

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

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Received June 26, 2003

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

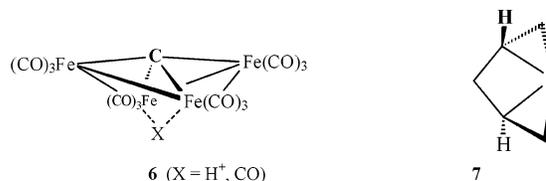
1. Introduction

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[2.1.0.0^{1,3}]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 σ -donor groups X in CH₂X₂ substantially narrow the energy gap between the lowest energy tetrahedral **1** and bisphenoidal **5** geometries. However, in no case did the calculations reveal compounds for which the XCX angle reached 180°.

The goal of the present study was to gain further insight into other structural types providing for perfect or approximate linearity of two bonds formed by a tetracoordinated carbon atom. The approach reported in this paper is based on growing the fragments of [*n*]prismanes (*n* = 3–6) **8–11** into columnar structures **8a–11a** and **8b–11b**, which may be termed poly[*n*]prismanes.

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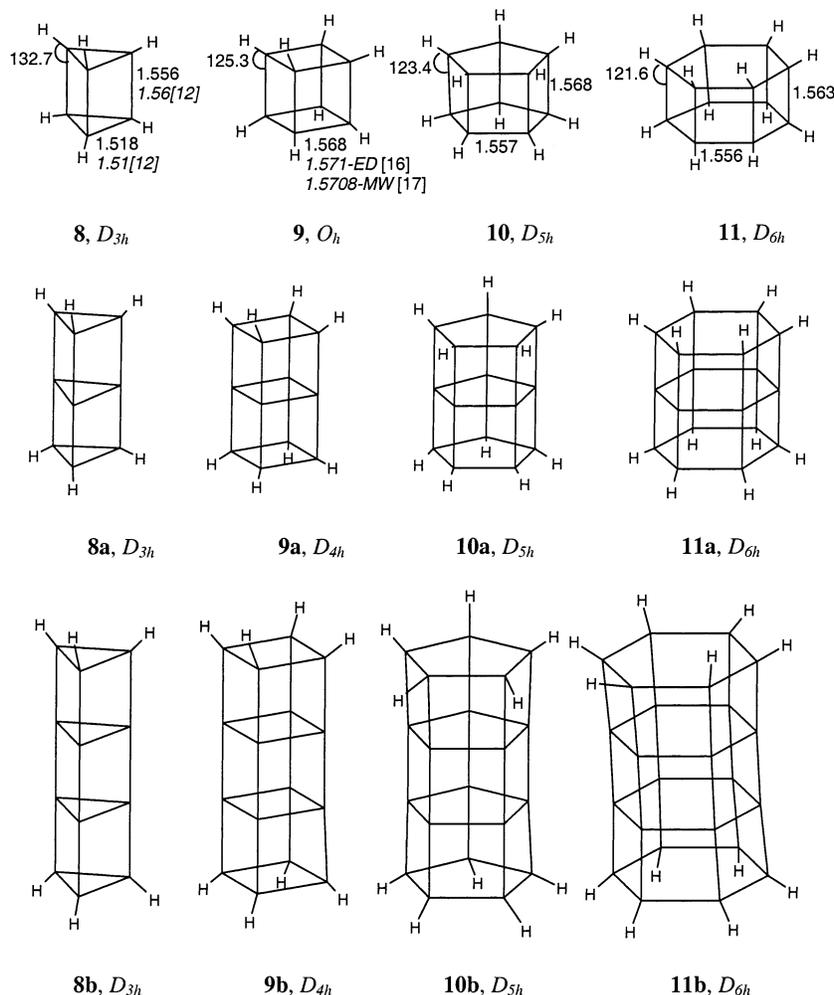
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CHART 1



2. Computational Methods

The calculations were carried out using the Gaussian98 system of programs.¹¹ The Becke-3 parameter density functional with the Lee–Yang–Parr correlation functional (B3LYP)^{12,13} 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).

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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,¹⁴ agree well with the experimental data available for derivatives of **8**¹⁵ and for **9**.^{16,17} 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_{nh} 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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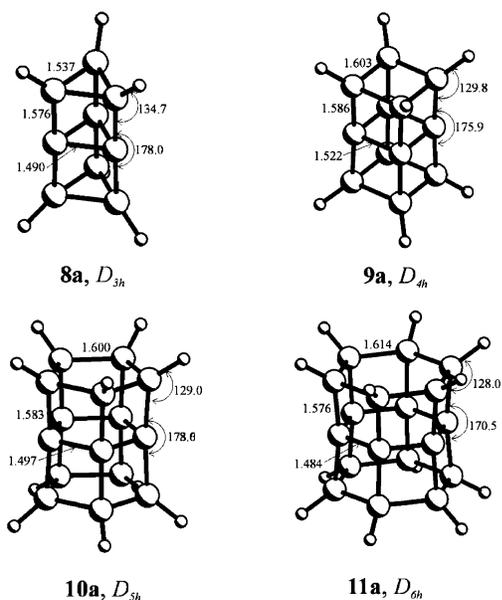


FIGURE 1. Structural parameters of bi[*n*]prismanes calculated by the B3LYP/6-311G(2df,p) method. Bond lengths are in Ångströms, angles in degrees.

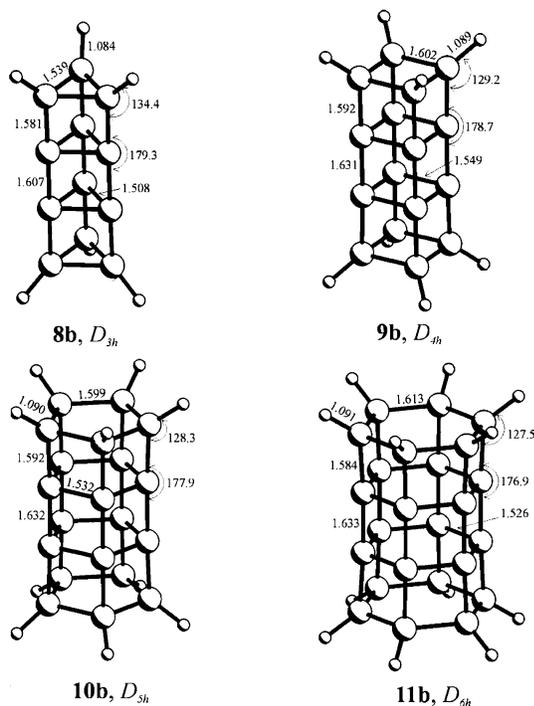


FIGURE 2. Structural parameters of tri[*n*]prismanes calculated by the B3LYP/6-311G(d,p) method. Bond lengths are in Ångströms, angles in degrees.

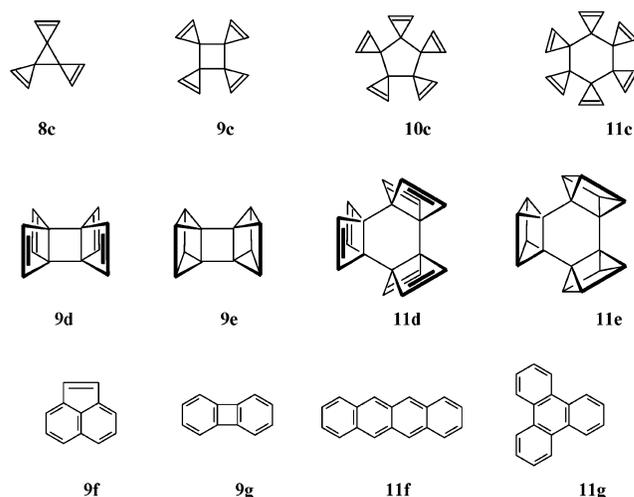
As may be seen from Figures 1 and 2, the (H)CCC(H) angles in **8a–11a** and the (H)CCC angles in **8b–11b** are very close to 180°, as in the ideal bisphenoid **5**. The CC bond lengths in the external basal (CH)_{*n*} rings of both bi[*n*]prismanes and tri[*n*]prismanes are 0.02–0.05 Å elongated, whereas 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-

TABLE 1. Total + ZPE and Relative Energies of Bi[*n*]prismanes **8a–11a** and Their Valence Isomers Calculated by B3LYP/6-311G(2df,p)

compound	$-(E_{\text{total}} + \text{ZPE}), \text{ au}$	$E_{\text{rel}}, \text{ kcal mol}^{-1}$
8a , bi[3]prismane	346.109 78	0
8c	346.196 82	–55
9a , bi[4]prismane	461.515 10	0
9c	461.664 58	–94
9d	461.729 52	–135
9e	461.555 06	–25
9f	462.062 23	–343
9g	462.007 22	–309
10a , bi[5]prismane	577.031 15	0
10c	577.111 15	–50
11a , bi[6]prismane	692.419 29	0
11c	692.533 45	–72
11d	692.709 13	–182
11e	692.527 20	–68
11f	693.124 34	–442
11g	693.138 45	–451

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 cyclopropanes 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 **11e** 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

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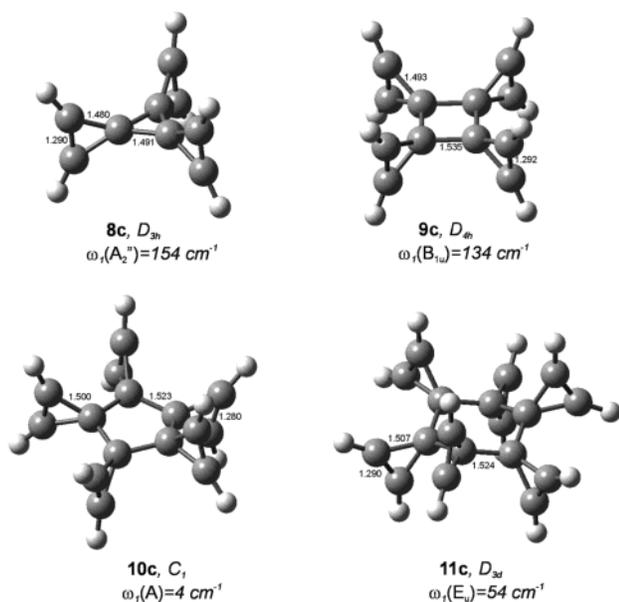


FIGURE 3. Structural parameters of the valence isomers of bi[*n*]prismanes **8c**–**11c** calculated by the B3LYP/6-311G(2df,p) method. Bond lengths are in Ångströms, angles in degrees.

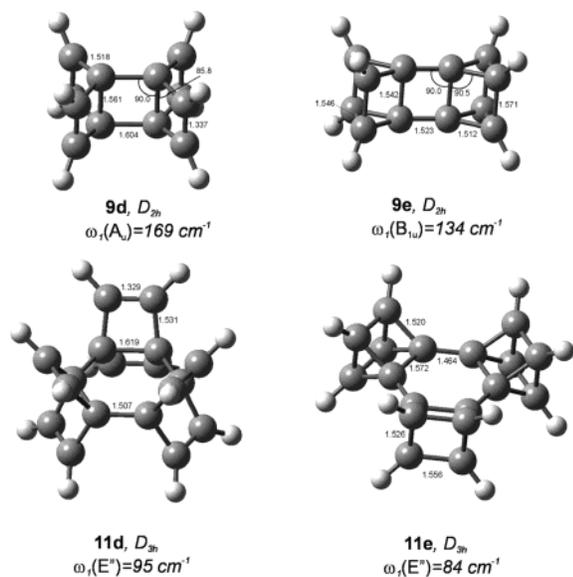


FIGURE 4. Structural parameters of the valence isomers of bi[4]prismane **9d** and **9e** and bi[6]prismane **11d** and **11e** calculated by the B3LYP/6-311G(2df,p) method. Bond lengths are in Ångströms, angles in degrees.

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 bisphenoidal methane **12a** and several other similarly distorted structures **12b**–**d** optimized in the

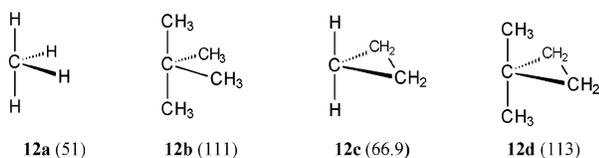


TABLE 2. Mulliken Charges at Carbon Atoms of [*n*]Prismanes and Poly[*n*]prismanes (q_C), Frequencies of the First Harmonic Vibrations (ω_1), Total Strain Energies (E_{str}), and Strain Energy per One CC Bond ($E_{\text{str}}^{\text{CC}}$) Calculated According to Equations 2–4 by the B3LYP/6-311G(2df,p) Method for [*n*]Prismanes and Bi[*n*]prismanes and by B3LYP/6-311G(d,p) Method for Tri[*n*]prismanes^a

[<i>n</i>]prismanes	<i>n</i> = 3 (8)	<i>n</i> = 4 (9)	<i>n</i> = 5 (10)	<i>n</i> = 6 (11)
q_C	−0.08	−0.06	−0.06	−0.10
E_{str} , kcal mol ^{−1}	136	151	129	163
$E_{\text{str}}^{\text{CC}}$, kcal mol ^{−1}	15.1	12.6	8.6	9.1
ω_1 , cm ^{−1} (symmetry)	647 (A ₁ '')	624 (E _u)	566 (E ₂ '')	389 (E _{2u})
bi[<i>n</i>]prismanes	<i>n</i> = 3 (8a)	<i>n</i> = 4 (9a)	<i>n</i> = 5 (10a)	<i>n</i> = 6 (11a)
$q_C(\text{outer})$	−0.15	−0.158	−0.159	−0.155
$q_C(\text{central})$	0.11	0.14	0.15	0.11
E_{str} , kcal mol ^{−1}	298	373	378	465
$E_{\text{str}}^{\text{CC}}$, kcal mol ^{−1}	19.9	18.7	15.1	15.5
ω_1 , cm ^{−1} (symmetry)	241 (E')	337 (E _u)	385 (E')	394 (E _{2g})
tri[<i>n</i>]prismanes	<i>n</i> = 3 (8b)	<i>n</i> = 4 (9b)	<i>n</i> = 5 (10b)	<i>n</i> = 6 (11b)
$q_C(\text{outer})$	−0.12	−0.11	−0.11	−0.10
$q_C(\text{central})$	0.01	0.01	0.00	−0.01
E_{str} , kcal mol ^{−1}	457	579	606	748
$E_{\text{str}}^{\text{CC}}$, kcal mol ^{−1}	21.8	20.7	17.3	17.8
ω_1 , cm ^{−1} (symmetry)	133 (E')	191 (E _u)	245 (E')	270 (E _{2u})

^a E_{tot} energies for CH₃–CH₃, HC(CH₃)₃, and C(CH₃)₄ are calculated as −79.858 95, −158.511 45, and −197.837 52 au by the B3LYP/6-311G(2df,p) method and −79.856 26, −158.505 89, and −197.830 75 au by the B3LYP/6-311G(d,p) method, respectively.

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

Whereas relative energies E_{rel} 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 E_{rel} calculated for **12a** and **12c** are, we think, mainly indicative of the first effect. By taking the value $E_{\text{rel}} = 52$ kcal mol^{−1} for the bisphenoidal methane **12a** (to be compared with 130–140 kcal mol^{−1} calculated by various methods for planar methane)^{1–4} 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 E_{str} 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

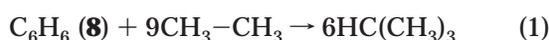
Several points of further interest are as follows. In **9c**, the four-membered cycle is planar, whereas the five-membered cycle of **10c** and the six-membered cycle in **11c** deviate from planarity with dihedral angles of 24° and 51°, respectively. The first harmonic vibration of the structure **10c** has the strikingly low value 4 cm^{−1}. This is related to the pseudorotation of the five-membered ring

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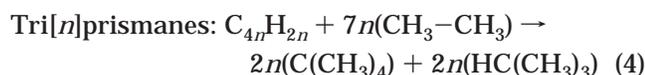
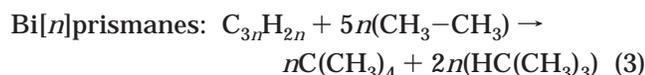
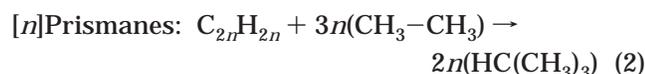
of **10c** with energy barriers between the five topomeric forms as low as 0.5 kcal mol⁻¹. The *D*_{5h} structure corresponds to a second rank saddle point (hilltop). A similar low-energy barrier (5-fold degenerate rearrangement) is characteristic of the singlet cyclopentadienyl cation, see ref 3 and 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



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.



The strain energies for prismane **8** and cubane **9**, evaluated as the energy difference of reagents and products in eq 2, fit well with those reported in the literature, calculated from experimental or computed heats of formation of components of selected homodesmotic reactions, 114–149 kcal mol⁻¹ for **8** and 157 kcal mol⁻¹ for **9**.^{1,19,22,24,25} Interestingly, when account is made

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TABLE 3. HOMO–LUMO Energetic Gaps (in eV) Calculated by the B3LYP/6-311G(d,p) Method for [*n*]prismanes, Bi[*n*]prismanes, and Tri[*n*]prismanes

<i>n</i>	[<i>n</i>]prismanes	bi[<i>n</i>]prismanes	tri[<i>n</i>]prismanes
3	7.8	4.9	3.7
4	7.3	4.6	3.5
5	7.9	5.0	3.8
6	7.0	4.7	3.3

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),^{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 tricongeners (**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)_{*n*} rings) is to be found in the strong π_σ–π_σ orbital interaction between the symmetry-adapted 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 σ way of π-antibonding MOs of the fragments. The determining role of such type π_σ–π_σ orbital interaction for stabilization of various polyhedral organic structures built up by parallel superposition of two or more fragment cyclic π-systems has been well established, [*n*]prismanes,^{1,26} [*n*]asteranes²⁷ (which may be viewed as [*n*]prismanes sandwiched by a polymethylene pseudocycle), organic molecular crystals,²⁸ and others.

The π_σ–π_σ 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 σ_π–σ_π orbital interaction between the radial MOs, formed by symmetry-adapted combinations of s, p_x, and p_y AOs.

Compounds with nonstandard stereochemical configuration of carbon centers may display unusual chemical properties.^{1–3,6,8,10} We have studied computationally the

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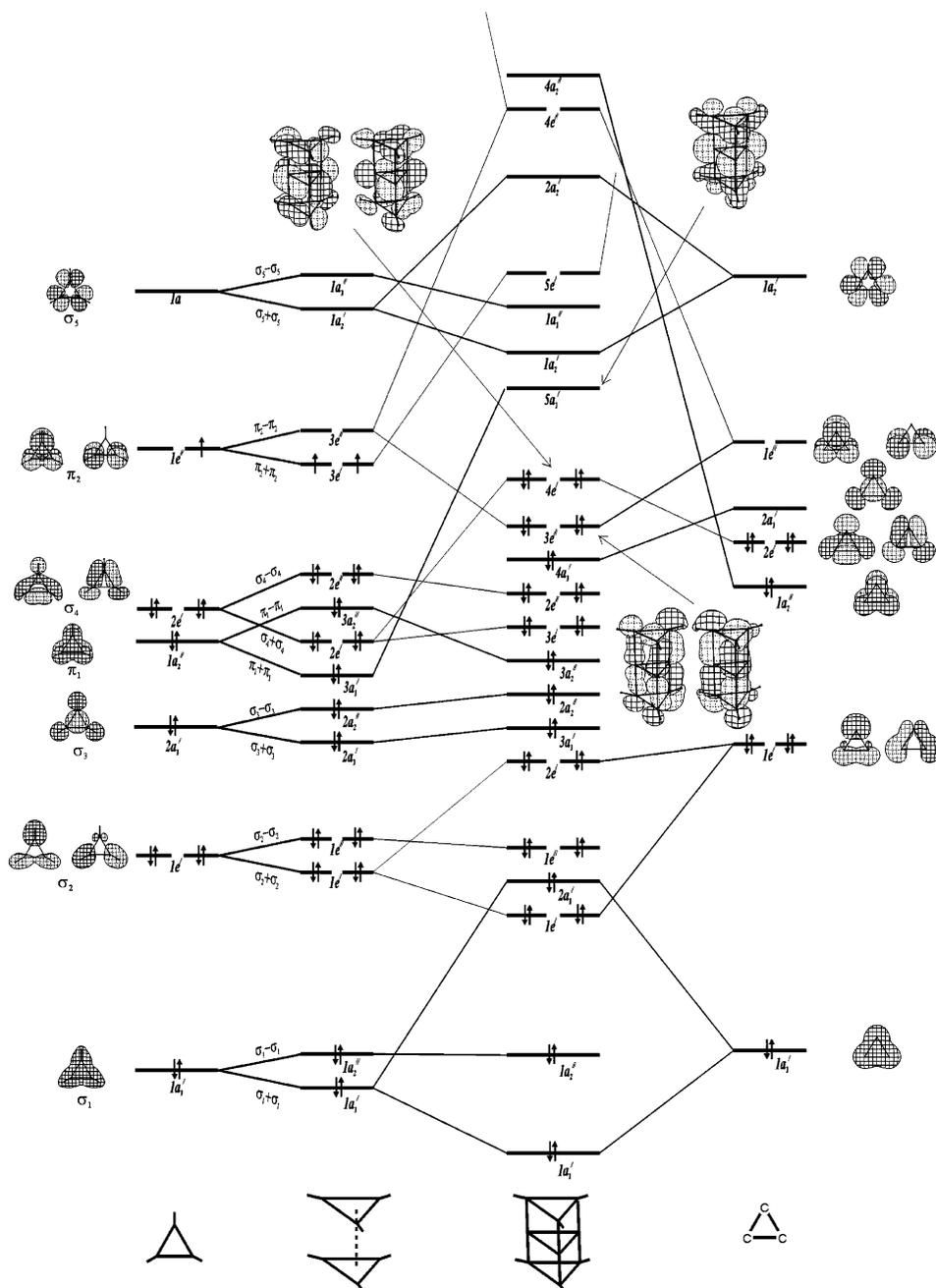
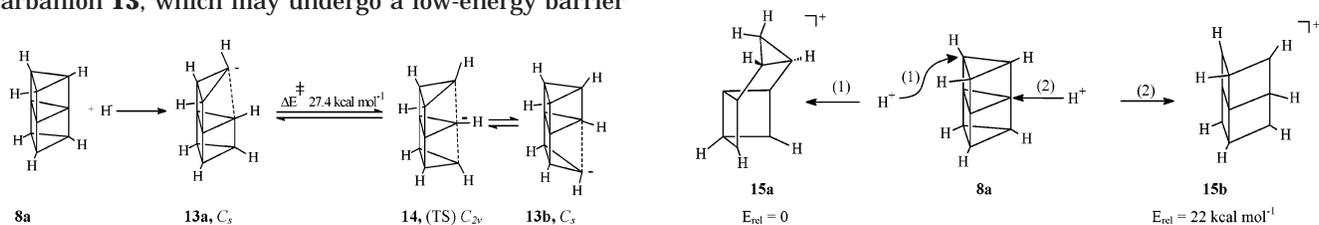


FIGURE 5. CACAO²⁹ drawing of the orbital interaction diagram depicting formation of MOs of bi[3]prismane **8a** from MOs of the fragments. The energy levels are calculated by the EHMO method³⁰.

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”³¹ 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



charged carbon atom of the central C_3 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 D_{nh} structures. The stability of the D_{nh} 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.³² 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.

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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 C_n and external $(CH)_n$ rings) half-planar (bisphenoidal) tetracoordinate carbon centers. The main factor providing for the stability of these compounds is the π_σ - π_σ orbital interaction between the parallel rings.

Acknowledgment. This work was supported by CRDF (Grant RC1-2323-RO-02) and the Russian Foundation for Basic Research (Grants 01-03-32546 and 02-03-33227). V.I.M. is also grateful to the Foundation for the Support of Russian Science.

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>.

JO034910L