

# Quantum-Chemical Investigation of Structure and Stability of $[n]$ -Prismanes and $[n]$ -Asteranes

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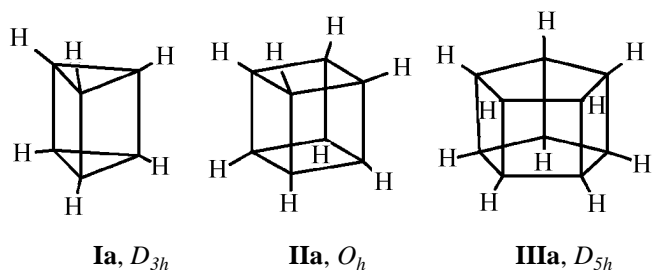
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**Abstract**—The study by DFT [B3LYP/6-311G(2df,p)] method of structural and energy characteristics peculiar to  $[n]$ -prismanes and  $[n]$ -asteranes demonstrated that prismanes of  $n = 3–10$  and asteranes of  $n = 3–7$  possessed a stable structure of  $D_{nh}$ -symmetry; the  $D_{nh}$ -geometry was distorted in the subsequent terms of the series.

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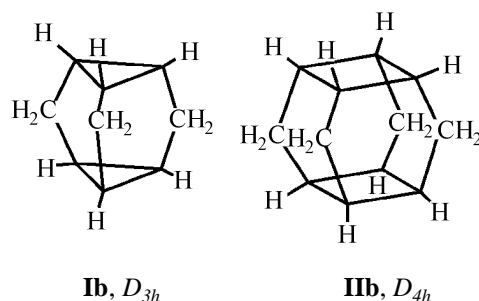
Hydrocarbons of prismane class are among the most interesting chemical compounds due to their unusual highly symmetrical structure [1, 2]. Prismane molecules  $C_{2n}H_{2n}$  built up of two parallel regular  $n$ -polygons joined by rectangular faces are highly strained framework structures with bond angles considerably deviating from the tetrahedral angle of an  $sp^3$ -hybridized carbon. By now three terms of the prismane series have been synthesized: triprismane (**Ia**) [3], cubane (**IIa**) [4], and pentaprismane (**IIIa**) [5].



One of outstanding prismanes properties is their uncommon kinetic stability suggesting that these highly strained compounds may be regarded as promising high-energy systems [6]. The structure and spectral characteristics of cubane (**IIa**) were investigated by versatile experimental and theoretical methods [6]. The structural parameters of triprismane (**Ia**) and pentaprismane (**IIIa**) were obtained from X-ray diffraction analysis of their derivatives [7, 8], and also from quantum-chemical calculations [9–11]. Theoretical methods remain yet the only instrument for the study of higher prismanes [10–12].

The steric strain in the prismane system may be considerably reduced by extending their framework introducing additional atom groups. As an example of thus extended prismane asterane molecules can be indicated [13] formed by introducing methylene groups into the lateral edges of prismanes.

By now triasterane (**Ib**) [14] and tetraasterane (**IIb**) have been obtained [15]. According to the quantum-chemical calculations the strain energy in the asterane system is lower than in the corresponding prismane analogs [13, 16].



A significant aspect of the prismane chemistry is the problem of the stability limits for the prismatic forms of  $D_{nh}$ -symmetry and the influence of  $n$  value on the prismane characteristics [10]. The results obtained by MM2 [17] and MM3 [18] procedures suggest that starting with octaprismane the prismatic geometry should be distorted. At the same time the calculations by MM4 method [18] suggest for octaprisman a  $D_{8h}$ -conformation. According to the calculations by STO-3G method [10], prismanes of  $n = 3–12$  are characterized by stable  $D_{nh}$ -

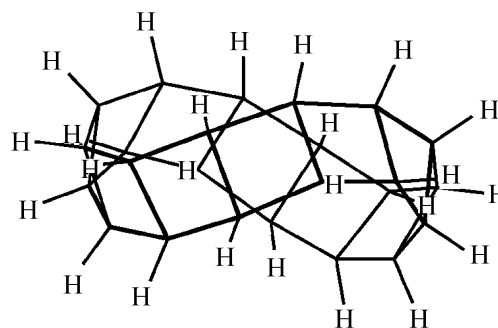
configuration. The calculations on the level SCF/6-31G\* confirmed the conclusion on the stability of prismanes up to  $n = 8$  [10], but the problem of the stability limits remained unsolved. The asterane systems were not investigated in this respect.

The target of the present study was investigation of the stability limits for prismane and asterane systems applying B3LYP/6-311G(2df,p) method [19] which ensured good agreement with experimental data, and also analysis of factors governing the structural and energy characteristics of these compounds.

Quantum-chemical calculation were performed by the method of density functional theory (DFT) employing three-parameter potential B3LYP in a valence-split basis 6-311G(2df,p) using the software package GAUSSIAN-98 [20]. Stationary points on the potential energy surface (PES) were identified by means of calculating the second derivatives matrix (force constants) performed analytically. The graphical images of the molecular structures represented in the figures were obtained with the help of a program PD (PLUTO mode) in the framework of the software package PC MODEL [21]; we used as parameters the final Descartes coordinates of atoms obtained by geometry optimization.

**Structure and stability of  $[n]$ -prismanes.** According to the calculation results the terms of the prismane series of  $n = 3-10$  possess a structure with  $D_{nh}$  symmetry and correspond to the energy minima ( $\lambda = 0$ , here and hereinafter  $\lambda$  means the number of the negative Gessian eigenvalues) on PES. At  $n > 10$  prismatic configurations

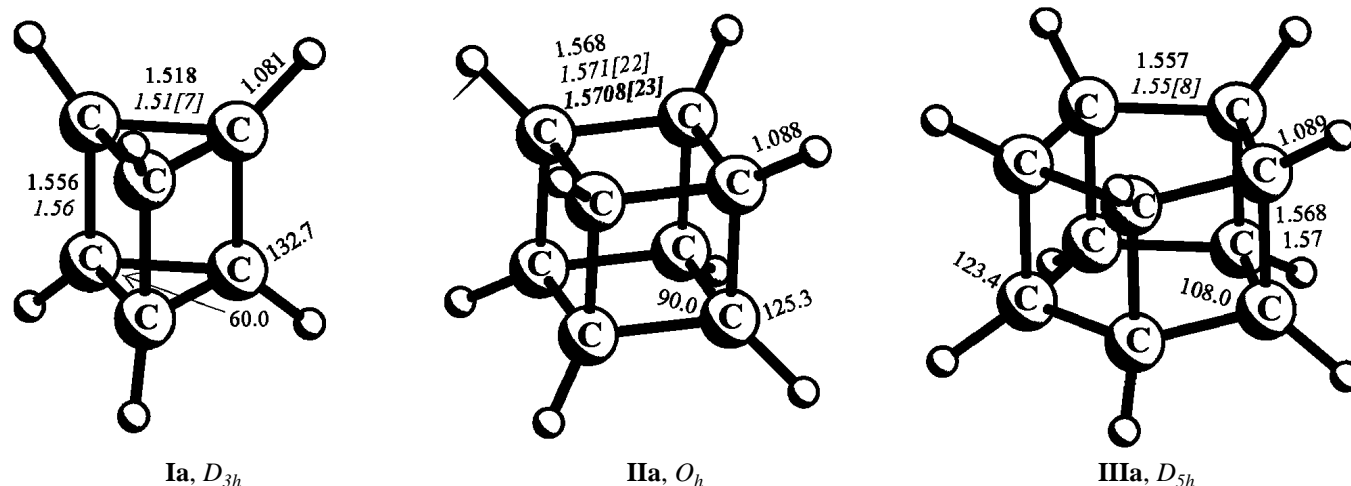
do not correspond to the energy minima on PES, whereas structures with a reduced symmetry correspond to stable systems. For instance, with 12-prismane a stable structure **IX** possesses  $S_4$  symmetry.



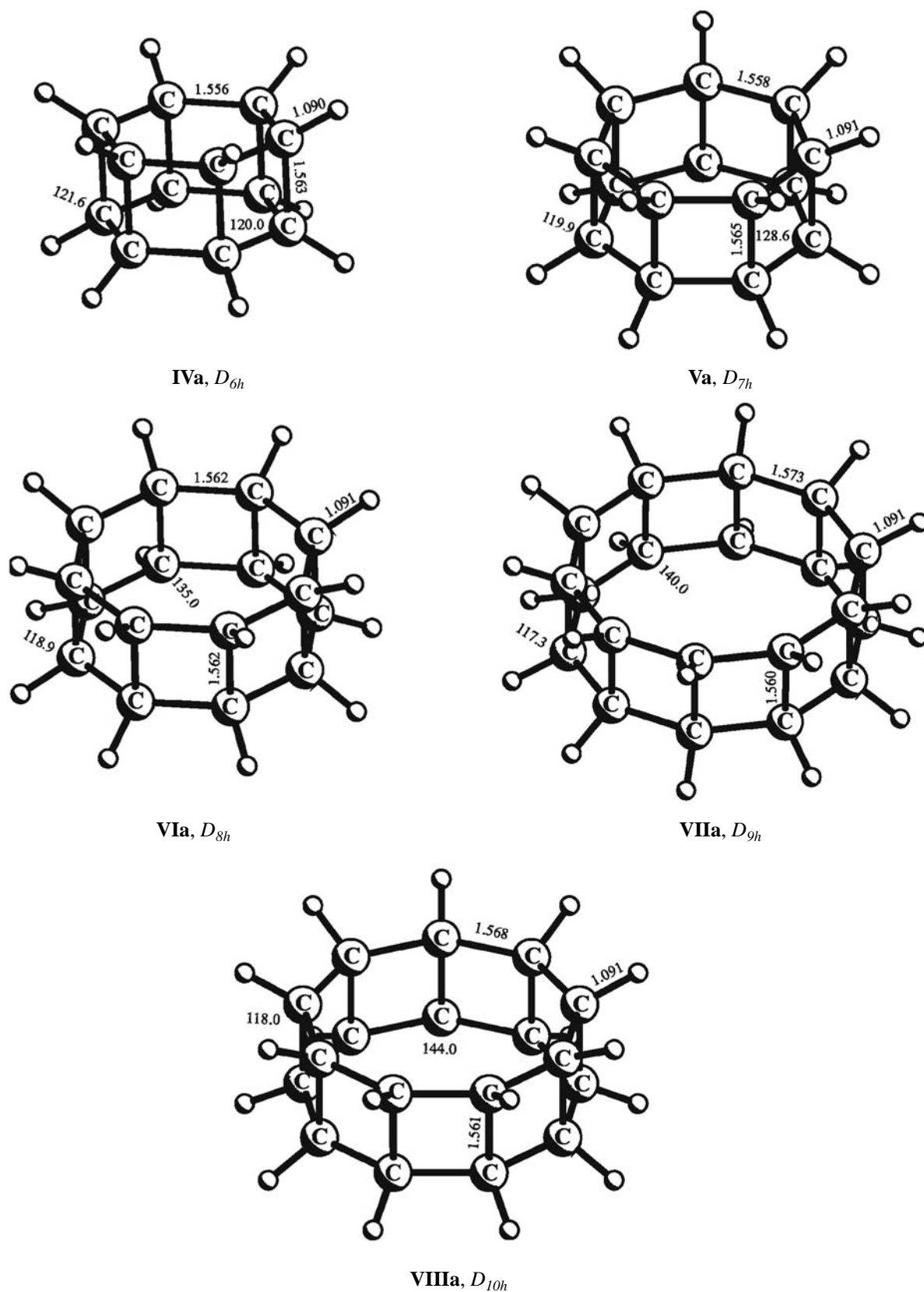
**IX**,  $S_4$

The structural characteristics of stable prismanes **Ia–VIIIa** are presented in Figs. 1 and 2, the energy characteristics are given in Table 1.

As seen from Fig. 1, the calculated structural characteristics of cubane are well consistent with the data of electron diffraction [22] and microwave spectroscopy [23]. The structural data obtained by X-ray diffraction analysis of substituted derivatives of triprismane [7] and pentaprismane [8] also are in agreement with the calculations. There is no constant trend in the variation of bond lengths CC in the series **Ia–VIIIa**: only in the higher prismanes **Va–VIIIa** the rise in  $n$  is accompanied with lengthening of the CC bonds of the  $n$ -member edges



**Fig. 1.** Calculated by B3LYP/6-311G(2df,p) method geometric characteristics of prismanes **Ia–IIIa** structures corresponding to the energy minima ( $\lambda = 0$ ) on the respective PES. Bond lengths are given in angstroms, bond angles, in degrees. Experimental data obtained by X-ray method for systems **Ia** [7] and **IIIa** [8] are printed in italics, data for system **IIa** obtained by electron diffraction [22] and microwave spectroscopy [23] are printed respectively in italics and bold italics.



**Fig. 2.** Calculated by B3LYP/6-311G(2df,p) method geometric characteristics of prismanes **IVa**–**VIIIa** structures corresponding to the energy minima ( $\lambda = 0$ ) on the respective PES. Bond lengths are given in angstroms, bond angles, in degrees.

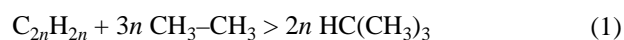
**Table 1.** Energy characteristics<sup>a</sup> of prismane systems **Ia–VIIIa** calculated by the B3LYP/6-311G(2df,p) method

| Structure                | $E_{\text{total}}$ | $\omega_1$ | $\omega_{\text{CH}}$ | $-E_{\text{HOMO-LUMO}}$ | $E_{\text{strain}}$ | $E_{\text{strain}}^{\text{CC}}$ |
|--------------------------|--------------------|------------|----------------------|-------------------------|---------------------|---------------------------------|
| <b>Ia</b> , $D_{3h}$     | -232.12205         | 647        | 3176                 | 7.8                     | 136                 | 15.1                            |
| <b>IIa</b> , $O_h$       | -309.54417         | 624        | 3087                 | 7.3                     | 151                 | 12.6                            |
| <b>IIIa</b> , $D_{5h}$   | -387.02474         | 566        | 3079                 | 7.9                     | 129                 | 8.6                             |
| <b>IVa</b> , $D_{6h}$    | -464.41721         | 389        | 3056                 | 7.0                     | 163                 | 9.1                             |
| <b>Va</b> , $D_{7h}$     | -541.77445         | 256        | 3038                 | 6.9                     | 218                 | 10.4                            |
| <b>VIa</b> , $D_{8h}$    | -619.11803         | 183        | 3026                 | 6.5                     | 283                 | 11.8                            |
| <b>VIIa</b> , $D_{9h}$   | -696.43747         | 113        | 3017                 | 6.6                     | 362                 | 13.4                            |
| <b>VIIIa</b> , $D_{10h}$ | -773.74945         | 53         | 3008                 | 6.3                     | 446                 | 14.9                            |

<sup>a</sup>  $E_{\text{total}}$  is the total energy, a.u., where 1 a.u. = 627.5095 kcal mol<sup>-1</sup>;  $\omega_1$  is the value of the least harmonic oscillation frequency, cm<sup>-1</sup>;  $\omega_{\text{CH}}$  is the value of oscillation frequency corresponding to the extension of the CH bond, cm<sup>-1</sup>;  $\Delta E_{\text{HOMO-LUMO}}$  is the energy gap value between the frontier orbitals, eV;  $E_{\text{strain}}$  and  $E_{\text{strain}}^{\text{CC}}$  are respectively total strain energy and strain energy calculated per a single CC bond, kcal mol<sup>-1</sup>.

and with shortening of the lateral edges. The growth of the CCC angle by growing size of prismanes is followed by continuous decrease in the bond angle HCC from 132.7 in triprismane **Ia** to 117.3 deg in decaprismane **VIIIa**. This trend is in agreement with the known effect of decreasing bond angle of a saturated carbon with the increasing opposite bond angle [10]. The decrease in the HCC angle results in minimization of the repulsion between hydrogen atoms belonging to the same  $n$ -membered ring which grows with the growing  $n$  [24]. For instance, the calculated vicinal distances H $\cdots$ H in triprismane **Ia** are 2.893 Å, whereas in decaprismane **VIIIa** they decrease to 2.173 Å. In the unstable  $D_{nh}$ -forms of undeca- and dodecaprismanes the distances H $\cdots$ H amount only to 2.128 and 2.091 Å respectively.

The terms of the prismane series are distinguished by shortened CH bonds caused by the high degree of the  $\sigma$ -character of the CH bond due to rehybridization of the carbon centers produced by steric strain. The growth of the CCC bond angle with the growing size of prismanes is accompanied by the reduction of the  $\pi$ -character of the CC bonds and consequently, by decreasing  $\sigma$ -character of CH bonds. Thus the increased  $n$  results in weakening of the CH bonds as seen the most obvious on the first five terms of the series (Figs. 1 and 2). The trend in reducing the  $\sigma$ -character of CH bonds on increasing  $n$  was confirmed by experimental data: the estimates based on the measurement of the coupling constants  $J_{\text{C}^{13}\text{-H}}$  showed that the  $\sigma$ -character of the CH bonds in systems **Ia**, **IIa**, and **IIIa** was respectively 36, 31, and 30% [5]. The lengthening of CH bonds at growing  $n$  is followed by a decrease in the oscillation frequency of bond extension  $\nu_{\text{CH}}$  (Table 1) that correlates with the experimental findings:  $\nu_{\text{CH}}$  for systems **Ia**, **IIa**, and **IIIa** is respectively 3066, 2992, and 2973 cm<sup>-1</sup> [5].



The least strain energy according to the calculations corresponds to pentaprismane (**IIIa**), where the angle strain in the five-membered face is virtually absent: the CCC angles are 108 deg and nearly ideally fit to the tetrahedral angle. In all the other terms of the series the growth of  $n$  is accompanied by monotonic increase in the strain energy, and it correlates with the growing number of strained four-membered faces. The calculated strain energy of cubane is close to the experimental value 157 kcal mol<sup>-1</sup> [26]. The trend obtained for the variation of the strain energy (Fig. 3) is consistent with the former estimates made previously for the first four terms of the series [9–12].

The convenient way of comparison of the strain energy in prismanes is the estimate of the strain energy per one bond CC ( $E_{\text{strain}}^{\text{CC}} = E_{\text{strain}}/3n$ ) [1]. This approach regards pentaprismane as the least strained system. Thus evaluated strain energy of the ultimate terms of the series is lower than the strain energy of the synthesized triprismane. At the same time the calculated strain energies of the unstable  $D_{nh}$ -forms of undeca- and dodecaprismanes amount respectively to 16.4 and 17.6 kcal mol<sup>-1</sup> and are considerably larger than the values obtained for stable systems **Ia–VIIIa**.

The repulsive interaction of the vicinal hydrogen atoms alongside the effect of the strained four-membered faces is a significant factor of destabilization for the higher terms of the prismanes series. The deformation of prismatic structures of  $n > 10$  to less symmetric forms results not only in the changes in bond angles, but also in considerable increase in the vicinal H $\cdots$ H distances. The diminishing stability of prismane systems at growing  $n$  is demonstrated in the continuous decrease in the value

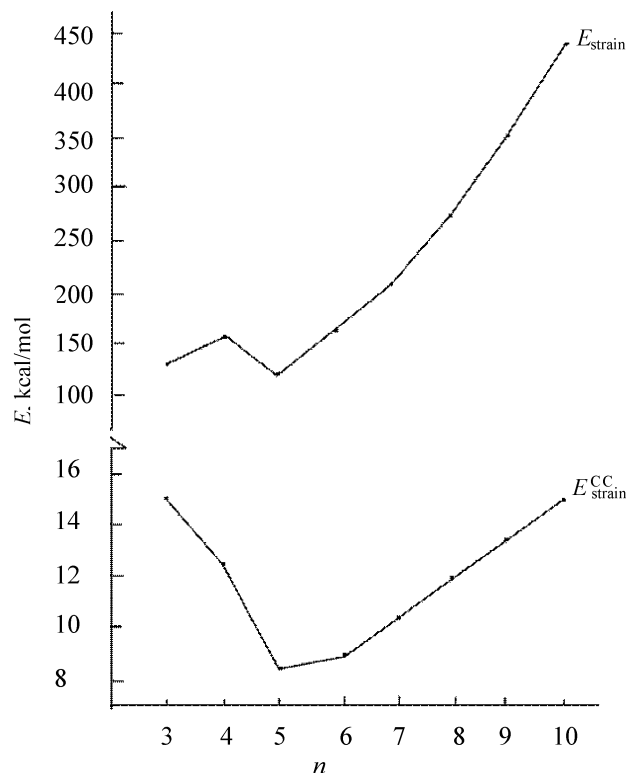


Fig. 3. The calculated strain energy as a function of the number of side faces in prismanes.

(2)

of the first harmonic oscillation frequency and in reduction of the gap between the frontier orbitals (Table 1).

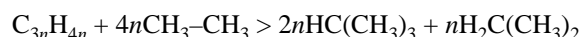
**Structure and stability of [n]-asteranes.** The calculation results demonstrated that asterane systems of  $C_n$   $n = 3-7$  possessed a stable structure ( $\lambda = 0$ ) of  $D_{nh}$  symmetry; at larger  $n$  the structures of  $D_{nh}$  symmetry did not correspond to the energy minima on PES. The geometric characteristics of stable asterane systems **Ib–Vb** are presented on Fig. 4, the energy characteristics are given in Table 2.

Table 2. Energy characteristics<sup>a</sup> of asterane systems **Ib–Vb** calculated by the B3LYP/6-311G(2df,p) method

| Structure              | $E_{\text{total}}$ | $\omega_1$ | $\Delta E_{\text{HOMO-LUMO}}$ | $E_{\text{strain}}$ |
|------------------------|--------------------|------------|-------------------------------|---------------------|
| <b>Ib</b> , $D_{3h}$   | -350.23583         | 234        | 7.5                           | 50                  |
| <b>IIb</b> , $D_{4h}$  | -467.00513         | 331        | 7.4                           | 52                  |
| <b>IIIb</b> , $D_{5h}$ | -583.79484         | 366        | 7.7                           | 41                  |
| <b>IVb</b> , $D_{6h}$  | -700.45507         | 259        | 6.9                           | 111                 |
| <b>Vb</b> , $D_{7h}$   | -817.02741         | 143        | 7.0                           | 236                 |

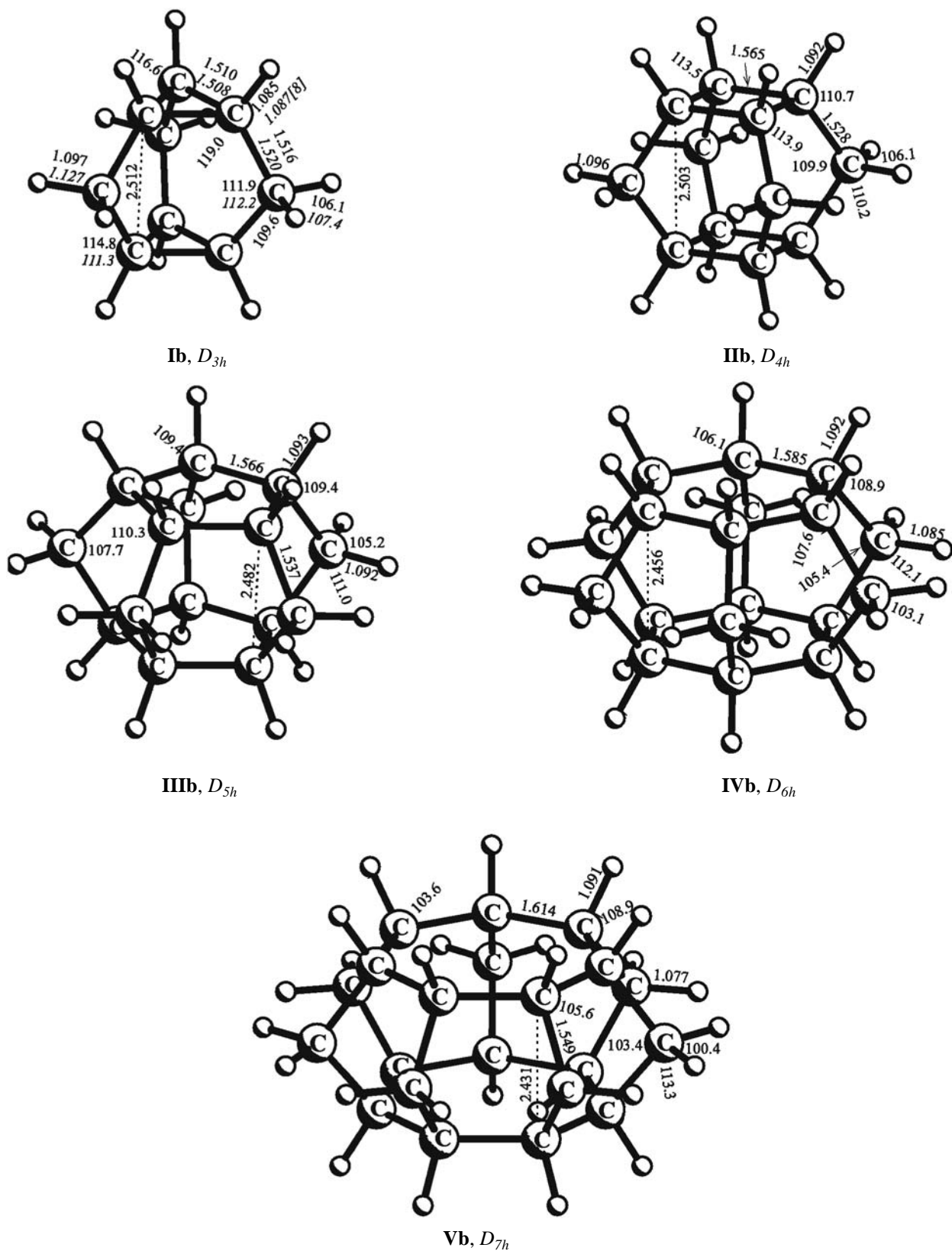
<sup>a</sup> See the note of Table 1.

As seen from Fig. 4, the calculated geometric characteristics of triasterane (**Ib**) are well consistent with the data of the electron diffraction [13]. Unlike prismanes distinguished by shortened CH bonds the CH bond, distances in the  $n$ -membered asterane rings, save **Ib**, correspond to the standard values of ordinary bonds. The introduction of methylene groups into the side faces resulted in decrease of the strain energy in asteranes compared to prismanes. The total strain energy of systems **Ib–Vb** calculated with the use of homodesmotic reaction (2) (Table 2) is notably lower than that of the prismane analogs **Ib–Vb**.



The variation of strain energy in the asterane series is similar to the trends found for prismanes. The calculated total strain energies of triasterane and tetraasterane are nearly equivalent, and the least strain energy belongs to pentaasterane (**IIIb**) whose bond angles virtually ideally coincide with tetrahedral angles. The results obtained are in contrast to the former calculations by MM3 [13] that ascribe the lowest strain energy (20 kcal mol<sup>-1</sup>) to triasterane (**Ib**), and in going to the next terms of the series the total strain energy steeply grows (86 and 85 kcal mol<sup>-1</sup> for tetra- and pentaasterane respectively).

Unlike prismanes suffering from the destabilizing effect of the strained four-membered side rings, the lateral faces of asteranes are built of relatively flexible cyclohexane structures that determines the reduction of the steric strain. Although the extension of the  $n$ -membered rings with growing  $n$  leads to the decrease of the bond angles HCC and CCC of the cyclohexane fragments, the deviation from the optimum tetrahedral values is relatively small and amounts just to several degrees (Fig. 4). These deviations are not sufficient for the destabilization of the higher terms of the asterane series. A more important destabilizing factor is the repulsive interaction of the hydrogen atoms from the neighboring methylene groups: according to calculations the increase in  $n$  results in sharp approach of the methylene hydrogens from 3.245 in triasterane (**Ib**) to 1.553 Å in heptaasterane (**Vb**). The approach of the methylene hydrogen atoms is partially compensated by lengthening of the CC bonds within the  $n$ -membered rings from 1.510 in **Ib** to 1.614 Å in **Vb**. A similar but less pronounced effect is also observed in prismane systems. Hence although the steric strain in asteranes is lower than in prismanes the class of the methylene-extended analogs is very limited and contains only five stable systems.



**Fig 4.** Calculated by B3LYP/6-311G(2df,p) method geometric characteristics of asteranes **Ib–Vb** structures corresponding to the energy minima ( $\lambda = 0$ ) on the respective PES. Bond lengths are given in angstroms, bond angles, in degrees. Experimental data obtained by electron diffraction method for system **Ib** [13] are printed in italics.

In the asterane series a trend in monotonic change in the flattening of the side faces is observed: whereas in triasterane (**Ib**) the *boat*-like cyclohexane fragment is sufficiently flattened (methylene atoms are deviated from a plane by 18.7 deg), in the heptaasterane (**Vb**) the deviation from a plane reaches 35.4 deg. The decrease in the bond angles of the cyclohexane fragments is followed by notable approach of the *n*-membered rings, from 2.512 in **Ib** to 2.431 Å in **Vb** and also by strong shortening of the methylene CH bonds, especially pronounced in the ultimate terms of the series (1.077 Å in heptaasterane). The destabilization of the higher asteranes at growing *n* results in smaller value of the first harmonic frequency (Table 2).

Thus the calculations performed demonstrated the growing destabilization of prismane and asterane systems with growing *n*, although the reason of the destabilization is different in these cases. At the same time sufficiently high values of the first oscillation frequencies of the higher representatives of both classes suggest the possibility to observe them experimentally.

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