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COMPUTATIONAL STUDIES OF PRISMANE, HELVETANE/ISRAELANE AND ASTERANE

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ABSTRACT. Lower members of the title series have been calculated with MM2' and AM1 methods in order to gain insights into the strain and structural features of these mostly unknown molecules.

1. INTRODUCTION

The past few years saw a sudden rush of papers on the computation of prismane and related hydrocarbons. Impetuses for these works are the assessment of synthetic possibilities and the evaluation of various computational techniques for the molecules with extremely high strain. We summarize below some of our recent results obtained in this field.

2. PRISMANES

The lower members of [n]prismanes, $(C_2H_2)_n$, $n=3$ to 14, have been overworked computationally(1-6). Interests are generated by two predictions that have been made based on MM2 calculations(1): [1] systematic variation of C-C bond lengths within and between the n-membered rings, and [2] instability of D_{nh} structure in the higher members. After several calculations with higher and higher precision, it appears that ab initio studies by Disch and Schulman(4) finally gave definitive answers to the questions: [1] the bond length variations predicted by the low-level computations are artefacts, and [2] the energy-minimum structures of the [n]prismanes with $n \leq 12$ are all D_{nh} , but the higher members have very low vibrational frequencies near 100 cm^{-1} .

Comparison of the results from AM1(2,3) and ab initio(4) calculations seems to support the contention of Dewar(8) that this new semiempirical molecular orbital method performs as good as the ab initio 6-31G* basis set.

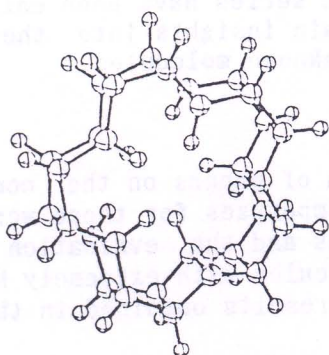
3. HELVETANES/ISRAELANES

These trivial names(9) so far referred to the two configurational isomers of [12]prismane wherein cyclobutane rings are all concatenated in all-cis fashion, which can be designated as (cis)₁₂. In israelane, the catenation is all-trans, (trans)₁₂. In helvetane, one cis-linkage replaces every third trans-linkage. According to our new notation,

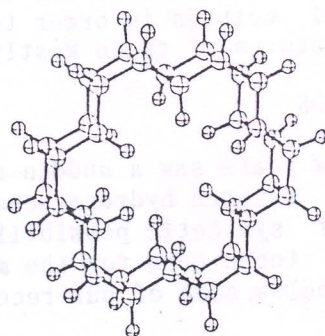
helvetane can be designated as $\{(trans)_2(cis)\}_4$.

The previous calculations(3,10) were limited to the two direct descendants of G. Dinsberg's original idea(9). However, the homologous series of these starshaped molecules should provide interesting submolecular environments, especially regarding the varying congestion in the inner cavity. As a preliminary step, we searched a part of the helvetane series, $\{(trans)_2(cis)\}_n$, $n=3-7$, using MM2'(11).

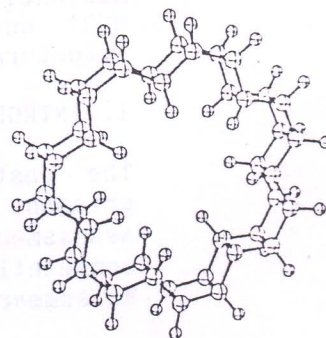
Triadhelvetane ($n=3$, $C_{18}H_{18}$) involves forbiddingly high congestion among the six inner protons and we have so far been unable to optimize the structure. Quadrihelvetane ($n=4$, $C_{24}H_{24}$) gave the same D_{2d} energy-minimum as obtained with AM1 and MM2(3). The inner congestion is still considerable in quinquhelvetane (1, $n=5$, $C_{30}H_{30}$) and hexadhelvetane (2, $n=6$, $C_{36}H_{36}$): they did not optimize into D_{nh} but ended up with C_2 and D_{3d} symmetries, respectively. Heptadhelvetane (3, $n=7$, $C_{42}H_{42}$) is the smallest member of the series that attains the planar D_{7h} structure.



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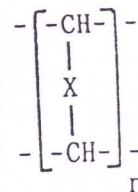


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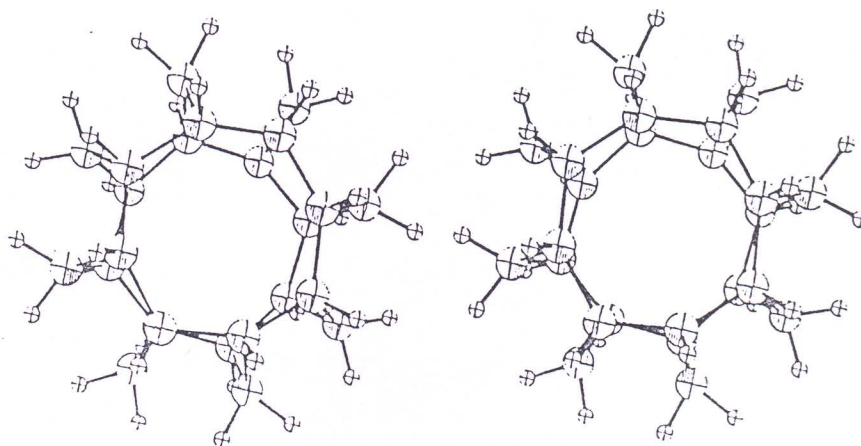
4. ASTERANES

The asterane series(12,13), having the general formula 4 [$X=CH_2$, $(C_3H_4)_n$, $n \geq 3$], provides novel means of straining a molecule by allowing less and less space between the bow and stern of boat cyclohexane ring in addition to the increasing angle strain similar to that of prismanes. Hence, the series should be, like the helvetanes, a good testing ground for the nonbonded H/H interaction potential function in molecular mechanics(14).

It has been predicted sometime ago that the energy minimum structure of asterane will lose D_{nh} symmetry at higher ($n \geq 8$) members based on molecular mechanics calculations(15). Exactly similar to the case of prismanes(1-4), AM1 calculations of asterane series again gave D_{nh} energy minima at least up to octaasterane ($n=8$). However, the lowest vibrational frequency of octaasterane occurs at 91 cm^{-1} .



4, Asterane, $X=CH_2$
Prismane, $X=\text{none}$



Stereo Pair of [8]Asterane, 4 ($X=CH_2$, $n=8$), in a Crown Conformation Obtained by Geometry Optimization with MM2'

The nonbonded H/H distances between bow and stern in the AM1-optimized structures of asteranes are significantly smaller than in the MM2'-optimized ones. For example, in hexaasterane ($n=6$), the distances are 1.707 and 1.832 Å, respectively. This indicates that the proton in MM2' may be still too hard and too large.

1. Reddy, V. P.; Jemmis, E. D. Tetrahedron Lett., 1986, 27, 3771-3774.
2. Jemmis, E. D.; Rudzinski, J. M.; Ōsawa, E. Chem. Express, 1988, 3, 109-112.
3. Miller, M. A.; Schulman, J. M. J. Mol. Struct. 1988, 163, 133-141.
4. Disch, R. L.; Schulman, J. M. J. Am. Chem. Soc. 1988, 110, 2102-2105.
5. Mehta, G.; Padma, S.; Ōsawa, E.; Barbiric, D. A.; Mochizuki, Y. Tetrahedron Lett., 1987, 28, 1295-1298.
6. Mehta, G.; Padma, S.; Jemmis, E. D.; Leela, G.; Ōsawa, E.; Barbiric, D. A. Tetrahedron Lett. 1988, 29, 1613-1616.
7. Ōsawa, E.; Barbiric, D. A.; Lee, O. S.; Kitano, Y.; Padma, S.; Mehta, G. submitted for publication in J. Chem. Soc., Perkin Trans. II.
8. Dewar, M. J. S.; O'Conner, B. M. Chem. Phys. Lett. 1987, 138, 141-145.
9. Nickon, A.; Silversmith, E. F. 'Organic Chemistry: The Name Game, Modern Coined Terms and Their Origins', Pergamon Press: New York, 1987.
10. Li, W.-K.; Luh, T.-Y.; Chiu, S.-W. Croat. Chem. Acta, 1985, 58, 1-3.
11. Jaime, C.; Ōsawa, E. Tetrahedron 1983, 39, 2769-2778.
12. Musso, H. Naturwiss. Rundschau, 1966, 19, 448; Umschau Wiss. Tech., 1968, 68, 209.
13. Miller and Schulman(3) called the starshaped helvetane and israelane as "asteranes", apparently without knowledge of the former occupants of the star. See, ref. 9.
14. Murrell, J. N. et al. 'Molecular Potential Energy Functions', John Wiley & Sons: New York, 1984.
15. Ōsawa, E.; Musso, H. Angew. Chem. Int. Ed. Engl. 22, 1-12.