Tetrahedron Letters,Vol.28,No.47,pp 5787-5790,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

THE STRUCTURES AND ENERGIES OF PENTAPRISMANE AND HEXAPRISMANE - AN AB INITIO STUDY[1]

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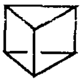
Summary: Ab initio calculations are reported for pentaprismane and hexaprismane using the 3-21G and 6-31G* basis set. The calculated structures and energies are compared with what is known experimentally and with the results of previous molecular mechanics calculations.

The [n]-prismanes are an aesthetically pleasing group of compounds which have received considerable experimental effort. Triprismane[2] (1), cubane[3] (2), and pentaprismane[4] (3) have been synthesized and are known experimentally to have D_{3h}[2], O_h[5], and D_{5h}[4] symmetry, respectively. The enthalpy of formation of cubane has also been determined.[6] There have been several reports on progress towards hexaprismane[7], a formal dimer of benzene, although the ring system is still unknown. Molecular mechanics calculations have been reported for cubane, pentaprismane and hexaprismane as well as some higher prismanes[8]. In addition, high level ab initio calculations on cubane[9], a minimal basis set calculation on pentaprismane[10] and an MNDO/minimal basis set ab initio study on hexaprismane[11] have all appeared. We report here the results of high level ab initio calculations for pentaprismane (3) and hexaprismane (4).

Ab initio calculations were performed for 3 and 4 using both the 3-21G and the 6-31G* basis set with complete geometry optimization[12] within the constraint of the appropriate (D_{5h} or D_{6h}) symmetry. The results are shown in Table 1 together with previous ab initio results for cubane[9] and molecular mechanics (MM2)[8] results for all three.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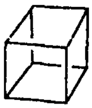
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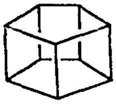
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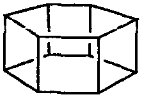
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Table 1. Optimized Structures and Energies for Cubane, Pentaprismane and Hexaprismane derived from ab initio and MM2 calculations.[a]

		theoretical method		
		ab initio basis set		
		3-21G	6-31G*	MM2
2	r(C-C)	1.577[f]	1.563[f]	1.557
	r(C-H)	1.074	1.085	1.114
	<HCC	125.26	125.26	125.26
	-E	305.69568[f]	307.39362[f]	
	ΔH_f	145.1[f]	147.1[f]	148.9
3	r(C-C)[b]	1.561	1.552	1.540
	r(C-C)[c]	1.582	1.558	1.566
	r(C-H)	1.077	1.082	1.115
	<HCC[d]	123.24	123.30	116.63
	-E	382.22481	384.34182	
	ΔH_f	115.4[g]	121.2[g]	114.7
4	r(C-C)[b]	1.558	1.551	1.532
	r(C-C)[c]	1.579	1.554	1.571
	r(C-H)	1.079	1.083	1.116
	<HCC[d]	121.13	123.04	112.94
	-E	458.63500	461.19570	
	ΔH_f	160.3[g]	154.5[g]	129.2

a. Bond lengths in angstroms, angles in degrees, total energies (E) in hartrees, enthalpy of formation in kcal/mol. b. Carbon-carbon bond perpendicular to the major axis. c. Carbon-carbon bond parallel to the major axis. d. Angle measured using the C-C bond parallel to the major axis. f. Reference 9. g. Calculated from the total energy according to reference 9.

Structures calculated at the 6-31G* level of theory are generally in good agreement with experimental values.[13] Cubane is predicted to have carbon-carbon bond lengths of 1.563 A^{o} while experimentally a value of 1.550 A^{o} is found.[5] For pentaprismane the C-C bonds in the five-membered rings are calculated to be slightly shorter (1.552 A^{o}) than the C-C bonds between the two five-membered rings (1.558 A^{o}). Experimentally[4] the C-C bonds within the five-membered rings of pentaprismane carboxylic acid average 1.548(8) A^{o} and the C-C bonds between the two five-membered rings average 1.565(4) A^{o}. The agreement is quite good. For hexaprismane both types of C-C bonds are predicted to be almost exactly the same length (1.551 and 1.554 A^{o}). This is in contrast to the results of MM2 calculations[8] which predict that the C-C bonds within the six-membered rings are shorter and the C-C bonds between the two six-membered rings are longer than those in pentaprismane. Hexaprismane is the first [n]-prismane in which the carbon atoms have C-C-C bond angles both less than (90^{o}) and greater than (120^{o}) the normal tetrahedral angle. There is relatively little known about compounds with saturated C-C-C angles in great excess of 109.5^{o}.[14]

The enthalpy of formation of pentaprismane and hexaprismane may be derived from the ab initio total energies using Wiberg's method[9] for converting total energies to enthalpies of formation. A very similar scheme has subsequently appeared.[15] The values derived using the 6-31G* basis set give results which are generally within 1 - 2 kcal/mol of the experimental values. Using the 6-31G* energies, Wiberg's method predicts values of 122.0 and 154.7 kcal/mol for the enthalpies of formation of pentaprismane and hexaprismane, respectively. A similar calculation for cubane predicts an enthalpy of formation of 147.1 kcal/mol. The measured value is 148.7 kcal/mol. It is interesting that values for the enthalpy of formation of cubane and pentaprismane derived from MM2 calculations agree fairly well with the values derived from the ab initio procedure but the MM2 value for the enthalpy of formation of hexaprismane is about 25 kcal/mol below the ab initio one. This is probably due to the fact that MM2 is not parameterized to deal with the saturated carbon-carbon-carbon angles of 120^{o} which are found in hexaprismane. MNDO calculations also greatly underestimate the value for the enthalpy of formation of hexaprismane with a prediction of 80.4 kcal/mol.[11]

The strain energies of cubane, pentaprismane and hexaprismane calculated from the 6-31G* total energies and the Benson group increment[16] ($C-(H)C_3$ = -1.90 kcal/mol) are 162.3, 140.2 and 177.3 kcal/mol respectively. The strain energies are roughly the number of four membered rings times the strain energy of cyclobutane (26.7 kcal/mol).

Using a value of 155 kcal/mol as the enthalpy of formation of hexaprismane, the reaction leading to two molecules of benzene (ΔH_f = 19.8 kcal/mol) is calculated to be exothermic by about 115 kcal/mol !

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$\Delta H_r = {}^{-}115$ kcal/mol

These predictions must now await experimental verification.

Acknowledgements. I am very grateful to the Research Fund at the University of Pennsylvania for partial financial support.

References

1. Dedicated to Professor Kenneth B. Wiberg on the occasion of his 60th birthday.
2. T. J. Katz and N. Acton, J. Am. Chem. Soc., 1973, 95, 2738.
3. P. E. Eaton and T. W. Cole, J. Am. Chem. Soc., 1964, 86, 3157.
4. P. E. Eaton, Y. S. Or and S. J. Branca, J. Am. Chem. Soc., 1981, 103, 2134; P. Engel, P. E. Eaton and B. K. Ravi Shankar, Z. fur Kristall. 1982, 159, 239; P. E. Eaton, Y. S. Or, S. J. Branca and B. K. Shankar, Tetrahedron 1986, 42, 1621.
5. F. B. Fleisher, J. Am. Chem. Soc., 1964, 86, 3889.
6. B. D. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave and J. L. Franklin, J. Am. Chem. Soc. 1966, 88, 626.
7. P. E. Eaton and U. R. Chakraborty, J. Am. Chem. Soc. 1978, 100, 3634; N. C. Yang and M. G. Horner, Tetrahedron Lett. 1986, 543; G. Mehta and S. Padma, J. Am. Chem. Soc. 1987, 109, 2212.
8. N. L. Allinger and P. E. Eaton, Tetrahedron Lett., 1983, 3697; V. P. Reddy and E. D. Jemmis, Tetrahedron Lett., 1986, 3771.
9. K. B. Wiberg, J. Comput. Chem. 1984, 5, 197 ; K. B. Wiberg, J. Org. Chem., 1985, 50, 5285.
10. E. Honegger, P. E. Eaton, B. K. Ravi Shankar, and E. Heilbronner, Helv. Chim. Acta, 1982, 65, 1982.
11. R. Engelke, P. J. Hay, D. A. Kleir and W. R. Wadt, J. Am. Chem. Soc., 1984, 106, 5439.
12. The calculations were carried out using the program GAMESS (M. Dupuis, D. Spangler, J. J. Wendoloski, National Resource for Computation in Chemistry Program QG01, 1982).
13. W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, "Ab Initio Molecular Orbital Theory", Wiley, New York, 1986.
14. P. G. Gassman and R. C. Hoye, J. Am. Chem. Soc. 1981, 103, 215 and references therein.
15. M. R. Ibrahim and P. v. R. Schleyer, J. Comput. Chem. 1985, 6, 157.
16. D. M. Golden, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neil, A. S. Rodgers, R. Shaw and R. Walsh, Chem. Rev. 1969, 69, 279.

(Received in USA 17 August 1987)