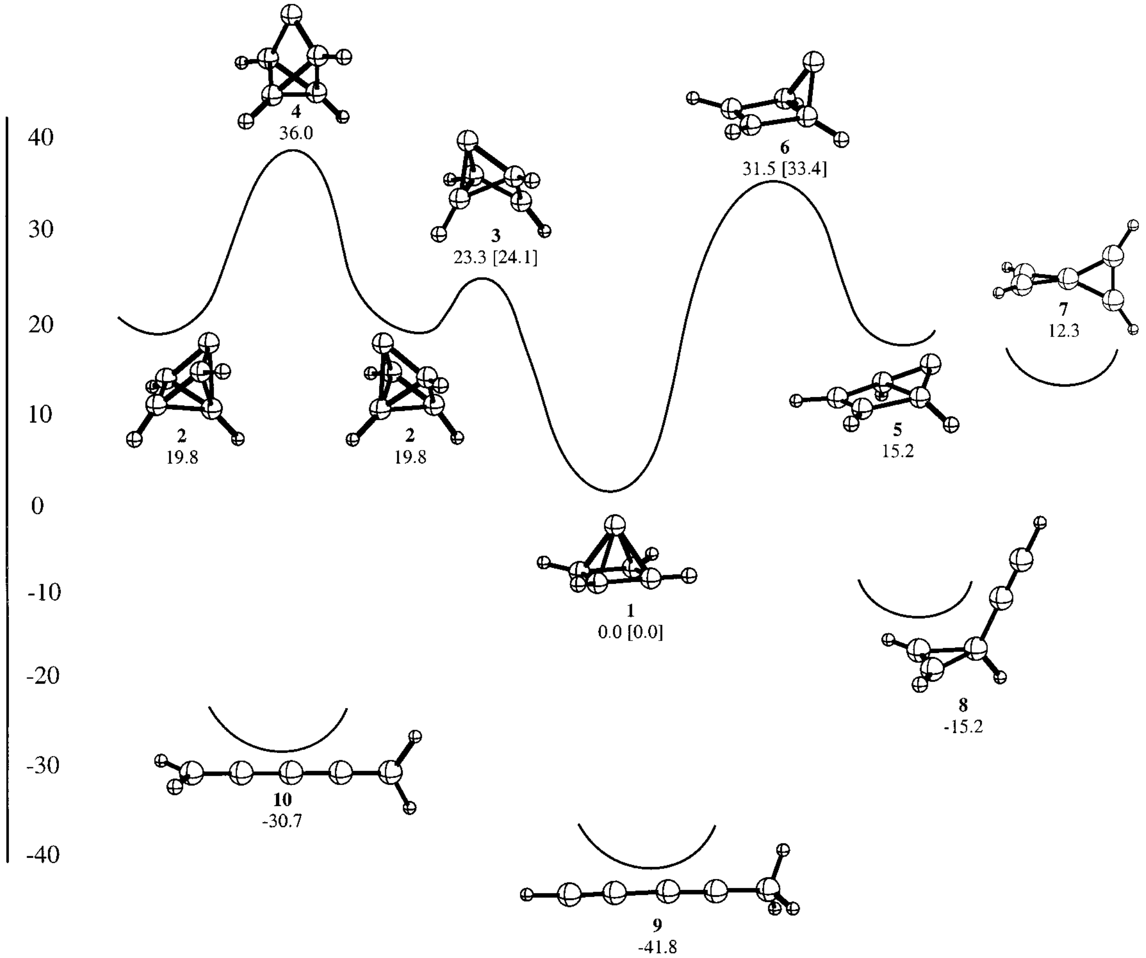

**Figure 11.** Representation of examined features of the $C_5H_4$ potential energy surface. Relative energies found at the CCSD(T)/DZP [CCSD(T)/TZ2P] level are given.

**TABLE 1: Coupled Cluster and DFT Relative Energies (kcal/mol) Including Zero-Point Corrections**

| | CCSD(T) | | B3LYP | BP86 |
|---|---|---|---|---|
| structure | TZ2P | DZP | DZP | DZP |
| **1** | 0.0 | 0.0 | 0.0 | 0.0 |
| **2** | | 19.8 | 16.6 | 17.4 |
| **3** | 24.1 | 23.3 | 20.8 | 20.2 |
| **4** | | 36.0 | 31.2 | 35.1 |
| **5** | | 15.2 | 10.5 | 15.4 |
| **6** | 33.4 | 31.5 | 27.0 | 32.6 |
| **7** | | 12.3 | 7.2 | 11.3 |
| **8** | | −15.2 | −18.6 | −10.4 |
| **9** | | −41.8 | −47.7 | −37.9 |
| **10** | | −30.7 | −45.7 | −38.9 |

**TABLE 2: Harmonic Vibrational Frequencies ($cm^{-1}$) and Infrared Intensities (in parentheses, km/mol) for Pyramidane**

| | CCSD(T)/DZP | B3LYP/DZP | BP86/DZP |
|---|---|---|---|
| $b_2$ | 370 (0) | 438 (0) | 397 (0) |
| e | 433(3) | 402 (5) | 429 (4) |
| $a_1$ | 735(44) | 727 (46) | 704 (44) |
| e | 785 (25) | 798 (24) | 758 (24) |
| $b_2$ | 865 (0) | 879 (0) | 844 (0) |
| e | 994 (15) | 984 (18) | 955 (18) |
| $b_1$ | 1005 (0) | 996 (0) | 967 (0) |
| $b_2$ | 1021 (0) | 1012 (0) | 979 (0) |
| $a_1$ | 1075 (110) | 1068 (121) | 1028 (119) |
| $a_2$ | 1183 (0) | 1169 (0) | 1124 (0) |
| $b_1$ | 1310 (0) | 1285 (0) | 1254 (0) |
| $a_1$ | 1321 (2) | 1314 (2) | 1282 (2) |
| e | 1405 (0.2) | 1386 (1) | 1343 (1) |
| $b_2$ | 3289 (0) | 3260 (0) | 3181 (0) |
| e | 3305 (0) | 3274 (1) | 3196 (0) |
| $a_1$ | 3325 (1) | 3294 (0.4) | 3215 (0.5) |

other directly accessible isomer, bicyclo[2.1.0]pent-2-ene-5-ylidene (**5**), was found to lie 15.2 kcal/mol above pyramidane. At 33.4 kcal/mol higher than pyramidane, the transition state to **5**, designated structure **6**, was found to lie 9.3 kcal/mol higher than the barrier to **2**. Structure **4**, the transition state between mirror image forms of structure **2**, completes the pyramidane portion of the singlet $C_5H_4$ surface. This structure was located 36.0 kcal/mol above pyramidane. These results show good agreement with the previous results of Lewars, confirming the viability of the pyramidane molecule.

In efforts toward determining the place of the pyramidane system in the global $C_5H_4$ surface, several other minima were examined. Spiropentadiene, strucuture **7**, seems to be a possible precursor to pyramidane. While silicon analogs of this structure have recently been isolated,[30] spiropentadiene and 1,1′-dichlorinated spiropentadiene decompose within 20 min at −100 °C.[31,32] Lewars was unable to locate a transition state connecting structures **1** and **7**.[14] Our attempts to locate a transition state at the B3LYP/DZP level were also unsuccessful. The first of the lower-lying isomers studied is 3-ethynylcyclopropene (**8**), an experimentally observed molecule whose structure has been of interest.[33−35] Our computations place this structure 15.2 kcal/mol below the pyramidane minimum.

Of all structures studied, those incorporating linear carbon chains were found to be energetically lowest-lying. At the CCSD(T)/DZP level 1,2,3,4-pentatetraene (**10**) was found to lie 30.7 kcal/mol below pyramidane. The most significant disagreements between coupled cluster and DFT energetics occurred for this structure. B3LYP and BP86 relative energies were −45.7 and −38.9 kcal/mol, differences with the coupled cluster results of −15.0 and −8.2 kcal/mol, respectively. At the CCSD(T)/DZP level, the lowest-lying structure examined was 1,3-pentadiyne (**9**). This structure was found to lie 41.8 kcal/mol below the pyramidane minimum. The B3LYP functional, predicting a relative energy of −47.7 kcal/mol, also places **9** lower than **10**, but only by 2.0 kcal/mol. The BP86 functional, however, places **9** 1.0 kcal/mol higher than **10** at −37.9 kcal/mol. The 1,3-pentadyine structure (**9**) is likely the global $C_5H_4$ minima.

## Conclusions

Despite the atypical bonding environments encountered in this study, both coupled cluster and DFT computations appear to give credible results which are certainly of qualitative use. While both the B3LYP and BP86 functionals reproduced coupled cluster geometries fairly well, agreement with coupled cluster relative energetics was found to be significantly better with the BP86 functional.

Our coupled cluster results show qualitative agreement with previous theoretical predictions. While the computed energetics may be subject to minor improvements by computations with larger basis sets, the general features of the pyramidane portion of the $C_5H_4$ singlet surface predicted by previous theoretical results are firmly established at the coupled cluster level. While a successful synthetic scheme may prove elusive, there is no doubt that the pyramidane structure is a true local minimum with substantial barriers to isomerization.

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## References and Notes

(1) Hogeveen, H.; Kwant, P. W. *Acc. Chem. Res.* **1975**, *8*, 413.

(2) Stohrer, W. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 1661.

(3) Minkin, V. I.; Zefirov, N. S.; Korobov, M. S.; Nivorozhkin, L. E.; Averina, N. V.; Boganov, A. M. *Zh. Org. Khim.* **1981**, *17*, 2616.

(4) Hart, H.; Kuzya, M. *J. Am. Chem. Soc.* **1972**, *94*, 8958.

(5) Minkin, V. I.; Minyaev, R. M. *Zh. Org. Khim.* **1979**, *15*, 225.

(6) Krogh-Jespersen, K.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Org. Chem.* **1980**, *45*, 1608.

(7) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781.

(8) Minkin, V. I.; Minyaev R. M. In *Molecular Structure and Conformation: Recent Advances, Progress in Theoretical Organic Chemistry*, Vol. 3; Csizmadia, I. G., Ed.; Elsevier, Amsterdam, 1982.

(9) Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 991.

(10) Minkin, V. I.; Minyaev, R. M.; Zacharov, I. I.; Avdeev, V. I. *Zh. Org. Khim.* **1978**, *14*, 3.

(11) Minyaev, R. M.; Minkin, V. I.; Zefirov, N. S.; Zhdanov, Y. A. *Zh. Org. Khim.* **1979**, *15*, 2009.

(12) Minkin, V. I.; Minyaev, R. M.; Orlova, G. V. *J. Mol. Struct. (THEOCHEM)* **1984**, *110*, 241.

(13) Balaji, V.; Michl, J., *Pure Appl. Chem.* **1988**, *60*, 189.

(14) Lewars, E. *J. Mol. Struct. (THEOCHEM)* **1998**, *423*, 173.

(15) Lewars, E. *J. Mol. Struct. (THEOCHEM)* **2000**, *507*, 165.

(16) Huzinaga, S. J. *J. Chem. Phys.* **1965**, *42*, 1293.

(17) Dunning, T. H., Jr. *J. Chem. Phys.* **1970**, *53*, 2823.

(18) Dunning, T. H., Jr. *J. Chem. Phys.* **1971**, *55*, 716.

(19) Purvis, G. D., III; Barlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(20) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(21) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513.

(22) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *167*, 609.

(23) Watts, J. D.; Gauss, J.; Bartlett, R. J. *Chem. Phys. Lett.* **1992**, *200*, 1.

(24) Stanton, J. F.; Gauss, J.; Lauderdale, W. J.; Watts, J. D.; Bartlett, R. J. *ACESII.* The package also contains modified versions of the MOLECULE Gaussian integral program of J. Almlöf and P. R. Taylor, the ABACUS integral derivative program written by T. U. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and P. R. Taylor, and the PROPS property evaluation integral code of P. R. Taylor.

(25) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(26) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(27) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(28) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(29) 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.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andes, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Brinkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision B.3*; Gaussian Inc.: Pittsburgh, PA, 1995.

(30) Iwamoto, T.; Tamura, M.; Kabuto, C.; Kira, M. *Science* **2000**, *290*, 504.

(31) Billups, W. E.; Haley, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 5084.

(32) Saini, R. K.; Litosh, V. A.; Daniels, A. D.; Billups, W. E. *Tetrahedron Lett.* **1999**, *40*, 6157.

(33) Baldridge, K. M.; Biggs, B.; Blaser, D.; Boese, R.; Gilbertson, R. D.; Haley, M. M.; Maulitz, A. H.; Siegel, J. S. *Chem. Commun.* **1998**, *1998*, 2547.

(34) Wesolowski, S. S.; Gonzales, J. M.; Schleyer, P. v. R.; Schaefer, H. F. *Chem. Commun.* **1999**, *1999*, 439.

(35) Dunitz, J. D. *Chem. Commun.* **1999**, *1999*, 2547.