Poly[n]prismanes: A Family of Stable Cage Structures with Half-Planar Carbon Centers

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A series of bi[n]prismanes and tri[n]prismanes (n = 3–6) containing n and 2n, respectively, tetracoordinated carbon centers with nonclassical bisphenoidal (half-planar) configuration has been designed computationally.

1. Introduction

People have been looking for novel organic structures containing main-group element centers with nonclassical valence bond configurations, with special attention being paid to tetracoordinated carbon atoms in nonstandard stereochemical environments.1–3 In addition to the classical tetrahedral topology 1, the nonclassical topological types considered include four configurations: planar 2, pyramidal 3, inverted (umbrella) 4, and bisphenoidal (half-planar) 5.

Poor carbon, one must say to be tortured—or seduced—in so many ways. The strategy of stabilization of planar tetracoordinate carbon centers originally developed by Hoffmann, Alder, and Wilcox4 has been successfully applied in the computational design of diverse molecules and ions containing such a center. That has been accompanied by experimental approaches to organic and organometallic examples. This work, as well as studies of tetracoordinated pyramidal carbon, first proposed by Minkin, Minyaev, and co-workers,5 has been recently reviewed.3 The first examples of organic compounds with an inverted umbrella-like configuration 4 of four bonds at a carbon center were computationally predicted and subsequently synthesized by Wiberg and co-workers.6 A carbon bond configuration very close to the bisphenoidal (butterfly) type 5 is observed in a number of carbide clusters, e.g., 6,7 and in other organometallic compounds (see refs 1–3 and 8 for reviews). It is also theoretically predicted for tricyclo[2.1.0.01,3]hexane 7.9

Electronic factors favoring stabilization of the bisphenoidal configuration 5 of tetracoordinated carbon were analyzed by Hoffmann, Gleiter, and co-workers.10 They found that strong o-donor groups X in CHX2 substan-

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2. Computational Methods

The calculations were carried out using the Gaussian98 system of programs. The Becke-3 parameter density functional with the Lee–Yang–Parr correlation functional (B3LYP) was used in conjunction with 6-311G(2df,p) or 6-311G(d,p) basis sets. All the structures were fully optimized using the key word "tight". Analytic harmonic frequencies at the same level of approximation were used to characterize the nature of the structures under study and to evaluate zero-point energy corrections (ZPE).

3. Results and Discussion

The optimized geometries of \([n]prismanes\) calculated by the DFT B3LYP/6-311G(2df,p) method, a reliable theoretical tool for accurate prediction of structural parameters, agree well with the experimental data available for derivatives of \(8\) and for \(9\). Calculations on bi\([n]prismanes\) \(8a–11a\) at the same level of approximation and tri\([n]prismanes\) \(8b–11b\) using the B3LYP/6-311G(d,p) scheme have shown that all these compounds possess stable \(D_{sh}\) structures (no imaginary frequencies) corresponding to relatively deep (high values of the first harmonic vibration frequencies) local minima on the respective potential energy surfaces. The optimized geometries of bi\([n]prismanes\) and tri\([n]prismanes\) are shown in Figures 1 and 2, respectively.

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CHART 1

Poly\([n]prismanes\): A Family of Stable Cage Structures

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As may be seen from Figures 1 and 2, the (H)CCC(H) angles in 8a–11a and the (H)CCC angles in 8b–11b are very close to 180°, as in the ideal bisphenoid 5. The CC bond lengths in the external basal (CH)ₙ rings of both bi[n]prismanes and tri[n]prismanes are 0.02–0.05 Å elongated, whereas those in the inner (C)ₙ rings are 0.03–0.07 Å shorter compared with the basal CC bonds in [n]-prismanes. The larger the size of the ring (larger n), the larger the difference. Relatively slight elongation is observed for the vertical HC–C bonds in the four-membered rings of bi[n]prismanes (0.013–0.018 Å) and tri[n]prismanes (0.021–0.025 Å). In contrast, the lengths of the C–C bonds in these rings of tri[n]prismanes are 0.05–0.07 Å longer than the HC–CH bonds in [n]-prismanes. Nevertheless, even the longest inner CC bond in tri[6]prismane 11b (1.633 Å) falls into the range of moderately stretched ordinary CC bonds.¹⁸ Bi[n]- and tri[n]prismanes have several lower energy valence isomers. We have considered some of these for the former set of compounds. Structures 8c–11c are cyclopropenes attached to a ring. Structures 9d and 11d are composed of, respectively, two and three Dewar benzene molecules linked by C–C bonds; 9e and 11e are the corresponding [3]prismane isomers. Bi[4]prismane 9a and bi[6]prismane 11a were also compared with their more conventional valence isomers, acenaphthylene 9f and biphenylene 9g and tetracene (naphthacene) 11f and triphenylene 11g, correspondingly. Table 1 contains the computational data on total and relative energies of bi[n]prismanes and their isomers. The optimized geometries of 8c–11c, 9d, 9e, 11d, and 11d are shown in Figures 3 and 4.

As may be seen from the values of E_rel in Table 1, the bi[n]prismane structures are at high energy compared

<table>
<thead>
<tr>
<th>compound</th>
<th>E_total + ZPE, au</th>
<th>E_rel, kcal mol⁻¹</th>
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<tbody>
<tr>
<td>8a, bi[3]prismane</td>
<td>346.109 78</td>
<td>0</td>
</tr>
<tr>
<td>8c</td>
<td>346.196 82</td>
<td>-55</td>
</tr>
<tr>
<td>9a, bi[4]prismane</td>
<td>461.515 10</td>
<td>0</td>
</tr>
<tr>
<td>9c</td>
<td>461.646 58</td>
<td>-94</td>
</tr>
<tr>
<td>9d</td>
<td>461.729 52</td>
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<tr>
<td>9e</td>
<td>461.555 66</td>
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<tr>
<td>9f</td>
<td>462.062 23</td>
<td>-343</td>
</tr>
<tr>
<td>9g</td>
<td>462.007 22</td>
<td>-309</td>
</tr>
<tr>
<td>10a, bi[5]prismane</td>
<td>577.031 15</td>
<td>0</td>
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<tr>
<td>10c</td>
<td>577.111 15</td>
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<td>692.419 29</td>
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<td>11c</td>
<td>692.533 45</td>
<td>-72</td>
</tr>
<tr>
<td>11d</td>
<td>692.709 13</td>
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<tr>
<td>11e</td>
<td>692.527 20</td>
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<tr>
<td>11f</td>
<td>693.124 34</td>
<td>-442</td>
</tr>
<tr>
<td>11g</td>
<td>693.138 45</td>
<td>-451</td>
</tr>
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</table>

FIGURE 1. Structural parameters of bi[n]prismanes calculated by the B3LYP/6-311G(2df,p) method. Bond lengths are in Ångströms, angles in degrees.

FIGURE 2. Structural parameters of tri[n]prismanes calculated by the B3LYP/6-311G(d,p) method. Bond lengths are in Ångströms, angles in degrees.

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**FIGURE 3.** Structural parameters of the valence isomers of bi[n]prismanes 8c–11c calculated by the B3LYP/6-311G(2df,p) method. Bond lengths are in Ångströms, angles in degrees.

**FIGURE 4.** Structural parameters of the valence isomers of tri[4]prismane 9d and 9e and bi[6]prismane 11d and 11e calculated by the B3LYP/6-311G(2df,p) method. Bond lengths are in Ångströms, angles in degrees.

To that of any valence-isomeric form. This is mainly due to the large angle strain at the half-planar carbon centers of 8a–11a. For a rough estimate of this strain, we considered biphenoxy methane 12a and several other similarly distorted structures 12b–d optimized in the

![Chemical structures](image)

**TABLE 2.** Mulliken Charges at Carbon Atoms of [n]prismanes and Poly[n]prismanes (qC), Frequencies of the First Harmonic Vibrations (ν1), Total Strain Energies (Estr), and Strain Energy per One CC Bond (Estr(CC)) Calculated According to Equations 2–4 by the B3LYP/6-311G(2df,p) Method for [n]prismanes and Bi[n]prismanes and by B3LYP/6-311G(d,p) Method for Tri[n]prismanes

<table>
<thead>
<tr>
<th></th>
<th>n = 3 (8)</th>
<th>n = 4 (9)</th>
<th>n = 5 (10)</th>
<th>n = 6 (11)</th>
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<tr>
<td>qC (outer)</td>
<td>0.15</td>
<td>−0.158</td>
<td>−0.159</td>
<td>−0.155</td>
</tr>
<tr>
<td>qC (central)</td>
<td>0.11</td>
<td>0.14</td>
<td>0.15</td>
<td>0.11</td>
</tr>
<tr>
<td>E1, kcal mol−1</td>
<td>298</td>
<td>373</td>
<td>378</td>
<td>405</td>
</tr>
<tr>
<td>E1, CC, kcal mol−1</td>
<td>19.9</td>
<td>18.7</td>
<td>15.1</td>
<td>15.5</td>
</tr>
<tr>
<td>ν1, cm−1 (symmetry)</td>
<td>241 (E′)</td>
<td>337 (Eu)</td>
<td>385 (E′)</td>
<td>394 (E′)</td>
</tr>
</tbody>
</table>

*E1 energies for CH3–CH3, H(CH3)₃, and C(CH3)₄ are calculated as −79.8585, −158.51145, and −197.83752 au by the B3LYP/6-311G(2df,p) method and −79.8596, −158.50889, and −197.83075 au by the B3LYP/6-311G(d,p) method, respectively.

geometries with an angle HCH or H₃CCCH₃ constrained at 180°. Relative energies (Erel) of structures 12a–d were calculated with respect to the fully optimized totally unconstrained ground-state structures possessing a tetrahedral configuration of the central tetrahodinated carbon atom.

Whereas relative energies Erel of 12b and 12d contain contributions from both angle strain at a half-planar carbon center and steric repulsion of the axial and basal methyl (methyl and methylene) groups brought closer together upon opening the H₃CCCH₃ angles, the values Erel calculated for 12a and 12c are, we think, mainly indicative of the first effect. By taking the value Erel = 52 kcal mol−1 for the biphenoxy methane 12a (to be compared with 130–140 kcal mol−1 calculated by various methods for planar methane) as an approximate measure of the angle strain at a half-planar carbon center, it is possible to estimate the combined effect of all such type centers in bi[n]- and tri[n]prismanes on their strain energy. This varies for bi[n]prismanes between ~160 kcal mol−1 for 8a (n = 3) and 310 kcal mol−1 for 11a (n = 6). These values are to be compared with the values Estr listed in Table 2 and the energy difference between benzene and its valence isomers (e.g., 117.5 kcal mol−1 as calculated by the MP2/6-31G* method for 3-prismane).19

Several points of further interest are as follows. In 9c, the four-membered cycle is planar, whereas the five-membered cycle of 10c and the six-membered cycle in 11c deviate from planarity with dihedral angles of 24° and 51°, respectively. The first harmonic vibration of the structure 10c has the strikingly low value 4 cm−1. This is related to the pseudorotation of the five-membered ring
of 10c with energy barriers between the five topomeric forms as low as 0.5 kcal mol\(^{-1}\). The D\(_{5h}\) structure corresponds to a second rank saddle point (hilltop). A similar low-energy barrier (5-fold degenerate rearrangement) is characteristic of the singlet cyclopentadienyl cation, see ref 3 and literature therein. It is worth noting that structures 9d and 9e contain inverted tetracoordinate carbon centers of type 4.

Though the prismanes are of high energy with respect to these isomers, there are still likely to be high activation energies hindering rearrangements. This conclusion is indirectly supported by relatively high values of the frequencies of the first harmonic vibrations of 8a–11a (241–394 cm\(^{-1}\)) and 8b–11b (133–270 cm\(^{-1}\)).

To evaluate in another way the cumulative effect of the strain due to the deformation of valence angles and bond stretching in [n]prismanes and poly[n]prismanes, we calculated the energy changes that accompany bond separation reactions converting sterically strained cage structures 8–11, 8a–11a, and 8b–11b into a set of standard unstrained molecules with the same number of bonds of each formal chemical bond type (isodesmic reactions).\(^{(20)}\) Of special interest are homodesmotic reactions,\(^{(21)}\) which account not only for an equal number of bonds in reactants and products but also for the exact environment of these bonds. Such easily devisable reaction schemes are often used for calculations of strain energies from computational data.\(^{(19,22,23)}\) For example, a homodesmotic reaction for [3]prismane may be written as

\[
C_2H_6 (8) + 9CH_3 \rightarrow 6HC(CH_3)_3 (1)
\]

Equation 2 is a generalization of eq 1 for the family of [n]prismanes. Equations (2) and (3) apply to bi[n]- and tri[n]prismanes. The results, based on the DFT total energies, are given in Table 2.

<table>
<thead>
<tr>
<th>n</th>
<th>[n]prismanes</th>
<th>bi[n]prismanes</th>
<th>tri[n]prismanes</th>
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<tbody>
<tr>
<td>3</td>
<td>7.8</td>
<td>4.9</td>
<td>3.7</td>
</tr>
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<td>7.3</td>
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<tr>
<td>6</td>
<td>7.0</td>
<td>4.7</td>
<td>3.3</td>
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for ZPE corrections, the values of \(E_{str}\) calculated by eqs 1–4 decrease by 12–15 kcal mol\(^{-1}\) for all the compounds under study. For both [n]prismanes and poly[n]prismanes, maximal steric strain is observed for the first members (n = 3, 4) of each family, and for each n, the strain increases with increase in the size of the structure. Both trends are obviously associated with the increasing number of the angle-strained three- and four-membered rings. Even for the most strained tri[n]prismanes 8b and 9b, the strain energy per CC bond is significantly lower than that for tetrahedrane (22–25 kcal mol\(^{-1}\)).\(^{(24)}\) for which many derivatives have already been prepared. The decrease in stability of a poly[n]prismane on passing from prismanes 8–11 to their bi- (8a–11a) and trircongeners (8b–11b) manifests itself also in a progressive decrease of the energy gap between frontier orbitals along this set of compounds. This tendency is illustrated by the data given in Table 3.

The origin of the relatively high stability of poly[n]prismanes containing (m – 2)n half-planar carbon atoms in sterically strained four-membered rings (where m is the number of stacked rings and n is the size of the inner C\(_n\) and external (CH\(_3\))\(_n\) rings) is to be found in the strong \(\pi_{\text{anti}}\) orbital interaction between the symmetry-adopted frontier MOs of the external annulene (CH\(_n\)) and the inner (C\(_n\)) rings. This is illustrated by an orbital interaction diagram (Figure 5) showing the formation of MOs of the simplest bi[n]prismane 8a from the MOs of its three parallel cyclic fragments. Much of the stability of the multilayer \(D_{3h}\) structure is provided by electron occupying of the 3e\(^-\) MO formed by the overlap in a \(\sigma\)-way of \(\pi\)-antibonding MOs of the fragments. The determining role of such type of \(\pi_{\text{anti}}\)–\(\pi\) orbital interaction for stabilization of various polycyclic frameworks built up by parallel superposition of two or more fragment cyclic \(\pi\)-systems has been well established, [n]prismanes,\(^{(18)}\) [n]asteranes\(^{(27)}\) (which may be viewed as [n]prismanes sandwiched by a polyethylene pseudocycle), organic molecular crystals,\(^{(28)}\) and others.

The \(\pi_{\text{anti}}\) orbital interaction shown in Figure 5 is the principal factor contributing to the stability of the columnar structures 8a–11a and 8b–11b. Less essential is the relatively weak \(\pi_{\text{anti}}\)–\(\sigma\) orbital interaction between the radial MOs, formed by symmetry-adopted combinations of s, \(\sigma\), and \(\pi\) AOs. Compounds with nonstandard stereochemical configuration of carbon centers may display unusual chemical properties.\(^{(1–3,6,10)}\) We have studied computationally the

\[\text{C}_2\text{H}_6 (\text{8}) + 9\text{CH}_3 \rightarrow 6\text{HC}(	ext{CH}_3)_3 (1)\]

\(\text{Equation 2 is a generalization of eq 1 for the family of [n]prismanes. Equations (2) and (3) apply to bi[n]- and tri[n]prismanes. The results, based on the DFT total energies, are given in Table 2.}\)

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<td>6</td>
<td>7.0</td>
<td>4.7</td>
<td>3.3</td>
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</table>


initial stages of the reactions of bi[3]prismane 8a with the simplest electrophile (proton) and nucleophile (hydride ion). The attack of 8a by a hydride ion is directed toward a positively charged (see Table 2) carbon center of the inner C3 ring. It leads to the formation of a stable carbanion 13, which may undergo a low-energy barrier degenerate rearrangement, a "narcissistic" bond-switch reaction through symmetrical transition state 14.

There exist two pathways for protonation of bi[3]-prismane; the one involving addition to a negatively

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**FIGURE 5.** CACAO\textsuperscript{29} drawing of the orbital interaction diagram depicting formation of MOs of bi[3]prismane 8a from MOs of the fragments. The energy levels are calculated by the EHMO method\textsuperscript{30}.
charged carbon atom of the central C₃ ring appears to be thermodynamically preferred.

Our preliminary DFT calculations showed that the tetra[n]prismane members of the poly[n]prismane family also possess relatively stable Dₘₙ structures. The stability of the Dₘₙ structures of bi-, tri-, tetra-, and even penta-[n]prismanes with (m – 2)n half-planar tetracoordinated carbon atoms (m is the number of stacked rings) has also been predicted by the semiempirical PM3 method. The geometric parameters of 8a–11a and 8b–11b obtained by this method almost coincide with the DFT values calculated for the stacked external and inner cycles, but the semiempirical method does not reproduce the lengthening of the “vertical” CC bonds in the four-membered rings of all poly[n]prismanes. At the same time different molecular mechanics force fields derive less symmetric poly[n]prismane structures containing pyramidal (type 3) and distorted tetrahedral (type 1) carbon centers.

4. Conclusions

The calculations performed reveal a new family of multilayered poly[n]prismane structures in which molecules contain (m – 2)n (where m is the number of stacked rings and n is the size of the inner Cₙ and external (CH)ₙ rings) half-planar (bisphenoidal) tetracoordinate carbon centers. The main factor providing for the stability of these compounds is the πᵦ–πᵦ orbital interaction between the parallel rings.

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Supporting Information Available: Total energies, frequencies, and atomic coordinates of optimized structures of 8a–c, 9a–g, 10a–c, 11a–c, 13a,b, 14, and 15a,b in PDF. This material is available free of charge via the Internet at http://pubs.acs.org.

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