Russian Chemical Bulletin, International Edition, Vol. 53, No. 9, pp. 1889—1893, September, 2004

Full Articles

Oligomers of $C_{20}H_8$ polyhedral molecule: a computer simulation

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DFT-PBE/DZ calculations of oligomers of $C_{20}H_8$ polyhedral molecule (derivative of C_{20} fullerene) were carried out. From the results obtained it follows that quasi-one-dimensional, quasi-two-dimensional, and three-dimensional polymers with compositions $[C_{20}H_8]_n$ can exist. The geometric parameters of the repeating units of these polymers were estimated.

Keywords: polyhedral molecules, C_{20} fullerene and its derivative $C_{20}H_8$, quantum-chemical calculations, density functional theory, DFT-PBE method.

The smallest fullerene, a polyhedral cluster C_{20} (**1**), was synthesized only recently,[1] whereas its derivatives (hydrocarbon molecules $C_{20}H_{20}$ and $C_{20}H_{18}Me_2$ with dodecahedral carbon skeletons[2,3]) were obtained long before the discovery of fullerenes. The C_{20} molecule has a highly strained structure, being therefore a highly reactive species. It was theoretically proved that a crystalline form of carbon (CFC) with a simple cubic lattice (**CFC-1**) built of covalently bound C_{20} fullerenes (see Ref. 4) and more dense orthorhombic and tetragonal phases (**CFC-2** and **CFC-3**, respectively)[5] can exist.

In all the known polymeric forms of fullerenes the repeating units (monomers) are linked to one another by four-membered rings that form as a result of [2+2]-cycloaddition to two double bonds of the reactant molecules. In C_{60} fullerene, there are six appropriate bonds with the midpoints located at the vertices of an octahedron. Because of this, the C_{60} molecules can form quasi-one-dimensional, quasi-two-dimensional, and three-dimensional structures (in particular, structures with simple cubic lattice).

Formally, dodecahedral molecule **1** also contains a group of six carbon—carbon bonds with the midpoints located at vertices of an octahedron (atoms involved in these bonds are shown by light circles in Fig. 1). Therefore, similarly to the C_{60} molecule, fullerene **1** can also be used to design quasi-one-dimensional, quasi-two-dimensional, and three-dimensional structures in which two clusters are connected through four-membered rings. Steric strain in the structure of cluster **1** can be relieved by attaching certain atoms or monovalent functional groups to the atoms located at the vertices of a cube (dark circles in Fig. 1). To date, various derivatives of fullerene **1** have been obtained, including η^2-complexes with transition

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1813—1817, September, 2004.

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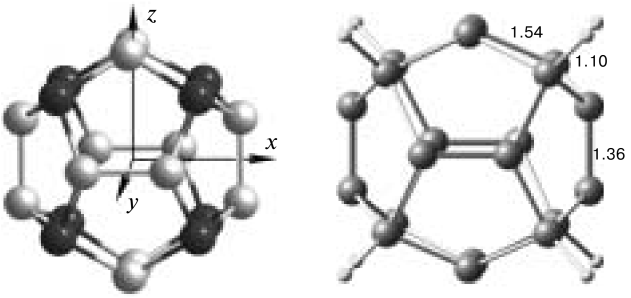


1 **2**

Fig. 1. Structure of C_{20} fullerene (**1**). The atoms located at the vertices of a cube are shown as dark circles. Carbon—carbon bonds that can be involved in [2+2]-cycloaddition of identical fullerenes are parallel to the faces of the cube. The coordinate axes pass from the center of the cube through the midpoints of the bonds mentioned above. Structure of molecule $C_{20}H_8$ (**2**) with T_h symmetry. Here and in Figs 2—7 the bond lengths are given in Å.

metals.[2,3,6] The synthesis of T_h-$C_{20}R_8$ molecules containing monovalent functional groups R attached to the atoms of fullerene **1** occupying the vertices of a cube also seems not to be unlikely.

Calculations of a $C_{20}R_8$ (R = Me) molecule thus designed revealed[7] a rather high stability of the species and a closed electron shell in the ground state. A procedure for generation of a hypothetical carbon allotrope $(C_{28})_n$ based on these molecules was also proposed.[7]

In this work we report on a study of oligomers of $C_{20}H_8$ polyhedral molecule (**2**, Fig. 1) with different spatial structures and discuss their molecular structures and stabilities. The geometric parameters of the repeating units of possible quasi-one-dimensional, quasi-two-dimensional, and three-dimensional polymers based on molecules **2** were also evaluated

Calculation Procedure

Density functional calculations of local energy minima on the potential energy surfaces of the clusters under study were carried out with full geometry optimization using the Perdew—Burke—Ernzerhof exchange-correlation potential (DFT-PBE),[8] the double-zeta (DZ) basis set, and the PRIRODA program.[9] Molecular geometry optimizations were performed with the BFGS algorithm.[10] The total energies were also estimated with inclusion of zero-point vibrational energies (ZPVE). The character of the stationary points located was checked by analyzing the spectrum of the Hessian matrix.

Results and Discussion

Molecule $C_{20}H_8$ (2). According to calculations, molecule **2** has a singlet ground state and T_h symmetry. All carbon atoms in the molecule can be divided into the atoms bonded to hydrogens and the atoms participating in the double bonds. There are also two types of carbon—carbon bonds in molecule **2**, namely, ordinary C—C(H) bonds 1.543 Å long and double bonds 1.360 Å long (this is much shorter than the corresponding carbon—carbon bonds in fullerene **1**).

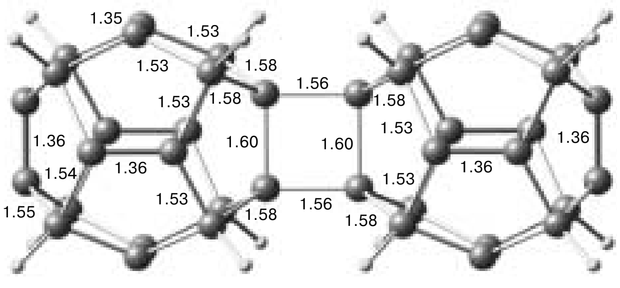


Fig. 2. Structure of dimer $(C_{20}H_8)_2$ (**3**) with D_{2h} symmetry.

The triplet state energy of molecule **2** is 54.1 kcal mol^{-1} higher than the singlet state energy. In the triplet molecule one double carbon—carbon bond becomes an ordinary bond 1.578 Å long (*cf.* 1.36 Å for the remaining double bonds). Each atom of this bond bears a spin density of 0.75 a.u., which must favor dimerization of molecule **2**.

Oligomers. The oligomers studied were $(C_{20}H_8)_2$ (**3**), $(C_{20}H_8)_3$ (**4**), $(C_{20}H_8)_5$ (**5**), $(C_{20}H_8)_7$ (**6**), and $(C_{20}H_8)_8$ (**7**). Their structures are shown in Figs. 2—6 and the main energy characteristics are listed in Table 1. According to calculations, oligomers **3—7** have singlet ground states with D_{2h} symmetry. In structures **3—7**, the repeating units are linked by four-membered rings that are formed as a result of [2+2]-cycloaddition to two double bonds of adjacent fullerene molecules. As a consequence, these bond lengths increase appreciably, being at the same time no greater than 1.61 Å (see Figs. 2—6); the Mulliken

Table 1. DFT-PBE/DZ calculated energy characteristics of oligomers of $C_{20}H_8$ molecule (E_t are the total energies, E^0_t are the total energies with inclusion of zero-point vibrational energy, ZPVE is the zero-point vibrational energy, ν_0 is the minimum frequency, and ΔE is the energy of the fullerene—fullerene bond)

Molecule, cluster	$-E_t$	$-E^0_t$	ν_0 /cm^{-1}	ZPVE	ΔE	E^0
	a.u.			kcal mol^{-1}		
C_{20} (**1**)	760.8795	760.7682	141	69.9	—	—
$C_{20}H_8$ (**2**)	765.7262	765.5176	465	131.0	—	—
$(C_{20}H_8)_2$ (**3**)	1531.5937	1531.1730	62	264.0	88.7	86.5
$(C_{20}H_8)_3$ (**4**)	2297.4611	2296.8289	38	396.7	88.6	86.6
$(C_{20}H_8)_5$ (**5**)	3829.1893	3828.1323	38	663.2	87.6	85.4
$(C_{20}H_8)_7$ (**6**)	5360.8920	5359.4105	34	939.6	84.6	82.3
$(C_{20}H_8)_8$ (**7**)	6127.4326	6125.7195	85	1075.0	84.9	82.6

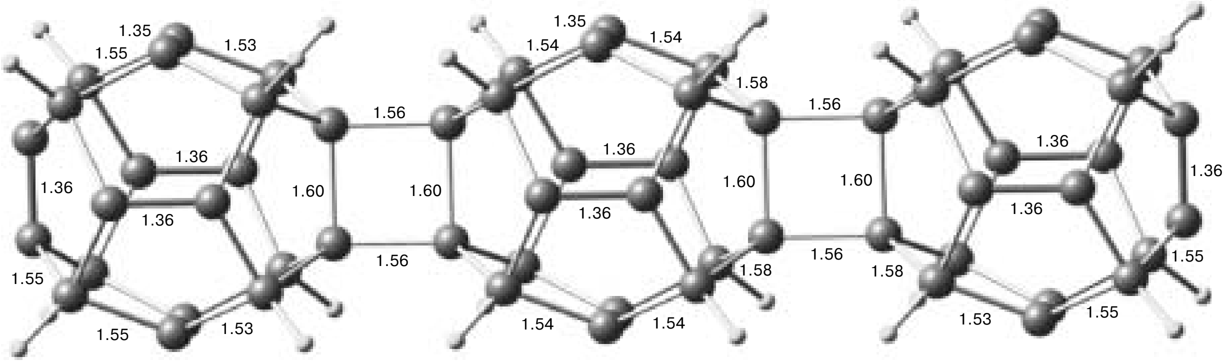


Fig. 3. Structure of linear trimer $(C_{20}H_8)_3$ (**4**) with D_{2h} symmetry.

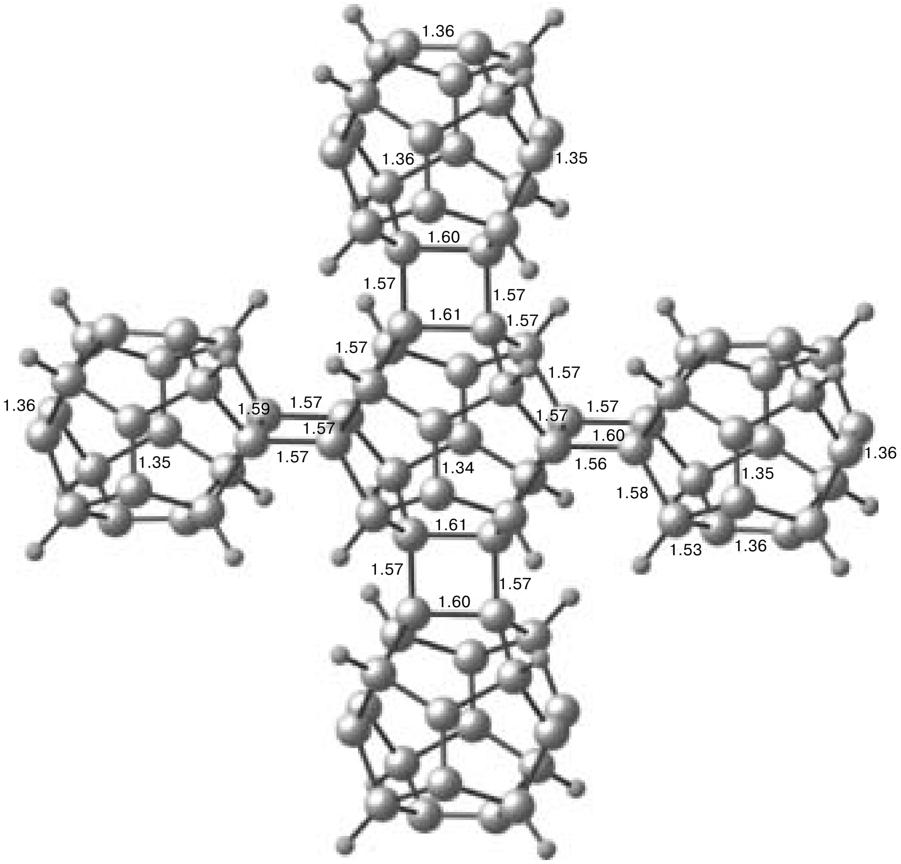


Fig. 4. Structure of pentamer $(C_{20}H_8)_5$ (**5**) with D_{2h} symmetry.

bond orders exceed 0.88 a.u. The bonds connecting the repeating units are 1.56—1.57 Å long in oligomers **3—6** and 1.59 Å long in molecule **7**. The average energies, ΔE and ΔE^0, of the C_{20}—C_{20} bonds were calculated as follows

$$\Delta E = [NE_t(1) - E_t(N)]/n, \Delta E^0 = [NE^0{}_t(1) - E^0{}_t(N)]/n,$$

where $E_t(N)$ is the total energy of the oligomer molecule comprised of N repeating units, n is the number of bonds between the repeating units, and the superscript "0" means that the energy was calculated with inclusion of zero-point vibrational energy (see Table 1). The fact that ΔE and ΔE^0 decrease only slightly with increasing N suggests the possibility for structures comprised of a rather large number of repeating units to exist. The inclusion of zero-point vibrational energies reduces the energies of the fullerene—fullerene bonds insignificantly; all the vibrational frequencies obtained from our calculations were real (see Table 1).

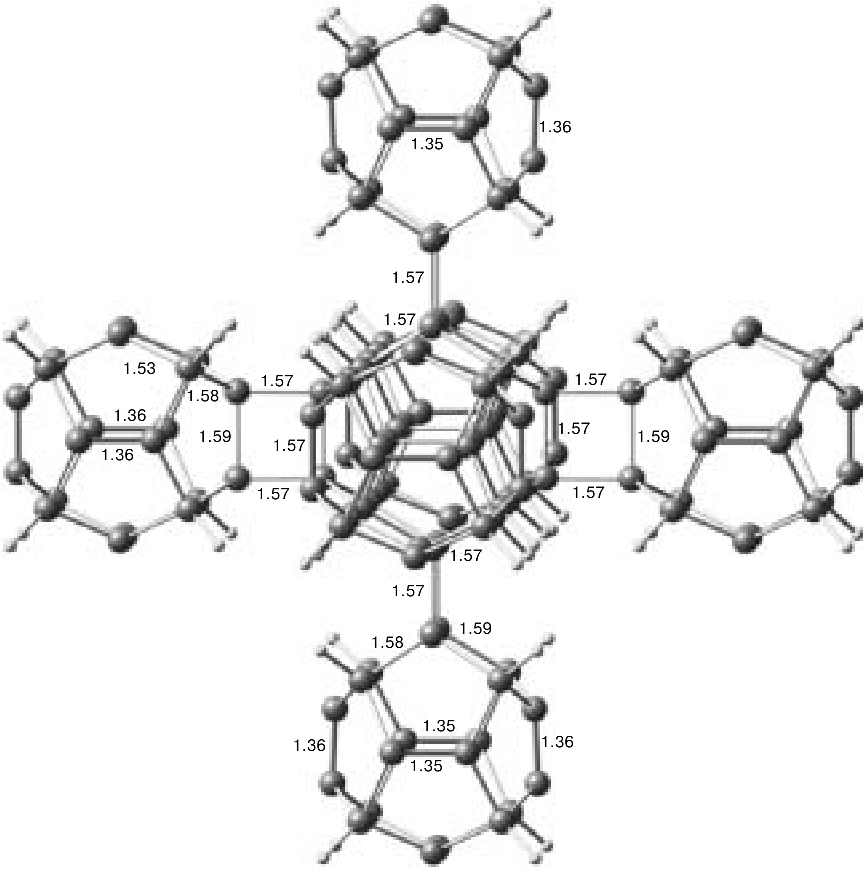


Fig. 5. Structure of oligomer $(C_{20}H_8)_7$ (**6**) with D_{2h} symmetry.

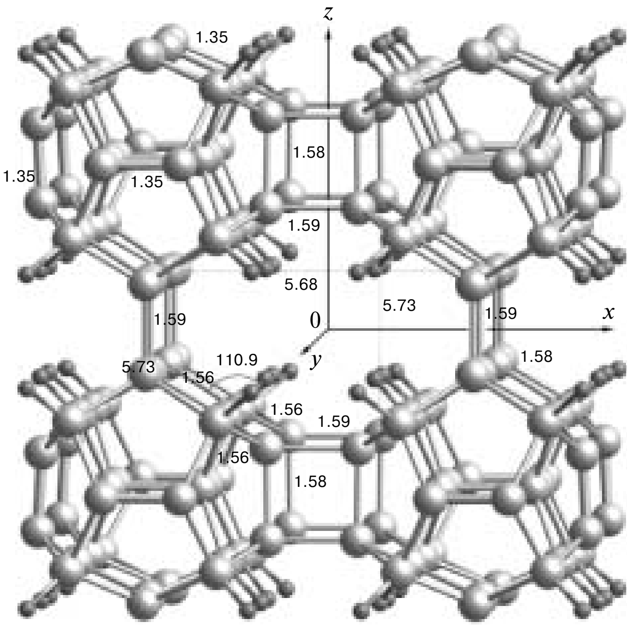
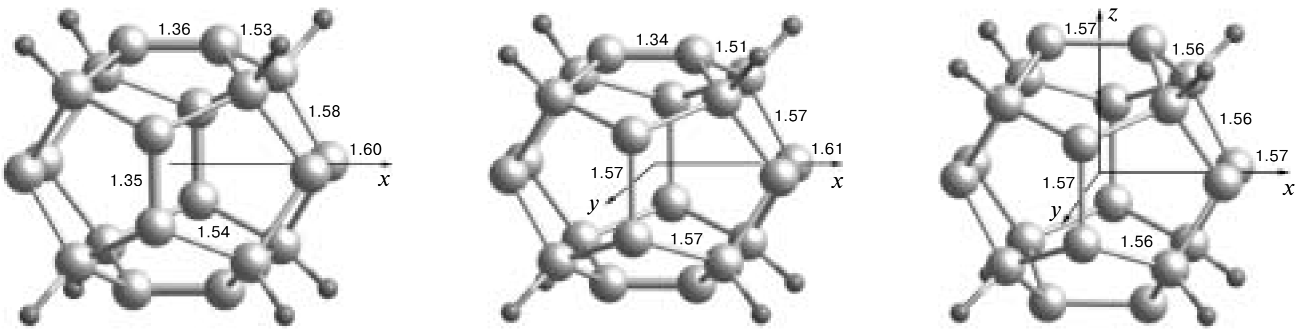


Fig. 6. Structure of oligomer $(C_{20}H_8)_8$ (**7**) with D_{2h} symmetry.

Dimer **3** and linear trimer **4** have a D_{2h} symmetry. Double carbon—carbon bonds in these systems must favor structure buildup in different directions upon successive attachment of the repeating units. This can lead to linear, two-dimensional, or three-dimensional polymerization. We estimated the energies of [2+2]-cycloaddition of the $C_{20}H_8$ repeating unit to linear oligomers $(C_{20}H_8)_3$ and $(C_{20}H_8)_4$. At $n = 3$ and 4, the reactions

$$(C_{20}H_8)_n + C_{20}H_8 \to (C_{20}H_8)_{n+1}$$

are exothermic; each of them is accompanied by a heat release of 88.7 kcal mol^{-1}, which is virtually equal to the corresponding energy for $n = 2$ (88.6 kcal mol^{-1}). The results obtained suggest the possibility of formation of linear polymers. It is appropriate to consider the central parts of trimer **4** (Fig. 7), pentamer **5**, and oligomer **6** as models for the repeating units of a quasi-one-dimensional polymer $(C_{20}H_8)_n$ (**8**), quasi-two-dimensional polymer $(C_{20}H_8)_n$ (**9**), and three-dimensional crystal $(C_{20}H_8)_n$ (**10**), respectively. According to calculations of the structure **6** comprised of seven repeating units, the inner fragment surrounded by six repeating units has a cubic symmetry. Analogously, a free monomer also has the cubic symmetry. Therefore, it is reasonable to assume that successive attachment of repeating units to oligomers with three-dimensional structure will also cause each



8: $L_x = 5.76$ Å **9**: $L_x = 5.68$ Å; $L_y = 5.76$ Å **10**: $L_x = L_y = L_z = 5.63$ Å

Fig. 7. Geometric parameters of the repeating units of one-dimensional (**8**), two-dimensional (**9**), and three-dimensional (**10**) crystals $(C_{20}H_8)_n$ with D_{2h} symmetry.

monomer surrounded by six adjacent repeating units (octahedral environment) to have the cubic symmetry and occupy sites of a simple cubic lattice. Our calculations predict that this crystal must have a simple cubic lattice. The lengths of the translation vectors of possible polymers **8—10** are shown in Fig. 7.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 02-07-90169), Russian Federation Ministry of Science and Education (under Contract No. 40.012.1.1.1147), and by the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Grant 05).

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Received April 30, 2004 ;
in revised form July 6, 2004