J. Org. Chem. **1995**, *60*, 1971−1974

Hypostrophene: An AM1 Study of Structure, Mechanism of Degenerate Cope Rearrangement, and Comparisons with Bullvalene and Other $C_{10}H_{10}$ Isomers

Benjamin M. Gimarc* and Ming Zhao

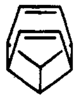
Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received September 2, 1994 (Revised Manuscript Received February 6, 1995[⊗]*)*

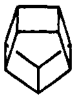
Hypostrophene (**1**) has been observed to undergo a degenerate Cope rearrangement similar to that well known to occur in bullvalene **3**, another $(CH)_{10}$ isomer. Neither the activation energy nor the detailed molecular structure of **1** has been determined experimentally. At elevated temperatures **1** rearranges to **4**, still another $(CH)_{10}$ isomer. We present geometry-optimized AM1 calculations for **1**, its Cope rearrangement transition state structure **1′**, and the related isomer **4**. We compare these results with those of similar calculations, already in the literature, for other $(CH)_{10}$ isomers, such as pentaprismane (**2**), bullvalene (**3**), and [10]annulene (**5**). The Cope rearrangement activation energy of **1** turns out to be larger than that for **3**, in agreement with the observations that the rearrangement of **3** is fast compared to **1**. Finally, we combine several pieces of data from experiment and theory to give consistent estimates of strain energies of the $(CH)_{10}$ isomers **1**−**5**.

Introduction

In 1971 Pettit and co-workers reported the preparation of hypostrophene **1**, $(CH)_{10}$.[1] Paquette and his group devised improved synthetic methods that raised the overall yield to 12%.[2] The motivation for that work was the expectation that hypostrophene might be the immediate precursor of pentaprismane **2**, another $(CH)_{10}$ isomer and a synthetic target of considerable interest at the time. Unfortunately, the anticipated isomerization of hypostrophene to pentaprismane does not take place. Ten years later, Eaton and co-workers ultimately achieved the synthesis of pentaprismane by other means.[3] Nevertheless, hypostrophene was found to have another interesting property; it undergoes a degenerate Cope rearrangement, eq 1, comparable to that which had been previously observed for bullvalene **3**, still another $(CH)_{10}$ isomer.[4,5] The chemistry of $(CH)_{10}$ turns out to be quite rich. Balaban has enumerated 93 possible isomeric structures in which 10 CH units can be linked together by single and double bonds following the normal valence rules for carbon and hydrogen.[6] Restricting the set to include only chemically realizable structures (planar graphs) reduces the number of possible isomers to 71, not counting stereoisomers.[7] Many of these isomers have already been prepared. Several recent reviews discuss their chemistry and isomerizations.[7−10]



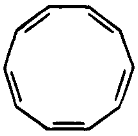
1



2

3

4



5

(1)

The degenerate Cope rearrangement of hypostrophene is too slow to be observed by NMR. That it occurs was verified by deuterium scrambling. Attempts to study the temperature dependence of the rearrangement revealed that at 80 °C, hypostrophene itself begins to undergo an intramolecular rearrangement to yet another $(CH)_{10}$ isomer with the proposed structure **4**.[1]

Despite these interesting properties, hypostrophene has been neglected. No detailed molecular structure has ever been reported. No estimate of its activation energy toward the degenerate Cope rearrangement, eq 1, has ever been made. Theoretical studies of hypostrophene appear to have been confined to interpretations of its photoelectron spectrum and the development of MO models to account for the failure of hypostrophene to isomerize photochemically to pentaprismane.[11,12] Finally, we have no idea of the position that hypostrophene occupies in energy relative to some of the other $(CH)_{10}$ isomers. We hope to rectify some of these omissions by presenting the results of quantum mechanical calculations for hypostrophene and few of its $(CH)_{10}$ valence isomers.

Calculations

We have carried out geometry-optimized semiempirical SCF MO calculations for **1**, **1′**, and **4**. We used the AM1

[⊗] Abstract published in *Advance ACS Abstracts*, March 15, 1995.

[1] McKennis, J. S.; Brener, L.; Ward, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1971**, *93*, 4957.

[2] Paquette, L. A.; Davis, R. F.; James, D. R. *Tetrahedron Lett.* **1974**, 1615.

[3] Eaton, P. E.; Or, Y. S.; Branca, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 2134. Eaton, P. E.; Or, Y. S.; Branca, S. J.; Ravi Shankar, B. K. *Tetrahedron* **1986**, *42*, 1621.

[4] Doering, W. v. E.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 115.

[5] Schröder, G. *Angew Chem., Int. Ed. Engl.* **1963**, *2*, 481; *Chem. Ber.* **1964**, *97*, 3140.

[6] Balaban, A. T. *Rev. Roum. Chim.* **1966**, *11*, 1097.

[7] Balaban, A. T.; Banciu, M. *J. Chem. Educ.* **1984**, *61*, 766.

[8] Maier, G.; Wiegand, N.; Baum, S.; Wüllner, R. *Chem. Ber.* **1989**, *122*, 781.

[9] Scott, L. T.; Jones, M., Jr. *Chem. Rev.* **1972**, *72*, 181.

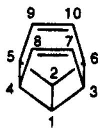
[10] Marchand, A. P. *Chem. Rev.* **1989**, *89*, 1011.

[11] Schmidt, W.; Wilkins, B. T. *Tetrahedron* **1972**, *28*, 5649.

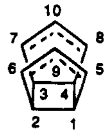
[12] Spanget-Larsen, J.; Gleiter, R.; Klein, G.; Doecke, C. W.; Paquette, L. A. *Chem. Ber.* **1980**, *113*, 2120.

0022-3263/95/1960-1971$09.00/0

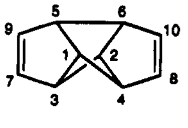
Table 1. Selected Structural Parameters and Heats of Formation from AM1 Calculations for Hypostrophene (1), Its Cope Rearrangement Transition State 1′, and the Isomerization Product



1, C_{2v}



1′, C_{2v}



4, C_2

bond distances (Å)		bond distances (Å)		bond distances (Å)	
1−2	1.553	1−2	1.580	1−3	1.598
1−3	1.571	1−4	1.550	1−4	1.570
3−6	1.576	1−5	1.514	1−5	1.585
3−7	1.498	5−9	1.400	3−7	1.493
7−8	1.351	5··8	2.253	5−6	1.587
7···10	2.797	9···10	2.905	5−9	1.507
1−H	1.092	1−H	1.101	7−9	1.352
3−H	1.105	3−H	1.088	1−H	1.091
7−H	1.091	9−H	1.093	3−H	1.102
				5−H	1.102
				7−H	1.089
				9−H	1.088
ΔH_f (kcal/mol) =	92.7		125.9		109.9

method, developed by Dewar and co-workers,[13] because the method is fast even for systems as large as $(CH)_{10}$, it produces heats of formation and structural parameters in reasonable agreement with experiment, results for several other $(CH)_{10}$ isomers have already been reported, and the routines are readily available as part of the GAUSSIAN 92 program package.[14] Miller and Schulman have presented AM1 results for pentaprismane (**2**).[15] Dewar and Jie have done AM1 calculations for bullvalene **3**, barbaralane, and semibullvalene and transition state structures which these molecules encounter during degenerate Cope rearrangements.[16] Schaefer and co-workers have carried out AM1 calculations for [10]annulene (**5**), another $(CH)_{10}$ isomer, in several different conformations.[17]

Table 1 contains bond distances and heats of formation obtained from symmetry-restricted geometry optimizations for **1**, **1′**, and **4**. Calculated vibrational frequencies are all real and positive for **1** (C_{2v}) and **4** (C_2) indicating that these structures correspond to local minima on the $(CH)_{10}$ energy surface. Results for **1′** (C_{2v}), however, include a single imaginary frequency revealing this structure to be a transition state as expected.

In the next section we discuss hypostrophene in terms of its AM1 calculated structural and energy parameters. Since neither structural nor thermochemical data for hypostrophene are available for comparison with calculated values, it is reasonable to take a few lines to evaluate the dependability of AM1 results for related $(CH)_{10}$ isomers. X-ray crystal structures have been reported for both bullvalene (**3**) and the carboxylic acid derivative of pentaprismane (**2**).[18,19] For these examples, AM1-calculated bond distances agree within 0.03 Å and are generally much better. For the 27 bonds of six different types in **2** and **3**, the average error in AM1 distances is 0.85%. For **3** comparisons of AM1 bond distances with gas phase electron diffraction data[20] are very similar to those for single crystal X-ray diffraction studies.[18] For both **2** and **3** AM1 bond distances show the same qualitative order as the experimental values.

AM1 calculations give directly heats of formation as the energy quantity. For the $(CH)_{10}$ isomers considered here, all heats of formation are positive. The lower the heat of formation, the lower the total energy. Månsson and Sunner have made a calorimetric study of bullvalene and found a heat of formation (gaseous state, 298.15 K) of 79.85 kcal/mol.[21] The AM1 result of Dewar and Jie is 75.4 kcal/mol.[16] For pentaprismane **2**, no experimental quantity is available for comparison, but several different theoretical methods have been used to estimate its heat of formation: ab initio SCF MO calculations with the 6-31G* basis set (119.6 kcal/mol;[22] 121.2 kcal/mol[23]), MM2 (114.7 kcal/mol[24]), MM3 (129.3 kcal/mol[25]), and AM1 (117.7 kcal/mol[15]). The average of these estimates is 120.5 kcal/mol with a spread of almost 15 kcal/mol. The AM1 result is within 3 kcal/mol of the average. We hope for comparable consistency in our results for **1**, **1′**, and **4**.

Discussion

The difference between heats of formation calculated for hypostrophene (**1**) and the Cope rearrangement transition state **1′** is 125.9−92.7 = 33.2 kcal/mol, a value which is only a raw estimate of the activation energy for eq 1. Dewar and Jie have carried out AM1 calculations to obtain activation energies for bullvalene, barbaralane, and semibullvalene, all of which are known to undergo degenerate Cope rearrangements and for which experimental measurements of activation energies are available.[16] In their comparisons of AM1-calculated activation energies with those from experiment for these three related systems, Dewar and Jie found that AM1 values are too high by about 15 kcal/mol. Assuming that the same systematic error applies to the hypostrophene rearrangement, an improved estimate of the activation energy is 18 kcal/mol. This estimate for hypostrophene is larger than the experimental activation energy for the bullvalene rearrangement, 13 kcal/mol,[26−30] a comparison which is consistent with the observations that at room temperature, the rearrangement of hypostrophene is slow while that of bullvalene is fast.

---

(13) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(14) Frisch, M. J; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. G.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*, Revision C.4, Gaussian, Inc., Pittsburgh, PA, 1992.

(15) Miller, M. A.; Schulman, J. M. *THEOCHEM* **1988**, *40*, 133.

(16) Dewar, M. J. S.; Jie, C. *Tetrahedron* **1988**, *44*, 1351.

(17) Xie, Y.; Schaefer, H. F., III; Liang, G.; Bowen, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 1442.

(18) Amit, A.; Huber, R.; Hoppe, W. *Acta Crystallogr.* **1968**, *B24*, 865.

(19) Engel, P.; Eaton, P. E.; Ravi Shankar, B. K. Z. *Kristallogr.* **1982**, *159*, 239.

(20) Andersen, B.; Marstrander, A. *Acta Chem. Scand.* **1967**, *21*, 1676.

(21) Månsson, M.; Sunner, S. *J. Chem. Thermodyn.* **1981**, *13*, 671.

(22) Disch, R. L.; Schulman, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 2102.

(23) Dailey, W. P. *Tetrahedron Lett.* **1987**, *28*, 5787.

(24) Reddy, V. P.; Jemmis, E. D. *Tetrahedron Lett.* **1986**, 27, 3771.

(25) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

(26) Schröder, G.; Merenyi, R.; Oth, J. F. M. *Tetrahedron Lett.* **1964**, 773.

(27) Günther, H.; Ulman, J. *Tetrahedron* **1974**, *30*, 3781.

(28) Nakanishi, H.; Yamamoto, O. *Tetrahedron Lett.* **1974**, 1803.

(29) Poupko, R.; Zimmerman, H.; Luz, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5391.

(30) Meier, B. H.; Earl, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 5553.

Table 2. Heats of Formation (kcal/mol) of Some $(CH)_{10}$ Isomers from AM1 Calculations

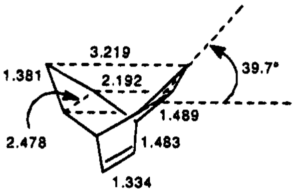
isomer	ΔH_f
pentaprismane (**2**)[a]	117.7
rearrangement product **4**[b]	109.9
hypostrophene (**1**)[b]	92.7
[10]annulene (twisted, C_2) (**5**)[c]	87.5
bullvalene (**3**)[d]	75.4

[a] Reference 15. [b] This work. [c] Reference 17. [d] Reference 16.

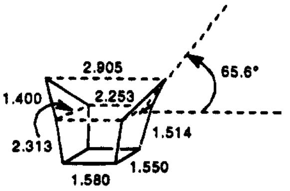
At elevated temperatures hypostrophene (**1**) isomerizes to the proposed product **4**. To our surprise, we find that the heat of formation of **4** is greater than that of hypostrophene (**1**) by almost 17 kcal/mol. Thus, the energies of isomer **4** and the Cope rearrangement transition state **1′** are quite close. We have not tried to locate the transition state of the **1** → **4** isomerization process and therefore we do not know the activation energy for the process. Table 2 contains AM1 heats of formation for the $(CH)_{10}$ isomers **1**–**5**. The results in Table 2 show that hypostrophene **1** is 25 kcal/mol more stable than pentaprismane **2**, exactly the difference found by Schmidt and Wilkins who used MINDO/2 calculations.[11]

Bond distances show some interesting trends. The 7–8 bond in **1** (1.351 Å) and the 7–9 bond in **4** (1.352Å) are in the range of normal C=C double bonds. Adjacent to these double bonds in both **1** and **4** are single bonds that are significantly shortened: 1.498 Å for 3–7 in **1**; 1.493 Å and 1.507 Å for 3–7 and 5–9 bonds, respectively, in **4**. The shortening of single bonds adjacent to double bonds is also apparent among AM1 and experimental results for bullvalene (**3**). The remaining bonds in **1** and **4** are somewhat elongated C–C single bonds. The longest of all bonds in **1**–**5** are those emanating from carbons 1 and 2 in **4**. In the hypostrophene transition state structure **1′**, the four bonds equivalent to 5–9 (1.400 Å) are clearly intermediate in length between standard CC single and double bonds.

Dewar and Jie describe AM1 calculations for a symmetric intermediate and transition state for the Cope rearrangement of bullvalene.[16] They note that the energy surface is very flat in the region of the intermediate and transition state. We wanted to compare in detail structures of the bullvalene symmetric intermediate **6** and the hypostrophene transition state **7**. Since Dewar and Jie did not report all the structural parameters of **6**, we attempted to reproduce their calculation. Optimizing the geometry of **6** under the constraint of C_{2v} symmetry, we found bond distances that were identical to the selected parameters of Dewar and Jie. In one instance, a nonbonded distance differed by 0.002 Å. Our heat of formation for **6** is 0.2 kcal/mol lower than the value Dewar and Jie reported for the symmetric intermediate, a difference that could be the result of a slightly different choice of conversion factors from hartrees to kcal/mol. When we calculated vibrational frequencies, we found two imaginary frequencies, indicating that **6** is neither a transition state nor an intermediate. Lowering the symmetry restriction to C_2 led back to the C_{2v} structure. Changing the optimization procedure gave the same result. In the following discussion we assume that **6** is a reasonable approximation of the bullvalene rearrangement transition state.



6



7

The transition states in the Cope rearrangements of bullvalene and hypostrophene have certain similarities. Both structures, **6** and **7**, involve boat-shaped hexagons of reorganizing bonds. In **7** (hypostrophene) the prow and stern of the boat are much more steeply pitched (65.6°) from a planar hexagon than they are in **6** (bullvalene) (39.7°), making them closer together in **7** (2.905Å) than they are in **6** (3.129Å). In **6** the hexagon is flanked by a pair of triangles; in **7** two 4-membered rings border the hexagon. The bonds around the hexagon in **7** are 0.02–0.06 Å longer than comparable bonds in **6**.

According to the bond additivity model, the energy differences between $(CH)_{10}$ isomers **1**–**5** should be related to the numbers of different types of bonds and the difference between bond energies of two C–C single bonds and one C=C double bond. Assume $2D(C-C) - D(C=C) = 25$ kcal/mol. Because a pair of single bonds is stronger than a double bond, the lowest energy structure according to the bond additivity model should be pentaprismane (**2**) with all C–C single bonds. Higher by 50 kcal/mol and with equal energy should be hypostrophene (**1**) and its rearrangement product **4**, each with two C=C double bonds. Next, at 75 kcal/mol above the pentaprismane base line would be bullvalene (**3**), with three C=C double bonds. Highest of all and 125 kcal/mol above the base line would be [10]annulene (**5**) which has five C=C double bonds. This order of stabilities is not what we find from AM1 heats of formation, Table 2. The structures of isomers **1**–**4** contain small rings in which bond angles are distorted from preferred valence arrangements causing these structures to be destabilized by strain. In [10]annulene (**5**), it is conceivable that the alternant arrangement of single and double bonds in the ring might allow resonance stabilization. These effects can be visualized in Figure 1.

Månsson and Sunner, who did the calorimetric study of bullvalene, estimated that the strain energy of bullvalene is 35 kcal/mol.[21] This value would put bullvalene above the level of three isolated C=C double bonds or 35 + 75 = 110 kcal/mol above the base line of all C–C single bonds. We can use the strain energy additivity rule[31–35] to estimate the strain energy of pentaprismane (**2**). This isomer is composed of five cyclobutane rings and two cyclopentane rings. Taking standard values of strain energies of individual rings,[35] the strain energy of pentaprismane is $5 \times 27.4 + 2 \times 7.3 = 152$ kcal/mol. This estimate places pentaprismane 152 kcal/mol above the all C–C single bond base line and 42 kcal/mol above bullvalene. The 42 kcal/mol difference is almost exactly the difference between AM1 heats of formation for **2** and **3**: 42.3 kcal/mol. Reddy and Jemmis give a somewhat lower estimate of pentaprismane strain

---

(31) Kybett, B. D.; Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, J. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 626.

(32) Benson, S. W. *Thermochemical Kinetics*, 2nd Ed.; Wiley: New York, 1976.

(33) Hassenrück, K.; Martin, H.-D.; Walsh, R. *Chem. Rev.* **1989**, *89*, 1125.

(34) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(35) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

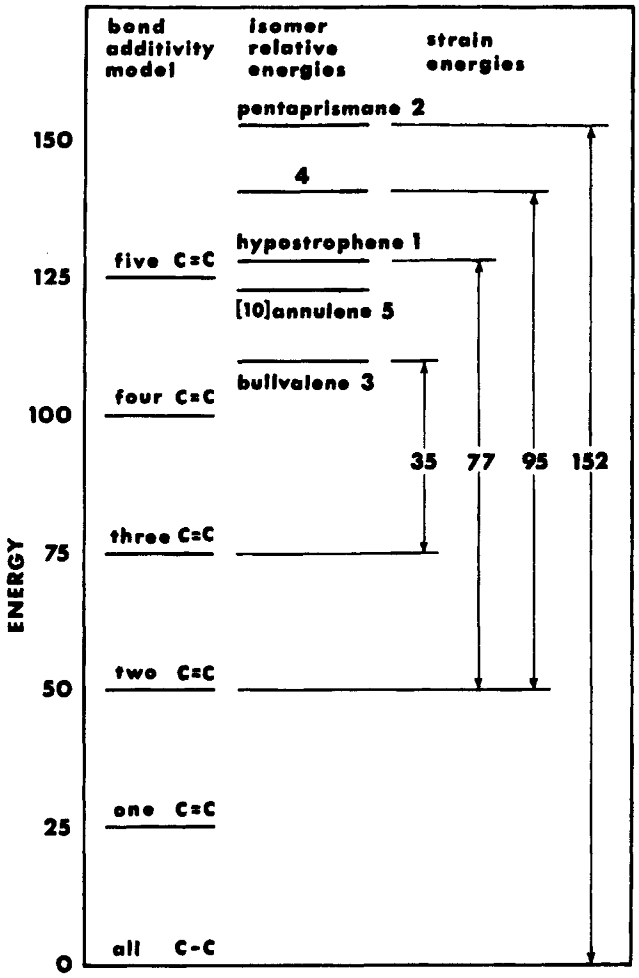
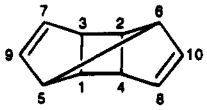


Figure 1. Relative energies of $(CH)_{10}$ isomers **1**–**5** from the strain-free bond additivity model and from AM1 calculations and estimates of strain energies of **1**–**4**. For **5**, strain and resonance effects appear to cancel each other to leave [10]-annulene at the energy of five C=C double bonds.

energy, 143.6 kcal/mol, from their MM2 calculations.[24] Hypostrophene (**1**) consists of two cyclobutanes and two cyclopentenes. Applying the strain energy additivity rule, 2 × 27.4 + 2 × 6.9 = 69 kcal/mol as an estimate of the strain energy of **1**. With two C=C double bonds (50 kcal/mol) plus strain energy (69 kcal/mol), hypostrophene should be 119 kcal/mol above the base line. The AM1-calculated heats of formation locate hypostrophene somewhat higher at 127 kcal/mol for an improved estimate of 77 kcal/mol for the strain energy. The AM1 heat of formation of the isomerization product **4** puts this isomer 35 kcal/mol above bullvalene and gives an estimated strain energy of 95 kcal/mol. This is a high strain energy for a structure that contains a single cyclobutane ring plus larger rings. Representing **4** by the planar graph **8** suggests considerable distortion due to the 5–6 bond. Recall that the bonds around atoms 1 and 2 are the longest C–C bonds in all the isomers considered here.



8

We have invoked the rule of Dewar and Jie that the AM1 method, for unknown reasons, overestimates the energy of transition structures, such as **1′**, by a systematic amount. The method might also be overestimating the energy of isomer **4**, but compared to the transition state **1′**, surely **4** is a much more conventional valence structure and is not likely to be overestimated by as much as 15 kcal/mol. Finally, [10]annulene (**5**), with five C=C double bonds, should be 125 kcal/mol above the base line in Figure 1. The AM1 results of Schaefer and coworkers[17] for the most stable, nonplanar C_2 conformation of **5** place this isomer 12 kcal/mol above bullvalene and 122 kcal/mol above the base line at almost exactly the level of the five C=C marker. In this structure, the five C–C single bonds show considerable shortening (average = 1.452 Å) compared to standard C–C bonds while the C=C double bonds (average = 1.342 Å) are essentially normal. The shortening of the C–C bonds might indicate some resonance stabilization. On the other hand, C=C–C bond angles around the ring average 125.6°, larger than the 120° angles expected for sp^2-hybridized carbon. If **5** is stabilized by resonance, the effect is almost exactly cancelled by strain destabilization.

Conclusion

For the degenerate Cope rearrangement of hypostrophene, semiempirical AM1 SCF MO calculations show that the activation energy is greater than that for comparable rearrangements of bullvalene, barbaralane, and semibullvalene, in agreement with the experimental observation that the rearrangement of hypostrophene is slow. Hypostrophene (**1**) is known to isomerize to **4** which AM1 results place 17 kcal/mol higher in energy than **1**. For neither **1** nor **4** had a detailed structure been determined. For both isomers, we present calculated structural parameters which appear to be normal. Transition state structures **6** and **7** for the degenerate Cope rearrangements of bullvallene and hypostrophene, respectively, are related but show differences in detail. The bond additivity model provides a strain-free basis for comparing strain energies of $(CH)_{10}$ isomers **1**–**5**. AM1 heats of formation, empirical estimates of strain energies, and the rule of ring strain additivity fit together nicely to form a consistent set of strain energy estimates for these isomers. Pentaprismane (**2**) has a large strain energy, 152 kcal/mol. In the nonplanar C_2 conformation of [10]annulene, angle strain in the ring may almost exactly cancel any resonance stabilization that might result from alternation of single and double bonds around the ring.

JO941520D