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A D_{4d} STRUCTURE FOR [8]-PRISMANE

V. Pitchi Reddy and Eluvathingal D. Jemmis*

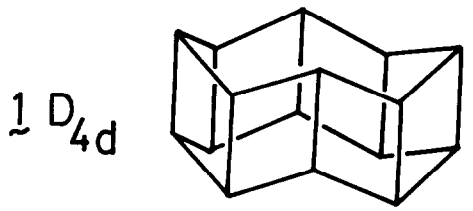
School of Chemistry, University of Hyderabad, Central University P.O.,

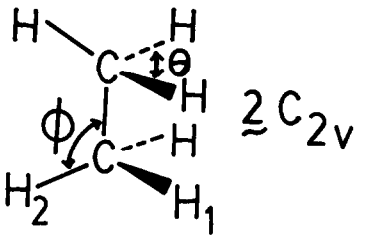
Hyderabad 500134, India.

Abstract: [n]-Prismanes, n>7,need not belong to D_{nh} point groups. Ab initio SCFMO Calculations on the model C_2H_6 and molecular mechanics calculations on [n]-prismanes indicate that [8]-prismane may adopt a D_{4d} structure, **1**.

[n]-Prismanes belong to D_{nh} point groups. The first three members of the series known experimentally have D_{3h},[1] O_h[2] and D_{5h}[3] symmetry. We present here theoretical studies which suggest that [8]-prismane prefers a D_{4d} structure, **1**. Higher prismanes should be less symmetric than D_{nh}.

Two approaches were used in this study. Initially an estimate of the relative strain energies of the prismanes were obtained by studying the model, ethane, in constrained geometries using ab initio calculations at the 3-21G level.[4] Previous experience has shown the advantage of such model calculations.[5] The strain energies, heats of formation and structures of the parent [n]-prismanes (n=3-8) are calculated using an empirical force field method.[6]





Model calculations: The [n]-prismanes are simulated by keeping θ=60, 90, 108, 120, 128.6 and 135° and H_1CC=90°, (**2**). All other parameters are optimized maintaining C_{2v} symmetry using the Gaussian76 series of programmes with the 3-21G basis set.[7] Table 1 shows the relative energies, and the angle, ϕ of the model **2**. The relative energy falls precipitously from θ=60 to θ=108, and then increases again, though with a decreased slope. This indicates that the higher prismanes are not unreasonable synthetic targets. The minimum in energy corresponding to θ=108° ([5]-prismane) as well as the inverse relation of θ to ϕ is well understood from the standard bond angles around carbon and an analysis of the Walsh diagram for variation of θ.[8] The value of θ determines the magnitude of the torsional strain arising from the C-H bonds of one ring with the other.[9] At θ=135° ([8]-prismane), ϕ is calculated to be 113.3° in the model. Since the CH bonds are necessarily eclipsed in the D_{nh} symmetries of the prismanes the torsional strain will be considerable. This model cannot include the torsional strain from CH bonds belonging to the same ring. Actual strain in the higher prismanes should be larger than this estimate. These are tested on the [n]-prismanes (n=3-8) by empirical force field calculations.

Strain Energy Calculations on [n]-Prismanes: We selected the molecular mechanics method for studying the parent prismanes as the molecules are too large to be optimized by the ab initio methods. The MM2 program with the standard set of potential functions[10] was used because this is known to work well for moderately strained systems.[11] The lower members of the [n]-prismanes have been studied previously by different theoretical methods[12]. Table 1 shows the geometric parameters, heats of formation and strain energies of [n]-prismanes with D_{nh} symmetry. Both the heat of formation and strain energy follow the same trend as that of the model studies. As anticipated the strain energy for a given prismane is larger than the relative energy estimated using the model for $n>5$ and less than the relative energy for $n<5$. The C-C bond lengths within the ring and between the rings change in the oposite direction but fall within the range 1.524 to 1.609 Å.[9]

The HCC angles involved in the top ring decreased from 133.8° in n=3 to 111.0° in n=8. The corresponding change in the HCC angles involving two rings is from 130.1 in n=3 to 110.4° in n=8. The latter values are comparable to that found from the model **2**. The two sets of angles together indicate a high degree of torsional strain for [8]-prismane in addition to the obvious angle strain due to internal CCC angles of 135°. Does it have a way out of the strain? We optimized the [n]-prismanes using the MM2 program relaxing all symmetry restrictions. The D_{nh} structure was retained by all [n]-prismanes except for n=8. The optimization changed the geometry of [8]-prismane to D_{4d}, **1**, with a ΔH_f of 6.8 kcal/mol

lower than that of the D_{8h} structure. **1** can be best described as a crown built from two cyclooctanes through axial-equatorial connections. The decrease in the angle strain accounts for most of the stabilization in going from D_{8h} to D_{4d}. The following angles are noteworthy. Within the eight membered ring the CCC angles alternate between 134.0° and 126.0°. The internal angles of the four membered rings are 80.2° and 99.8° instead of 90°. The HCCH dihedral angles of the eight membered rings are around 3.5°. If these values are any indication [8]-prismane should represent a dynamic system at accessible temperatures. The current interest in prismanes will, no doubt, be enriched by attempts at synthesizing higher prismanes.[13]

Isoelectronic prismanes are known among organometallic compounds where CH is replaced by RAlNR pairs. $(RAlNR)_6$ has a pseudo D_{6h} symmetry.[14] Unlike the organic prismanes these are not made by stepwise synthetic routes. The increased strain of [7] and [8]-prismanes are reflected in the non prismane structures obtained in these almost self-assembly reactions.[15]

Theoretical studies of the structure and energetics of higher prismanes, their alternatives, and various methods of reducing their strain energies are underway.

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Table: Structure and energy of the model C_2H_6, (3-21G) and the [n]-Prismanes(MM2). Energy (kcal/mol), bond lengths (A), Angles(degrees).

n	θ	C_2H_6, **2**		[n]-Prismanes					
		Rel. Energy[a]	φ	<HCC[b]	<HCC[c]	C-C[b]	C-C[c]	ΔH_f	Rel.strain
3	60	328.9	136.5	130.1	133.8	1.609	1.549	303.2[d]	**176.0**
4	90	69.1	127.9	125.3	125.3	1.557	1.557	148.8	27.9
5	108	0.0	122.5	116.6	121.7	1.566	1.540	114.7	0.0[e]
6	120	8.0	118.5	112.9	117.4	1.571	1.532	129.2	20.8
7	128.6	49.0	115.7	111.3	113.9	1.573	1.526	173.8	71.7
8	135	118.0	113.3	110.4	111.0	1.575	1.524	243.0	147.1

[a]The corresponding total energy is -78.72503 a.u. The relative energies are multiplied by n. [b]The CC bond parallel to the C_n axis. [c]The CC bond forms a part of the n-membered ring. [d]Optimized without the cyclobutane option. [e]The total steric energy corresponding to [5]-prismane is 143.6 kcal/mol.

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