Two-dimensional lattice oligomers of diboraspiropentadiene: a quantum chemical study*

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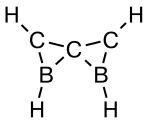
According to B3LYP/6-311G(d,p) density functional calculations, the most energetically favorable method of assembling diboraspiropentadiene molecules into dimers, trimers, tetramers, and higher two-dimensional (2D) oligomers is to join the diboraspiropentadiene units with the formation of C—B bonds and the diboraspiropentadiene units *trans*-arranged relative to these bonds. Using this procedure, stable 2D lattice structures comprising 4, 7, 9, 16, or 25 monomer units were constructed in such a manner that each unit retains a nonclassical planar configuration of four bonds formed by the central carbon atom. Enlargement of the planar oligomers results in narrowing of the HOMO—LUMO gap and a considerable increase in the dipole moment. High negative NICS values suggest that the three-membered rings retain their aromaticity, whereas the ten-membered rings formed involving different monomer units in constructing oligomeric structures are strongly antiaromatic.

Key words: planar tetracoordinate carbon atom, diboraspiropentadiene oligomers, energetically favorable isomers, 2D lattice structure, quantum chemical calculations, density functional theory, B3LYP functional.

At present, molecular engineering of and research on two-dimensional (2D) π-conjugated structures with valuable electrical and mechanical properties, *e.g.*, graphene[1,2] and its boron and silicon[3—5] analogs, have been key avenues of the design of new-generation materials for micro- and nanoelectronics. Unusual physicochemical properties of such structures are to a great extent due to unusual stereochemical configurations of their atomic centers. For instance, extremely high cohesive energies, as well as the semiconducting or metallic properties of so-called face-decorated graphene nanoribbons (graphene sheets functionalized at edge carbon atoms) are due to the formation, on the nanoribbon faces, of planar tetracoordinate carbon centers on which the frontier MOs are localized.[6] In this connection, organic and organoelement compounds with planar, bisphenoidal, and pyramidal tetracoordinate carbon atoms, as well as other nonclassical structures formed by carbon atoms and other atoms of main-group elements of the periodic system, attract increased attention of researchers.[7—10] Such compounds can serve as building blocks for the design of 3D and extended 2D molecular systems containing atoms with unusual stereochemical configurations of valence bonds.

The main method of molecular design of such systems[8—13] is to join blocks (monomer units) containing single nonclassically coordinate atoms. In this connection, theoretical research should also be aimed to search for thermodynamically or kinetically stable structures corresponding to minima on the potential energy surface (PES). This procedure for the assembly of stable oligomers was successfully used in the design of ribbon,[10—12] planar,[3,6,11,12] and 3D cage[10,13] structures containing planar tetracoordinate and hypercoordinate carbon centers.

In this work, we used the diboraspiropentadiene molecule as the initial "monomer" unit. According to B3LYP/6-311+G(d,p) and MP2(full)/6-311++G(d,p) calculations,[14,15] isomer **1** is the most stable among all possible isomers of diboraspiropentadiene containing the tetracoordinate carbon atom. Possible types of joining monomer units **1** resulting in extended 2D graphene-like structures covering the entire plane are presented in Scheme 1. We have theoretically studied (1) all possible types of dimerization following Scheme 1; (2) the most promising trimers built of the energetically most favorable dimer; and (3) tetramers and higher oligomers suitable for assembling extended 2D structures.



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* Dedicated to Academician of the Russian Academy of Sciences O. M. Nefedov on the occasion of his 80th birthday.

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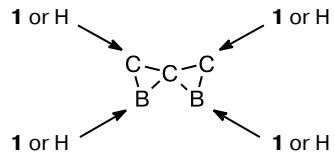
Scheme 1



Calculation Procedure

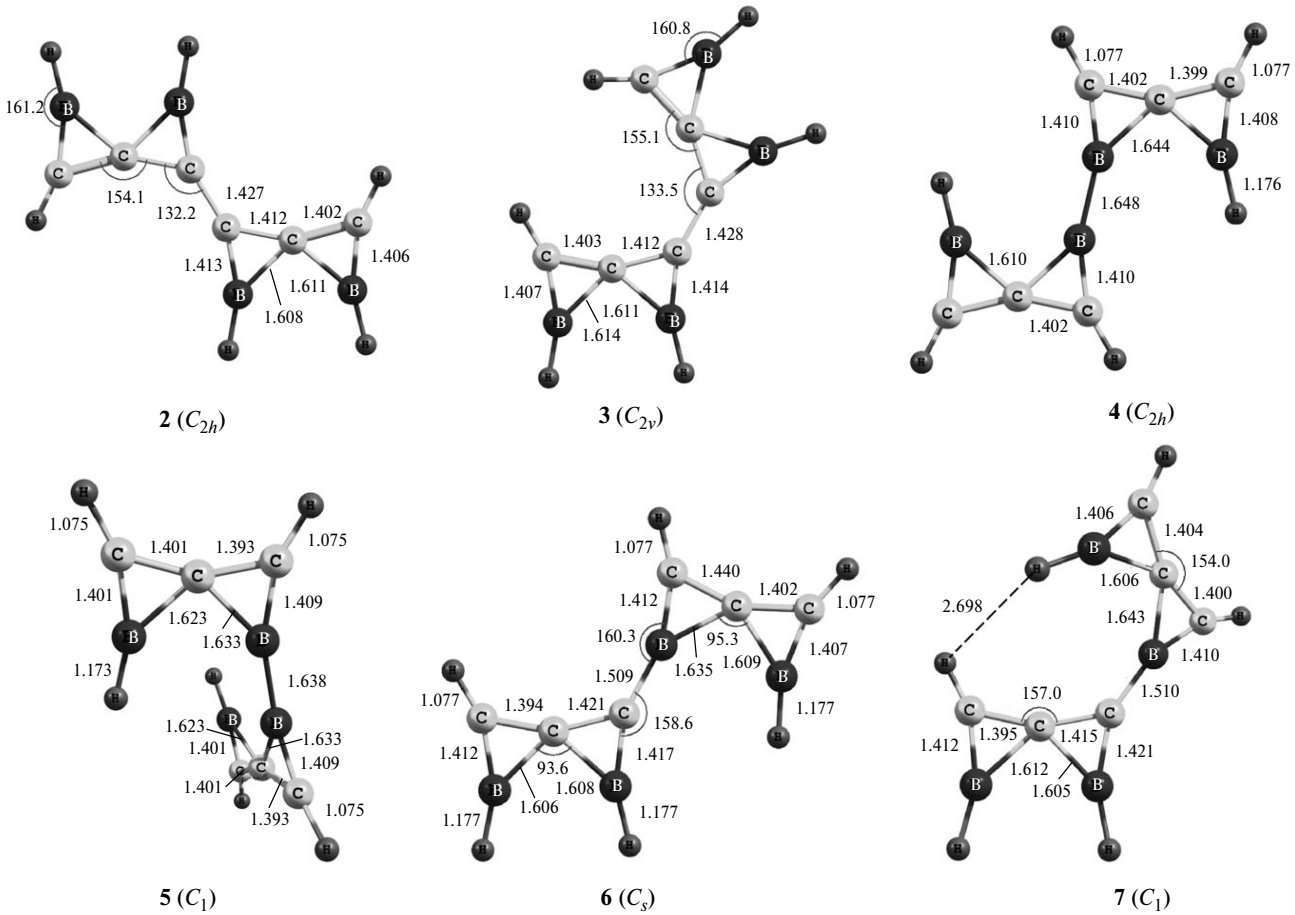
Quantum chemical calculations were carried out within the framework of the density functional theory (DFT) with the B3LYP three-parameter functional[16—18] and the 6-311G(d,p) split-valence basis set[19,20] using the Gaussian 03 program.[21] Numerical integration was carried out using an ultrafine integration grid (key word Integral, Grid=UltraFine). Geometry optimization was performed in the "tight" mode.

All wave functions at stationary points were checked for stability of the solution.[22] The nature of the stationary points was determined using analytical calculations of the force constant matrices. The nucleus-independent chemical shift (NICS) values were calculated following a known procedure.[23] Positive and negative NICS values corresponded to antiaromatic and aromatic character of the rings considered, respectively. Graphical images of the molecular structures were obtained using the ChemCraft program[24] for which the optimized Cartesian atomic coordinates were used as the input parameters.

Results and Discussion

By joining the monomer units at carbon or boron atoms in the positions labeled by arrows (see Scheme 1) one can obtain six diboraspiropentadiene dimers **2**—**7** (structures obtained by joining two, three, and more C_3B_2 units are then respectively denoted as dimers, trimers, *etc.*). The calculated geometric parameters of systems **2**—**7** are shown in Fig. 1 and their energy characteristics are presented in Table 1.

Among the dimers **2**—**7**, isomer **6** with the monomer units linked by the C—B bond is the most stable. For all pairs of conformers (**2** and **3**, **4** and **5**, **6** and **7**), *trans*-orientation of the monomer units relative to the bond connecting them in dimer **6** is energetically more preferable than the *cis*-orientation because of steric repulsion which causes deplanarization of the *cis*-isomers. One can



2 (C_{2h}) **3** (C_{2v}) **4** (C_{2h})

5 (C_1) **6** (C_s) **7** (C_1)

Fig. 1. Geometric parameters of diboraspiropentadiene dimers **2**—**7** obtained from B3LYP/6-311G(d,p) calculations. Here and in Figs 2—6 the bond lengths and interatomic distances are given in Å and the angles are given in degrees.

assume that the most energetically favorable method of assembling an oligomeric system based on diboraspiropentadiene is to build up the monomer units using the pattern of dimeric structure **6**, *i.e.*, by *trans*-joining at B—C bonds.

The third monomer unit can be added to dimer **6** in three ways which lead to trimeric structures **8**—**10**. The optimized geometric parameters of these structures are shown in Fig. 2 and their energy characteristics are presented in Table 1.

Trimer **9** is the most energetically favorable. The relative energies of the other two isomers are at most 1.2 kcal mol^{-1}.

By adding the next monomer unit to trimer **9** at two C—B bonds one can obtain a tetramer **11**, the primary building block for assembling a 2D structure with the energetically favorable type of bonding. Another route to tetramer **11** involves the addition of the C_3B_2 unit to the energetically least favorable trimeric structure **8**. The calculated geometric parameters of structure **11** are presented in Fig. 3 and its energy characteristics are listed in Table 1.

The addition of the fourth monomer unit causes an increase in the stereochemical rigidity of the polycyclic system in which N monomer units are linked by N rather than $N-1$ bonds as in the linear oligomer. Also, it leads to a more efficient conjugation of the π-systems of the monomer units.

Table 1. Relative energies of isomeric structures (ΔE), relative energies calculated with inclusion of zero-point vibrational energies (ΔE_{ZPE}), minimum vibrational frequencies (ω_1), and the energy differences between the HOMO and LUMO ($\Delta_{HOMO-LUMO}$) for structures **2**—**11** and **13**—**17**

Structure (symmetry group)	ΔE	ΔE_{ZPE}	ω_1 /cm^{-1}	$\Delta_{HOMO-LUMO}$ /eV
	kcal mol^{-1}			
2 (C_{2h})	9.2	8.5	44	4.83
3 (C_{2v})	9.9	9.2	42	4.77
4 (C_{2h})	7.1	7.5	22	4.65
5 (C_1)	7.2	7.6	35	5.39
6 (C_s)	0	0	35	4.84
7 (C_1)	1.1	1.0	29	4.89
8 (C_{2v})	1.2	1.2	19	4.27
9 (C_s)	0	0	17	4.27
10 (C_s)	0.4	0.4	22	4.51
11 (C_{2v})	—	—	17	3.45
13 (C_s)	0	0	9	2.85
14 (C_{2v})	4.9	4.7	6	3.16
15 (C_{2h})	—	—	9	2.54
16 (C_{2h})	—	—	5	1.95
17 (C_{2h})	—	—	3	1.50

Note. The total energies (E/au) of structures **6**, **9**, **11**, **13**, **15**—**17** are −331.550172, −496.738507, −660.743277, −1155.127943, −1483.139930, −2633.554151, and −4111.986337, respectively.

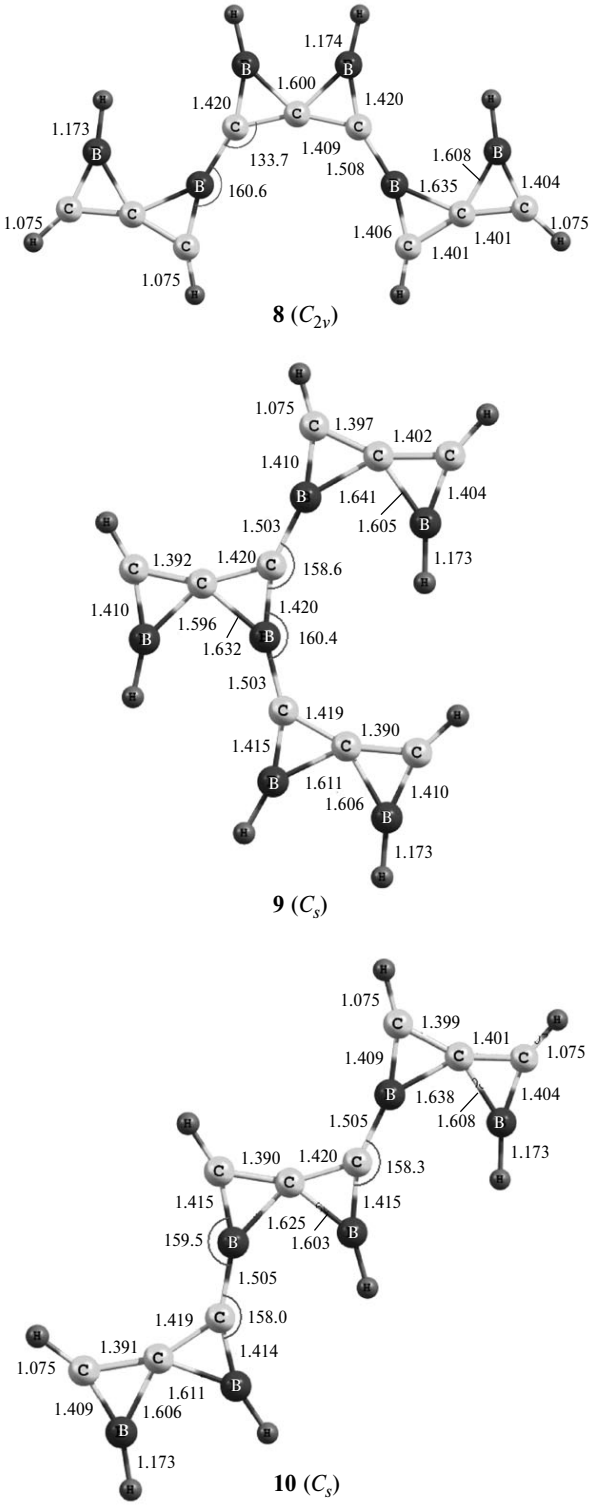
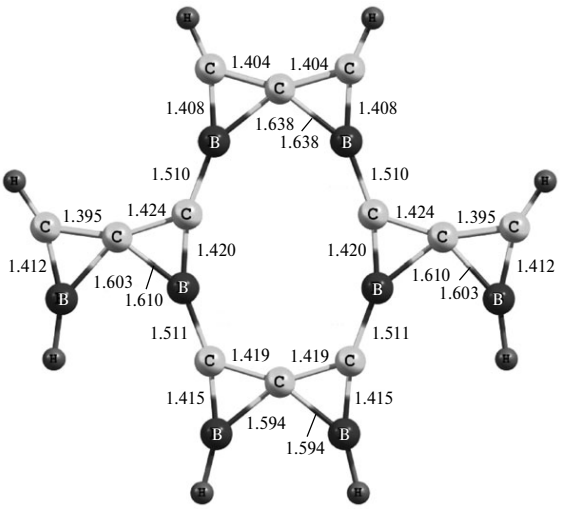


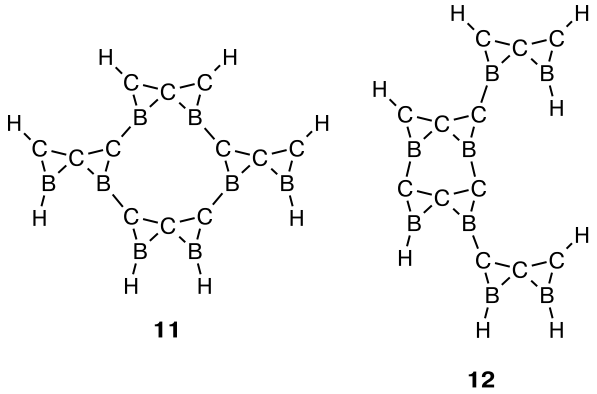
Fig. 2. Geometric parameters of diboraspiropentadiene trimers **8**—**10** obtained from B3LYP/6-311G(d,p) calculations.

The energy of tetramer **11** is 10.0 kcal mol^{-1} lower than that of isomer **12**. Structures **11** and **12** can be compared as follows: in isomer **12**, two outermost monomer



11 (C_{2v})

Fig. 3. Geometric parameters of tetramer **11** obtained from B3LYP/6-311G(d,p) calculations.



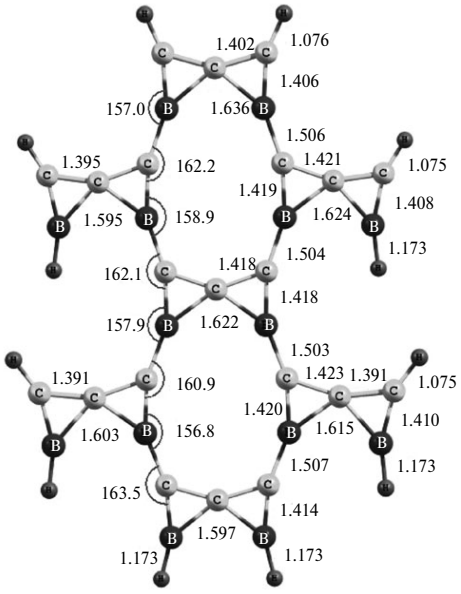
11 **12**

units are linked through single C—B bond each (in the most energetically favorable *trans*-conformation, as in dimer **6** and trimer **9**), whereas two central units are linked through two C—B bonds.[11,12] In tetramer **11**, all C_3B_2 units are *trans*-oriented relative to one another, as in dimer **6**.

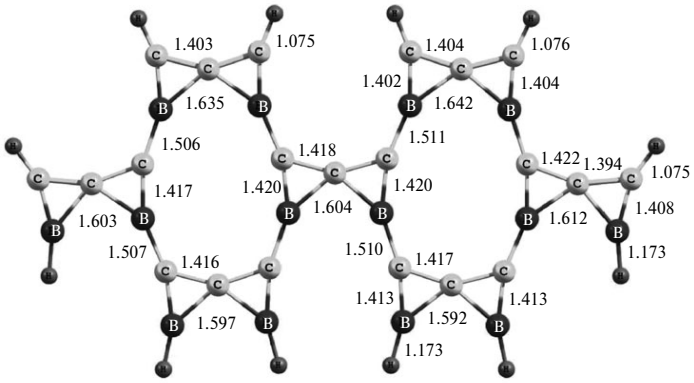
Thus, oligomerization of diboraspiropentadienyl units **1** using the structural pattern **11** is energetically more favorable compared to the structural pattern **12** studied earlier.[11,12] This seems to be due to considerable angular strain in the type-**12** structures which manifests itself when comparing the directions of the outer C—H and B—H bonds in compound **1** (or, *e.g.*, inter-unit C—B bonds in trimer **8**) and inter-unit C—B bonds in the central unit of tetramer **12**. In the monomer unit **1**, the angle between C—H (B—H) bonds is 58.5° (24.2°). The angle between the inter-unit bonds in the central unit of structure **12** is 3.9° (the straight lines converge along the C→B direction), *i.e.*, the directions of the bonds formed by C atoms change by 31.2° on the average (*cf.* 10.2° for the directions of the bonds formed by B atoms).

A similar type of bonding involving some units structurally similar to system **11** was proposed earlier[4] to build up the wall of a boron-carbon nanotube.

The addition of three monomer units **1** to structure **11** results in heptamers **13** or **14** depending on the buildup procedure. The calculated geometric parameters of structures **13** and **14** corresponding to minima on the PES are presented in Fig. 4 and their energy characteristics are listed in Table 1.

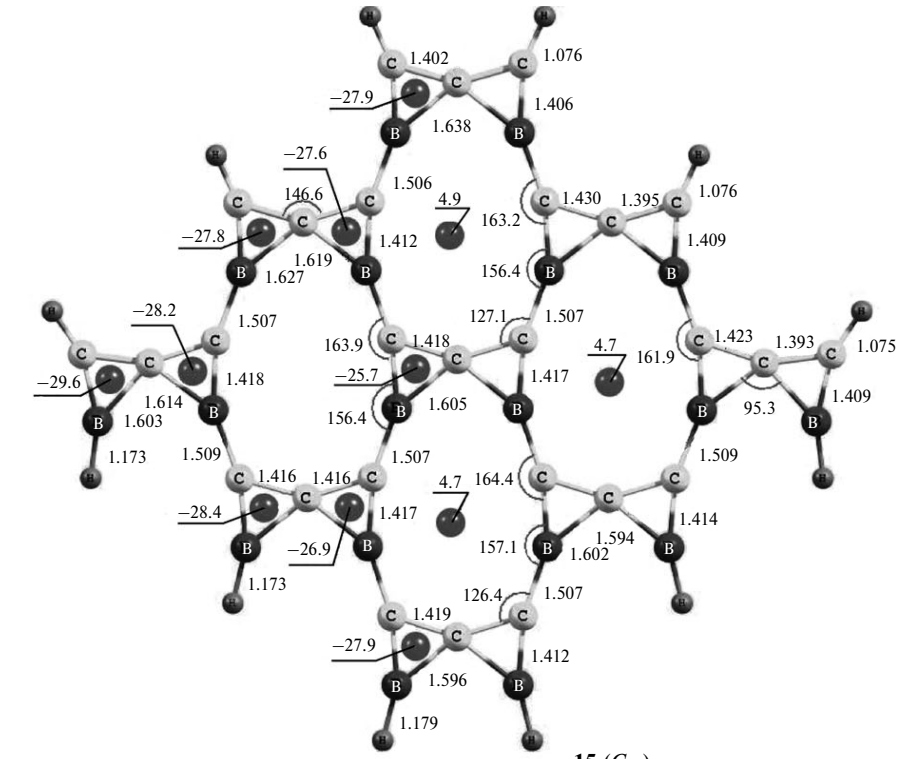


13 (C_s)

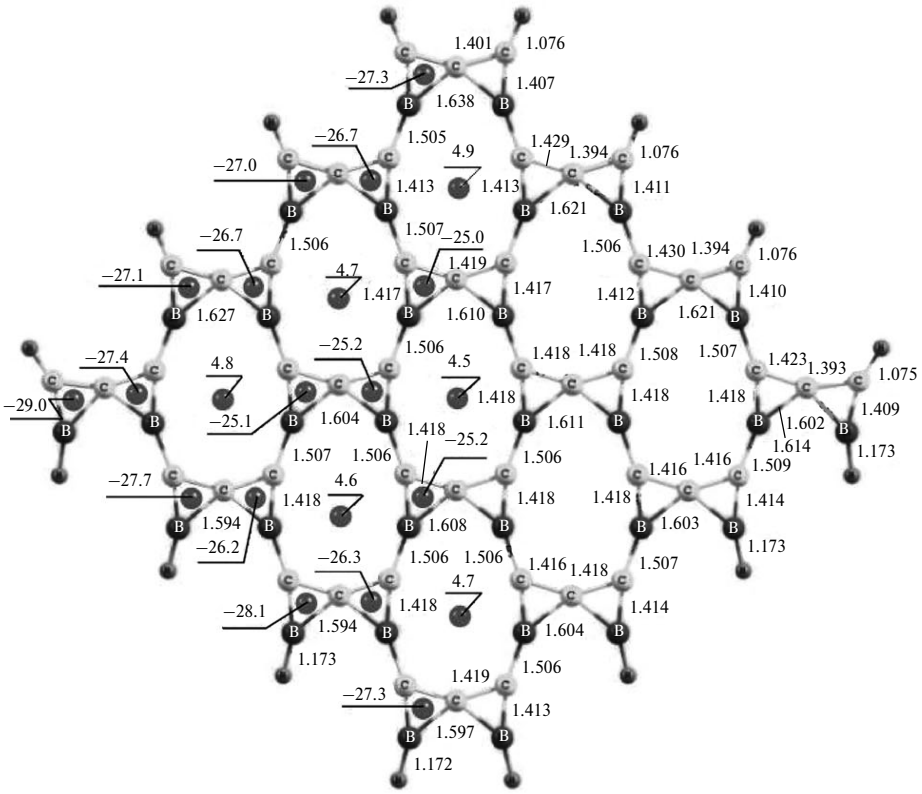


14 (C_{2v})

Fig. 4. Geometric parameters of heptamers **13** and **14** obtained from B3LYP/6-311G(d,p) calculations.



15 (C_{2v})



16 (C_{2v})

Fig. 5. Geometric parameters and NICS values obtained from B3LYP/6-311G(d,p) calculations of structures **15** and **16**.

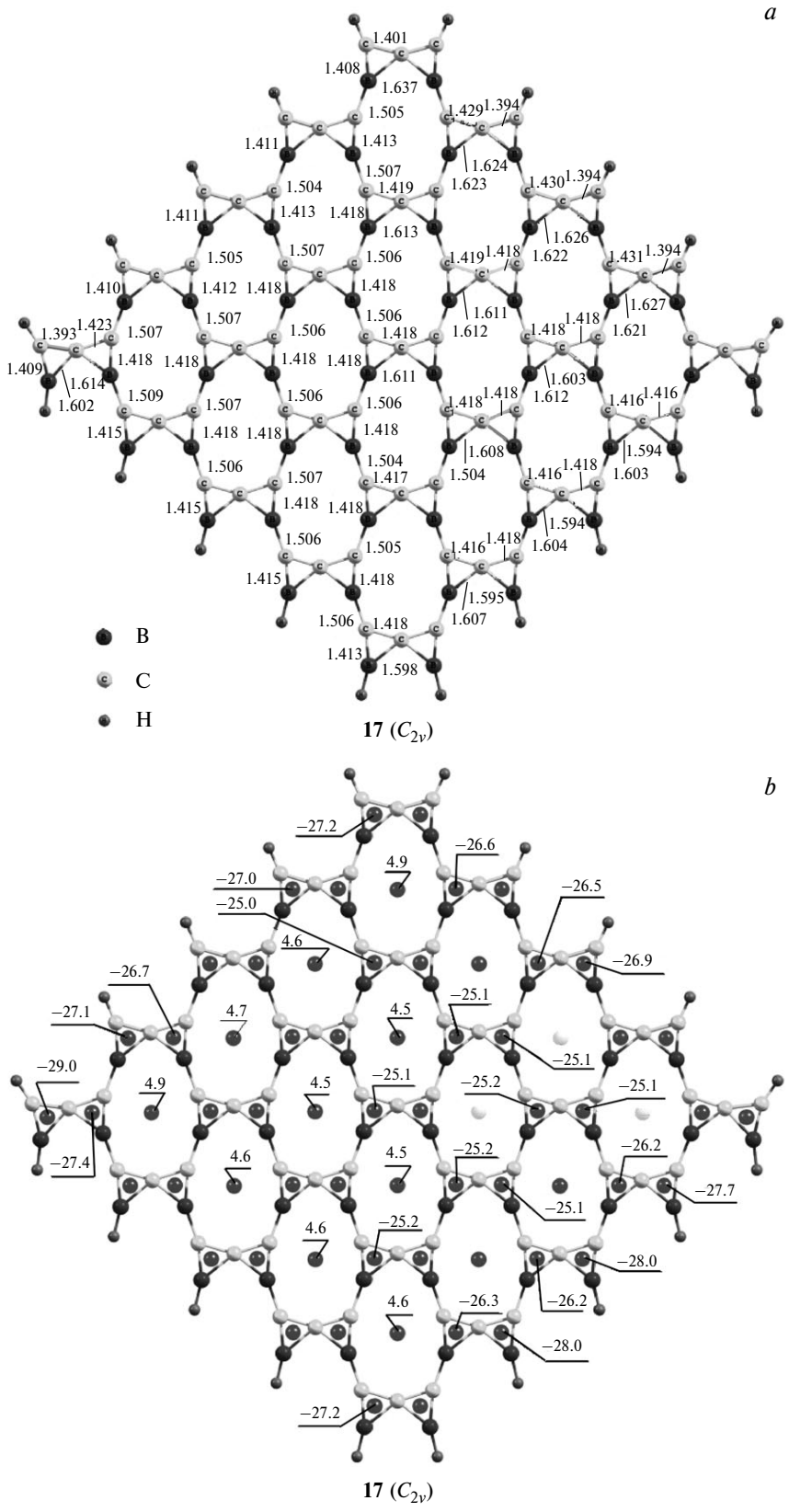


Fig. 6. Geometric parameters (*a*) and NICS values (*b*) obtained from B3LYP/6-311G(d,p) calculations of structure **17**.

Structure **13** is nonplanar, the side diboraspiropentadiene units deviate "up" and "down" from the plane of Fig. 4. The planar structure corresponds to the transition state of inversion of heptamer **13** relative to this plane. The calculated energy barrier to inversion is extremely low (0.01 kcal mol^{-1}).

Structure **14** is planar, *i.e.*, it is more structurally rigid than heptamer **13**. Therefore, it is more stereochemically favorable for assembling higher sterically unstrained oligomers by replacing hydrogen atoms by new monomer units.

This type of replacement results in nonamer **15** (rhombus with an edge length of three monomer units), hexadecamer **16** (rhombus with an edge length of four monomer units), and pentaduodecamer **17** (rhombus with an edge length of five monomer units). The calculated geometric parameters of structures **15**—**17** are presented in Figs 5 and 6 and their energy characteristics are listed in Table 1.

In the series **11**—**15**—**16**—**17**, the 2D sheet being formed retains its planar conformation. Also, individual monomer units, as constituents of oligomers, do not experience significant structural distortions and retain the nonclassical planar configuration of the four bonds formed by the central carbon atom in each unit. The lengths of the bonds within the monomer units and those of the inter-unit bonds vary from 0.006 to 0.048 Å with an increase in the number of the monomer units, the variations being the largest for the peripheral units.

The dipole moments of the oligomers monotonically increase with the size of the system. They are equal to 1.2 (**11**), 5.6 (**15**), 13.4 (**16**), and 24.9 D (**17**). On going from the monomer unit **1** (0.5 D) to tetramer **11** the direction of the dipole moment is reversed (Fig. 7) due to the dominant contribution of the dipole moments of the inter-unit C—B bonds compared to the contributions of the dipole moments of individual monomer units.

As mentioned earlier,[12] the calculated NICS values[23] (see Figs 5, 6, and 8) suggest very high aromaticity of the three-membered rings in the monomer unit **1** and in dimers **2** and **3** (*cf.* −8.0 and −22.8 for the NICS values calculated at the center of the benzene ring and at the center of the ring in the cyclopropenyl cation, respectively). The three-membered rings included in the oligomeric structures retain their aromaticity. As the size of the 2D system increases, the NICS values become increasingly more differentiated, *viz.*, they are higher for the peripheral monomer units (down to −29.6 for nonamer **15**), being lower for the central monomer units (down to −25.0 for structures **16** and **17**). At the same time, the central ten-membered rings formed by four neighboring monomer units in the oligomers **6**, **11**, **15**—**17** are antiaromatic.

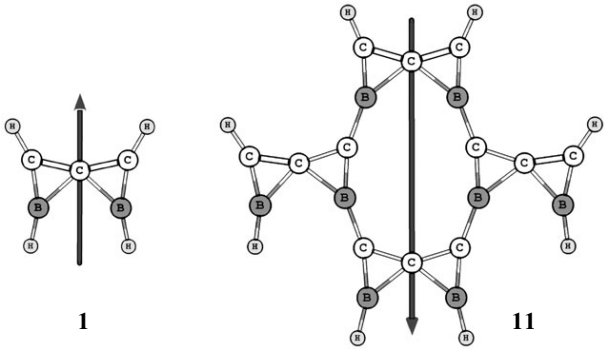


Fig. 7. Directions of the dipole moments of structures **1** and **11**.

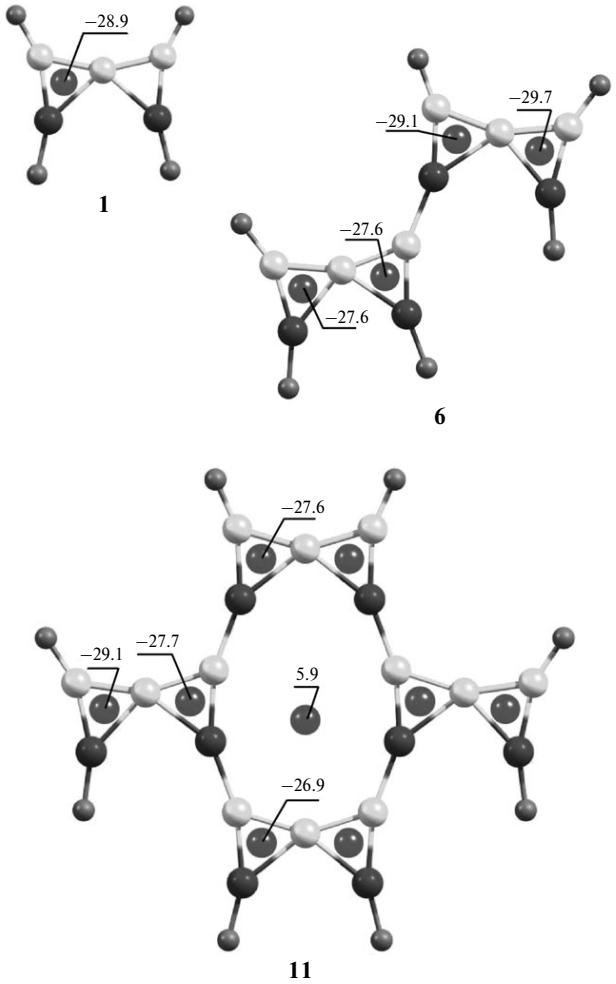


Fig. 8. NICS values calculated for structures **1**, **6**, and **11**.

Summing up, our B3LYP/6-311G(d,p) calculations demonstrated the most energetically favorable method of joining diboraspiropentadiene units which involves the formation of the C—B bond and *trans*-arrangement of monomer units relative to this bond. When constructing a linear chain from the monomer units **1**, structure **9** with vertically arranged chain of monomer units appeared to be the most energetically favorable. The addition of the fourth monomer unit linked to two other blocks through two C—B bonds led to the stereohemically rigid structure **11**, a basic building block for assembling extended 2D poly-

meric structures. Taking isomeric heptamers **13** and **14** as examples, it was shown that more stable extended 2D structures are formed when the oligomer is assembled using the diagonal rather than vertical pattern. The monomer units **1** were used to assemble stable 2D structures comprising 9, 16, and 25 monomer units using the structural pattern of tetramer **11**. In these systems, each monomer unit retains the nonclassical planar configuration of the four bonds formed by the central carbon atom.

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