Russian Chemical Bulletin, International Edition, Vol. 60, No. 8, pp. 1525—1530, August, 2011

Stability and properties of oligomeric organoboron structures with six-coordinate carbon atoms at centers of hydrocarbon frameworks

V. E. Avakyan,* R. M. Minyaev, and V. I. Minkin

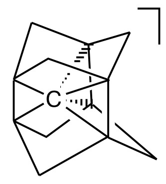
Institute of Physical and Organic Chemistry at Southern Federal University,
194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation.
E-mail: avakyan@ipoc.rsu.ru

Quantum chemical B3LYP/6-311G** calculations revealed that oligomers of a system containing a six-coordinate carbon atom at the center of a carbon framework composed of three 3,6-diboracyclohexa-1,4-diene rings annelated at double bonds remain energetically stable as the number of monomer units increases up to four. All oligomers have triplet ground states, the singlet states lying about 20 kcal mol^{-1} higher in energy. Similar systems with B—B groups replaced by unsaturated (C=C) and saturated (HC—CH) hydrocarbon fragments lose their stability as the length of the oligomer chain increases.

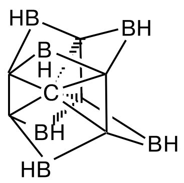
Key words: hypercoordinate carbon, organoboron compounds, quantum chemical calculations, density functional theory (DFT), B3LYP functional, effect of oligomerization on stability, triplet ground state.

Compounds with nonclassically coordinated atoms of main-group elements (*e.g.*, compounds of planar four-coordinate or hypercoordinate carbon) are promising for the design of materials with unusual physical (magnetic and electrical) properties.[1—3] A possible strategy of molecular design of this type of compounds is to annelate the available stable fragments[1—8] with nonclassical planar or six-coordinate center in order to compose oligomers and polymers and thus form extended one-, two-, and three-dimensional structures.[9,10]

Earlier,[7,8] the framework systems **1** and **2** containing a six-coordinate carbon atom at the center of a carbon (**1**) or organoboron (**2**) framework were studied. When composing an oligomeric system using **1** as building blocks, accumulation of positive charge involves considerable intramolecular electrostatic repulsions, which leads to destabilization of the multiply charged ion. Electrical neutrality of molecule **2** (an isoelectronic analog of system **1**) allows one to reduce intramolecular electrostatic repulsions and to design stable extended electrically neutral systems based on **2**.

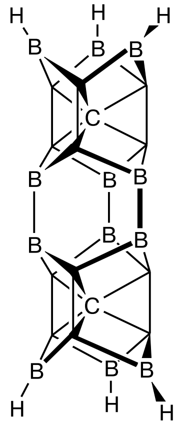


1

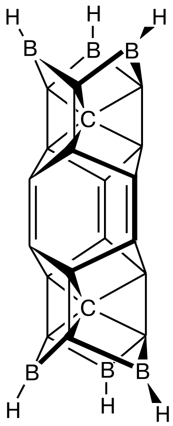


2

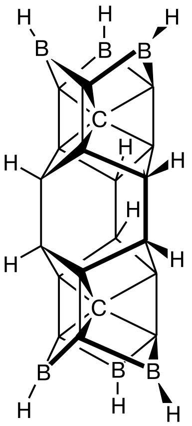
Dimer **3** comprised of type-**2** blocks as well as dimers **4** and **5** built of mixed blocks with B—B bridging groups replaced by C=C and HC— CH groups, respectively, are highly symmetric stable structures.[9] For these systems, reactions of extrusion of endohedral carbon atoms are highly endothermic.



3



4



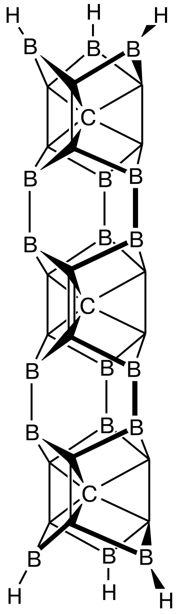
5

In this work, within the framework of the density functional theory (DFT), we studied the geometries, electronic structures, and stabilities of novel systems including trimers **6**—**8** and tetramers **9**—**11** built of monomers **2** and **1**, respectively.

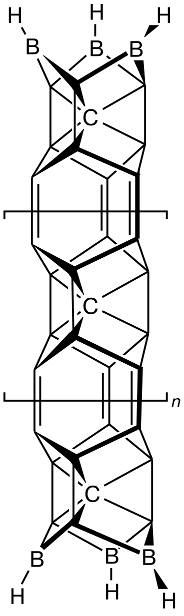
Calculation Procedure

Quantum chemical calculations were carried out within the framework of DFT with the B3LYP three-parameter functional[11—13] and the 6-311G(d,p) split-valence basis set[14,15] us-

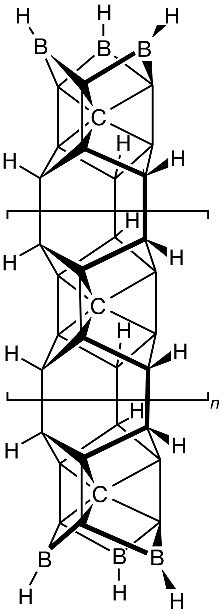
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1501—1506, August, 2011.



6, 9

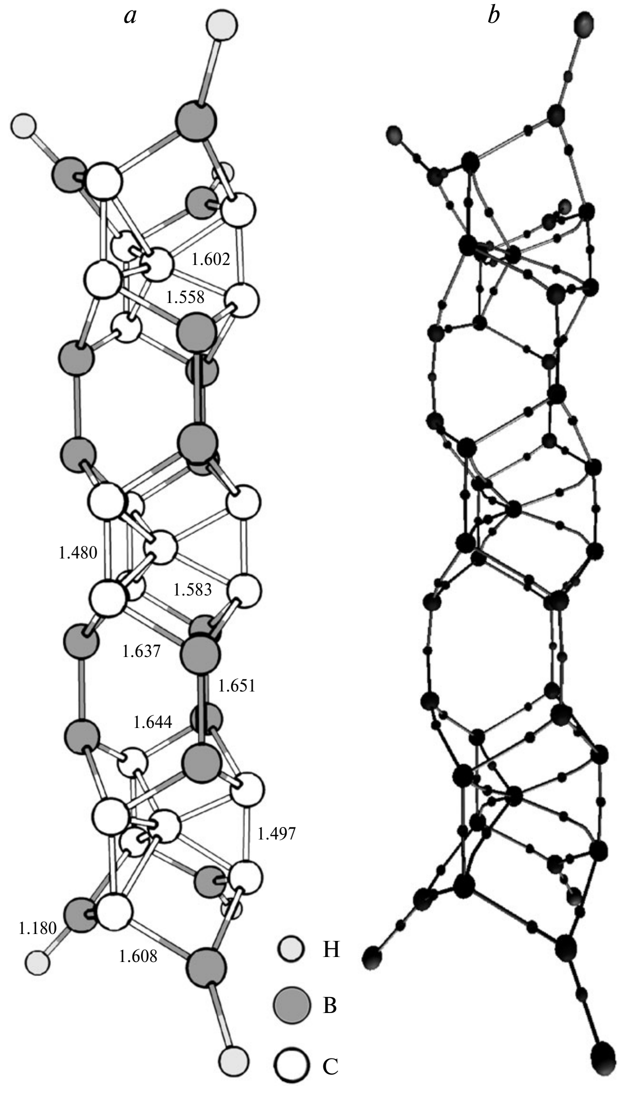


7, 10



8, 11

n = 1 (**6—8**), 2 (**9—11**)



6, D_{3h}

Fig. 1. Geometric parameters of the triplet state of structure **6** obtained from B3LYP/6-311G** calculations (*a*) and the molecular graph of this structure (*b*) according to the results of AIM analysis. In Figs 1—6, the bond lengths and some interatomic distances are given in Ångstrøms. Here and in Figs 3—5, lines connecting atoms denote the bond paths and circles in these lines denote the bond critical points.

ing the Gaussian-03 program.[16] Numerical integration was performed on a higher density grid (key word Integral, Grid=UltraFine). Geometric parameters were optimized in the "tight" mode.

All wave functions are stable at stationary points. The stationary points were identified analytically by calculating the force constant matrix; the number of imaginary vibrational frequencies is denoted by the Greek letter λ.

Topological analysis of the total electron density distribution (AIM analysis)[17] was carried out using the AIMPAC software.[18] Graphical images of molecular structures were obtained using the ChemCraft software for which the Cartesian atomic coordinates determined from geometry optimization served as input parameters.

Results and Discussion

According to calculations, structure **6** is highly symmetric (D_{3h}) and has a triplet ground state; the geometric parameters of this system are shown in Fig. 1. From the results of AIM analysis it follows that carbon atoms at the centers of frameworks are connected to peripheral carbon atoms by bond paths; this suggests that the central atoms are six-coordinate. Small negative values of the Laplacian at bond critical points (from −0.178 to −0.113 au; *cf.* −0.532 au for the Laplacian at the critical point of the single C—C bond in ethane molecule) indicate a covalent character of these bonds. Small Laplacian values can be due to essential multicenter (and, hence, electron-deficient) character of these bonds.

The energy minimum on the singlet-state potential energy surface (PES) is 19.5 kcal mol^{-1} higher than on the PES of the triplet ground state. The structure corresponding to the singlet-state minimum also has a D_{3h} symmetry; its geometric parameters are rather close to the parameters of the ground electronic state of trimer **6** (bond lengths and bond angles differ by at most 0.05 Å and 0.6°, respectively).

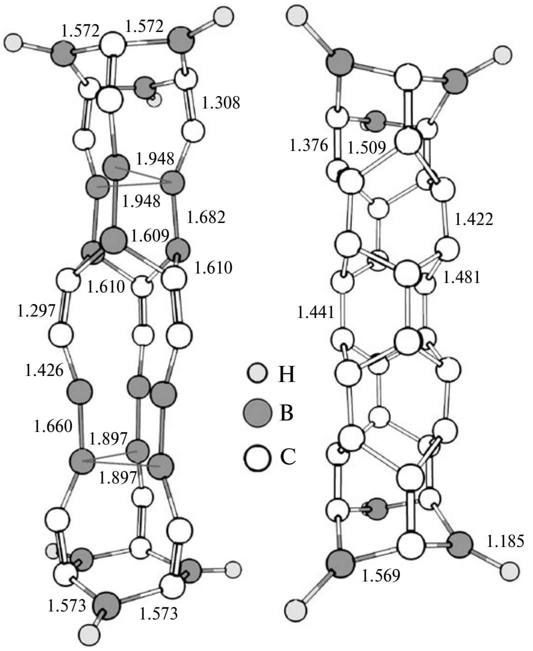
The next energy minimum corresponds to a quintet electronic state of system **6**. Its energy is 10.0 kcal mol^{-1} higher than that of the singlet state. The corresponding structure has a reduced symmetry C_1.

Structure **12** differs from trimer **6** in the lack of central six-coordinate carbon atoms at the centers of frameworks (Fig. 2). This is a classical Lewis structure, although highly strained; *viz.*, the C—B bonds at the sp^2-hybridized carbon atoms are highly pyramidalized (the sum of the bond angles at these atoms is by 23—30° smaller than 360°) while the bonds at the sp-hybridized carbon atoms are bent compared to the bonds in allene $H_2C=C=CH_2$ (bending angle ranges from 26° to 33°). Removal of the six-coordinate atoms from the centers of the frameworks is a highly endothermic process, which points to a higher stability of system **6** with nonclassical coordination compared to the classical Lewis system **12**.

$$\mathbf{6} \longrightarrow \mathbf{12} + 3\ \mathrm{C}\ (-106.4\ \mathrm{kcal\ mol^{-1}}) \tag{1}$$

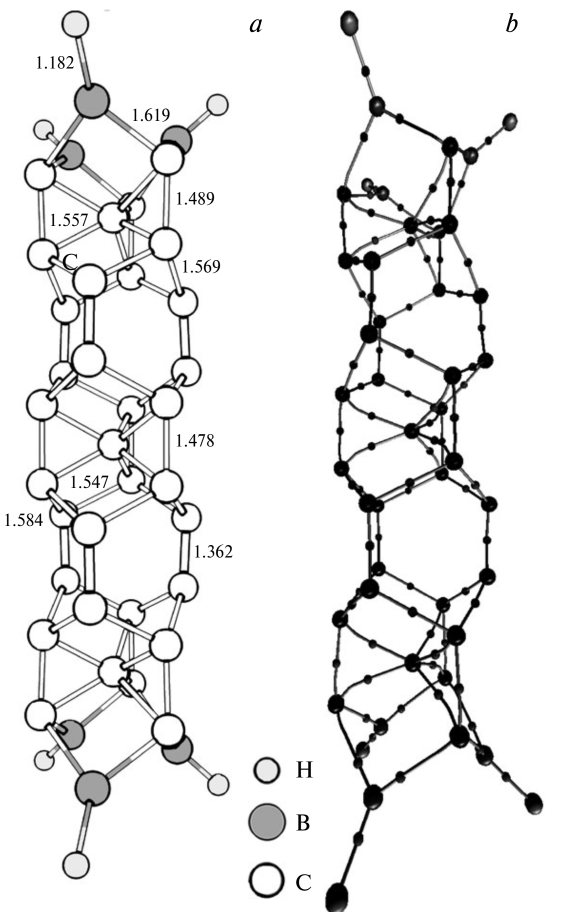
Structure **7** also has a D_{3h} symmetry and a singlet rather than triplet ground electronic state. This is in contrast with trimer **6**. The calculated geometric parameters of system **7** are shown in Fig. 3. The PES minimum of the triplet state of structure **7** is 12.8 kcal mol^{-1} higher in energy than that of the singlet state. The symmetry of the triplet state of system **7** is reduced to C_{2v}.

The reaction of extrusion of endohedral atoms from the centers of the corresponding frameworks is analogous to reaction (1) considered above. This reaction is also endothermic and results in structure **13** whose geometric parameters are shown in Fig. 2, but the thermal effect of the reaction is much lower in absolute value. This suggests a lower stabilization energy of trimer **7** compared to trimer **6**.



12, C_1 **13**, D_{3h}

Fig. 2. Geometric parameters of structures **12** and **13** containing no endohedral carbon atoms and corresponding to minima on corresponding PES obtained from B3LYP/6-311G** calculations.



7, D_{3h}

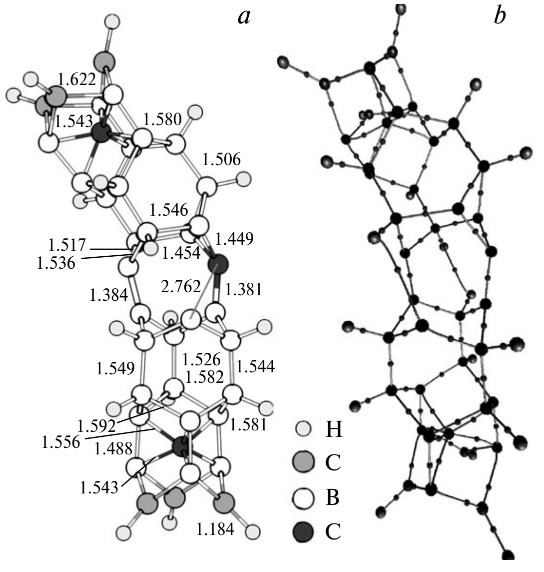
Fig. 3. Geometric parameters of structure **7** obtained from B3LYP/6-311G** calculations (*a*) and the molecular graph of this structure (*b*) according to the results of AIM analysis.

$$\mathbf{7} \longrightarrow \mathbf{13} + 3\ \mathrm{C}\ (-22.8\ \mathrm{kcal\ mol^{-1}}) \tag{2}$$

According to calculations, structure **8** with D_{3h} symmetry is unstable ($\lambda = 4$ for the corresponding stationary point on the singlet-state PES) while structure **8´** derived from system **8** and corresponding to an energy minimum has a C_1 symmetry with one endohedral atom escaped from the cage on the outer face (Fig. 4).

According to AIM analysis, endohedral carbon atoms in the outermost monomeric blocks of the distorted structure **8´** are six-coordinate, but the central carbon atom is tricoordinate (calculated bond paths are shown in Fig. 4). Transition **8** → **8´** accompanied by symmetry violation and escape of the central six-coordinate carbon atom from the cage leads to significant stabilization of the structure (by 203.7 kcal mol^{-1}).

The addition of yet another block **2** to structure **6** leads to tetrameric system **9** (Fig. 5). According to calculations,



8´, C_1

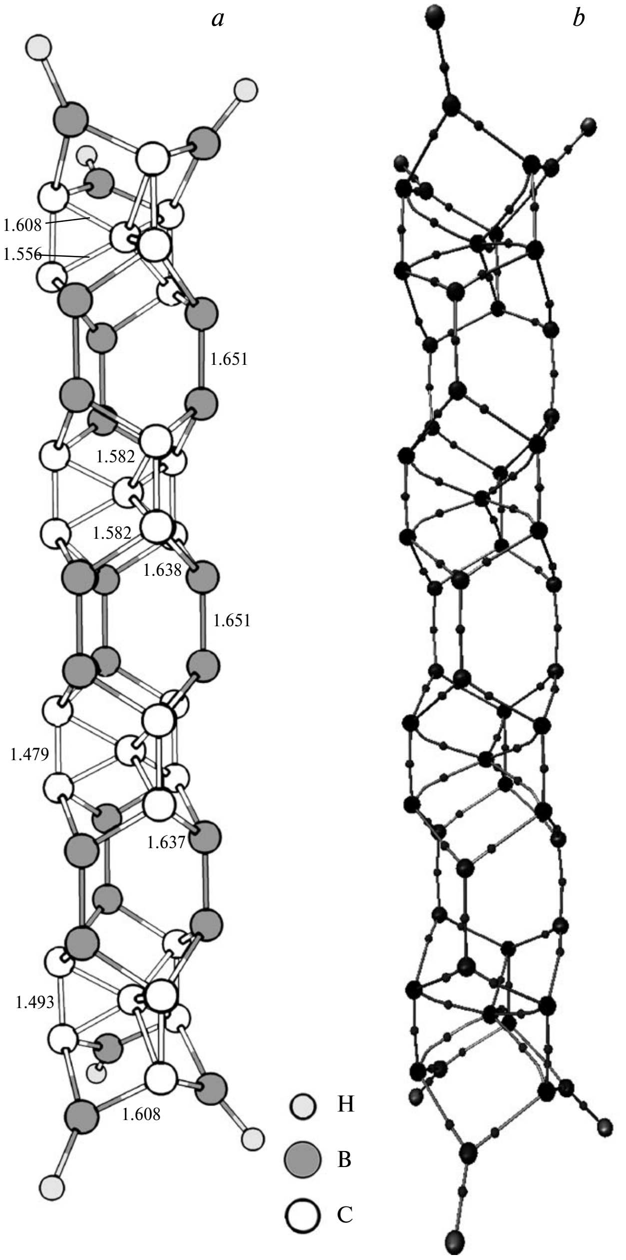
Fig. 4. Geometric parameters of structure **8**´ obtained from B3LYP/6-311G** calculations (*a*) and the molecular graph of this structure (*b*) according to the results of AIM analysis.

tetramer **9** with D_{3h} symmetry corresponds to an energy minimum. As for the dimer **3** (see Ref. 9) and trimer **6**, the triplet state of system **9** is 20.2 kcal mol^{-1} lower in energy than the singlet state. The structure corresponding to a minimum on the singlet-state PES also has a D_{3h} symmetry and its geometric parameters are close to the corresponding parameters of the triplet-state structure (bond lengths and bond angles differ by at most 0.006 Å and 0.9°, respectively).

The structure corresponding to the energy minimum of the next quintet state of system **9** lies 17.6 kcal mol^{-1} higher than the singlet-state minimum on the energy scale and has a reduced symmetry C_{2v}.

Tetramer **10** with C=C bridging groups has a singlet ground state and the structure with C_s symmetry where one six-coordinate central carbon atom becomes five-coordinate (structure **14**, Fig. 6). Structure **10** with D_{3h} symmetry (see Fig. 6) also corresponds to a minimum on the singlet-state PES but lies 19.5 kcal mol^{-1} higher on the energy scale. The two structures are separated by an energy barrier of 0.4 kcal mol^{-1} with respect to the highly symmetric structure **10**, *i.e.*, the transition **10** → **14** is almost barrierless. Thus, the trend of the system with C=C bridges to reduce the number of the six-coordinate central atoms will preclude the formation of stable extended linear polymers containing six-coordinate carbon atoms in each framework at $n > 2$.

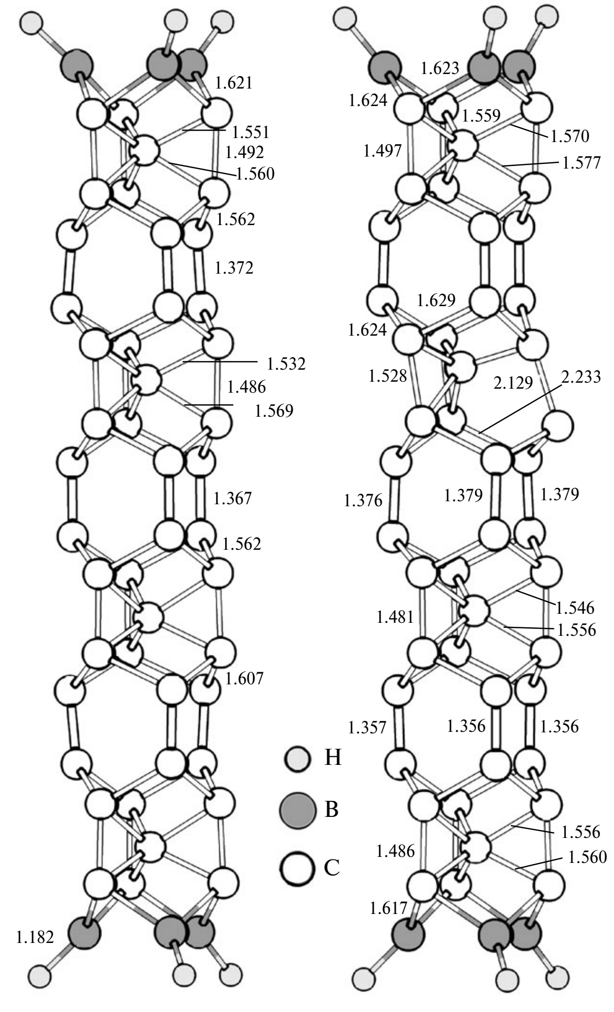
Our AIM analysis showed that all central carbon atoms in structure **10** are six-coordinate. In system **14**, one central carbon atom located in the distorted monomeric block is five-coordinate, which agrees with the expected bond length distribution suggested from the numerical values of interatomic distances.



9, D_{3h}

Fig. 5. Geometric parameters of structure **9** obtained from B3LYP/6-311G** calculations (*a*) and the molecular graph of this structure (*b*) according to the results of AIM analysis.

When calculating tetramer **11** with saturated hydrocarbon bridges HC—CH, we failed to locate the structure with six-coordinate central carbon atoms corresponding to an energy minimum on the singlet- or triplet-state PES. Highly symmetric structure **11** (D_{3h}) corresponds to a hill on the PES (λ = 8). A descent from this point along the vectors with imaginary frequencies leads to a number of



10, D_{3h} **14**, C_s

Fig. 6. Geometric parameters of structures **10** and **14** obtained from B3LYP/6-311G** calculations.

structures with reduced symmetry. They are still characterized by a few imaginary frequencies, have broken frameworks in two inner monomer units, and the central carbon atoms in them are no longer six-coordinate. Based on this fact, we suggested no formation of the desired structure of extended linear oligomer similar to, *e.g.*, structure **9** and stopped the search for an energy minimum.

The thermodynamic stabilities of structures **6—9** containing six-coordinate carbon atoms were evaluated by comparing their total energies with the sums of the total energies of structures **12—14** and those of the corresponding number of carbon atoms according to reactions (1) and (2). The calculated values and similar results obtained for structures **3—5** (shown for comparison, see Ref. 9) are listed in Table 1.

Among the systems with B—B bridges (**3**, **6**, **9**), the stabilities of the structures with six-coordinate C atoms calculated per carbon atom differ only slightly. The stabilities of the compounds with C=C (**4**, **7**, **10**) and HC—CH (**5**, **8**, **11**) bridges significantly decrease on going from the dimer to trimer; highly symmetric tetramers with six-coordinate central atoms are unstable (see above).

Table 1. Total (ΔE_{tot}/kcal mol^{-1}) and specific (ΔE_{sp}/kcal mol^{-1}) energy effects of fragmentation reactions (1) and (2) and similar reactions reported earlier[9]

Structure	B—B (bridge)		C=C (bridge)		HC—CH (bridge)	
	ΔE_{tot}	ΔE_{sp}	ΔE_{tot}	ΔE_{sp}	ΔE_{tot}	ΔE_{sp}
Dimer	71.5 (64.4)	35.8	56.7 (52.5)	28.4	82.0 (77.2)	41.0
Trimer	106.4	35.4	22.8	7.6	54.9	18.3
Tetramer	152.2	38.0	—	—	—	—

Note. The specific effect is the total energy effect divided by the number of six-coordinate C atoms removed from the centers of frameworks during the reaction.

Summing up, monomer **2** can serve as a basis building block for composing stable extended structures containing rows of six-coordinate carbon atoms, but corresponding systems with C=C and HC—CH bridging bonds are inappropriate for these purposes.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 10-03-00332), the Ministry of Education and Science of the Russian Federation (Grant RNP.2.2.1.1.2348), and the U.S. Civilian Research and Development Foundation (Grant RUC1-2889-RO-07).

References

1. R. Keese, *Chem. Rev.*, 2006, **106**, 4787.
2. L.-M. Yang, Y.-H. Ding, C.-C. Sun, *J. Am. Chem. Soc.*, 2007, **129**, 1900.
3. P. M. Esteves, N. B. P. Ferreira, R. J. Corrêa, *J. Am. Chem. Soc.*, 2005, **127**, 8680.
4. K. Ito, Zh. Chen, C. Corminboeuf, Ch. S. Wannere, X. H. Zhang, Q. Sh. Li, P. v. R. Schleyer, *J. Am. Chem. Soc.*, 2007, **129**, 1510.
5. Y.-B. Wu, H.-G. Lu, S.-D. Li, Zh.-X. Wang, *J. Phys. Chem. A*, 2009, **113**, 3395.
6. V. I. Minkin, R. M. Minyaev, R. Hoffmann, *Usp. Khim.*, 2002, **71**, 989 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2002, **71**].
7. R. M. Minyaev, T. N. Gribanova, V. I. Minkin, *Dokl. Akad. Nauk*, 2004, **396**, 628 [*Dokl. Chem.* (*Engl. Transl.*), 2004, **396**].
8. V. I. Minkin, R. M. Minyaev, *Mendeleev Commun.*, 2004, **14**, 43.
9. R. M. Minyaev, A. G. Starikov, V. E. Avakyan, V. I. Minkin, *Dokl. Akad. Nauk*, 2007, **416**, 486 [*Dokl. Chem.* (*Engl. Transl.*), 2007, **416**].
10. P. D. Pancharatna, M. A. Méndez-Rojas, G. Merino, A. Vela, R. Hoffmann, *J. Am. Chem. Soc.*, 2004, **126**, 15309.

11. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
12. B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.
13. P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
14. R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.
15. A. D. McLean, G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639.
16. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, *Revision E.01*, Gaussian, Inc., Wallingford, CT, 2004.
17. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, 1990.
18. J. R. Cheeseman, T. A. Keith, R. F. W. Bader, *AIMPAC Program Package*, McMaster University, Hamilton, Ontario (Canada), 1992.

Received June 28, 2010