Physical Chemistry

Molecular and electronic structures of some trimers of polyhedral carbon clusters

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Geometries and electronic structures of four crimped linear carbon clusters were modeled by the MNDO/PM3 method. Three of these clusters (C_{180} clusters) are trimers of I_h-C_{60} fullerene, which differ from each other by the mode of linkage of the monomers. The fourth cluster (C_{172} pseudo-trimer) consists of two C_{58} fragments of C_{60} fullerene linked to each other through the C_{56} cluster. The optimum geometric parameters, heats of formation, and ionization potentials were calculated for the above-mentioned systems as well as for the corresponding C_{120} and C_{116} dimers. The possibility of extrapolation of the data on dimers and trimers to linear oligomers of the C_{60} and C_{56} clusters with a larger number of repeating fragments is discussed. The character of linkages of monomers was analyzed for the two trimers under consideration, which have the most complex mode of binding of the C_{60} fullerene molecule and its fragments, using the $C_{60}H_{20}$ and $C_{72}H_{24}$ molecules (whose carbon skeletons model the structures of these linkages) as examples.

Key words: fullerenes, dimers, trimers; quantum-chemical calculations, MNDO/PM3 method.

Synthesis of C_{60} and C_{70} fullerenes in macroscopic amounts[1] open up considerable possibilities of constructing new compounds, which consist of polyhedral carbon clusters linked to each other *via* chemical bonds. These compounds can be obtained by photopolymerization and plasma-induced polymerization[2,3] as well as by action of high pressure on crystals of C_{60}.[4] Depending on the experimental conditions, dimers, oligomers that contain up to 10 monomer units, polymer chains, and three-dimensional structures characterized by a high degree of hardness can be obtained.[4] The spatial and electronic structures of some dimers of C_{60} fullerene have been discussed in a series of theoretical works[5—10] that considered the dumbbell-like dimers of C_{60}, as well as systems that consist of two C_{60} monomers linked to each other through one or two covalent bonds. In these clusters, the bonds between atoms of monomeric C_{60} fragments form skeleton structures.

It is of interest to assess changes in the geometry, electronic structure, and energy characteristics of oligomers of polyhedral carbon clusters as the number of monomeric fragments increases. In this work, this prob-

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lem was solved by semiempirical quantum-chemical methods using the $[C_{60}]_2$ and $[C_{58}]_2$ dimers, the linear $[C_{60}]_3$ trimers, and the $[C_{58}]_2C_{56}$ quasi-trimer as examples.

Calculation Procedure

Calculations were carried out on a DEC 3000 Alpha-AXP 400X workstation by the MNDO/PM3[11] and AM1[12] methods using the GAMESS program.[13] The atomic coordinates of the above-mentioned systems, which were determined by molecular mechanics (MM2) using the ALCHEMY program, were used as the first approximations in calculations.

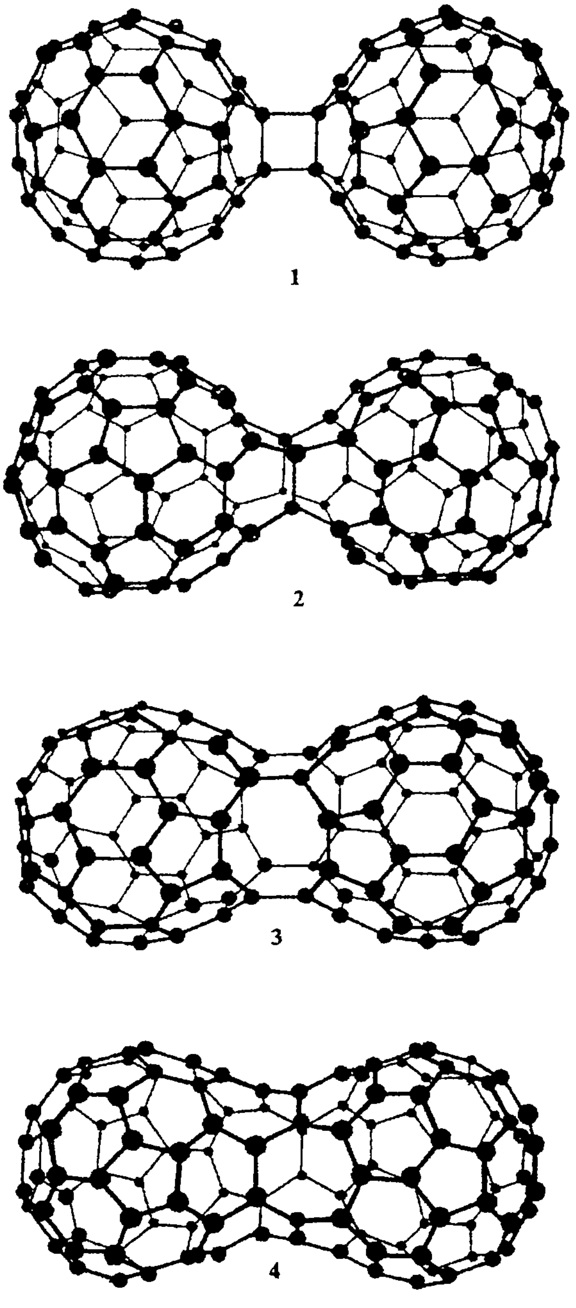


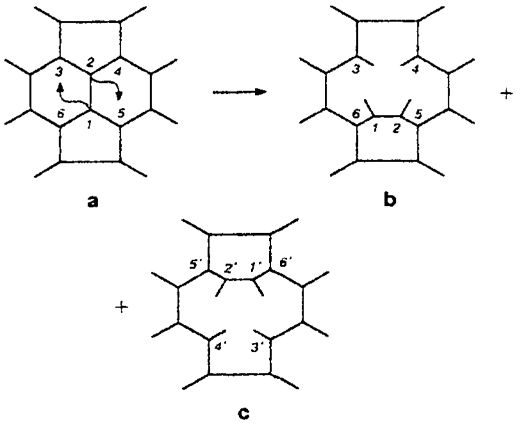
Fig. 1. Structures of dimers **1**—**4**.

Results and Discussion

Modes of binding of polyhedral clusters. Previously,[5—10] a number of modes of binding of two polyhedral C_{60} carbon clusters have been suggested. For example, formation of C_{120} was interpreted[5,8] as cycloaddition of cyclohexatrienyl fragments of two C_{60} fullerene molecules. Dimers obtained by [1,2+1,2], [1,4+1,4], and [1,2+1,4] cycloaddition were considered. The structure of the first of these dimers (**1**) is shown in Fig. 1 from which it can be seen that two C_{60} monomers are linked to each other through a four-membered ring. It was demonstrated[7,8] that dimers of C_{60} obtained by cycloaddition contain rather strained fragments, which link spheroidal C_{60} monomers. Therefore, the authors suggested[7] that these dimers can undergo further conversions to form more stable dumbbell-like C_{120} or C_{116} clusters. The latter cluster can be considered as a dimer of C_{58} fullerene, which is formally obtained according to the following scheme: $C_{120} \Rightarrow C_{116} + 2\ C_2$.

Among the described dimers of C_{60},[7] the energetically most favorable dimer has D_{2h} symmetry (see Fig. 1, structure **2**). The formation of this dimer from two C_{60} clusters can be schematically represented as follows. Let us consider the naphthalene fragment of the C_{60} cluster and transform its structure in the vicinity of the bond *1—2*, which links two five-membered rings in the fullerene molecule (Scheme 1, **a**). Then let us break the bonds *1—6*, *1—5*, *2—3*, and *2—4*, "rotate" the bond *1—2* by 90°, form new bonds *1—6* and *2—5* (Scheme 1, **b**), and join the atoms *1*, *2*, *3*, and *4*, which have two adjacent atoms each, to the atoms *1′—4′*, which belong to an analogous fragment of the second monomer (Scheme 1, **c**) so that the bonds *3—1′*, *4—2′*, *2—4′*,

Scheme 1

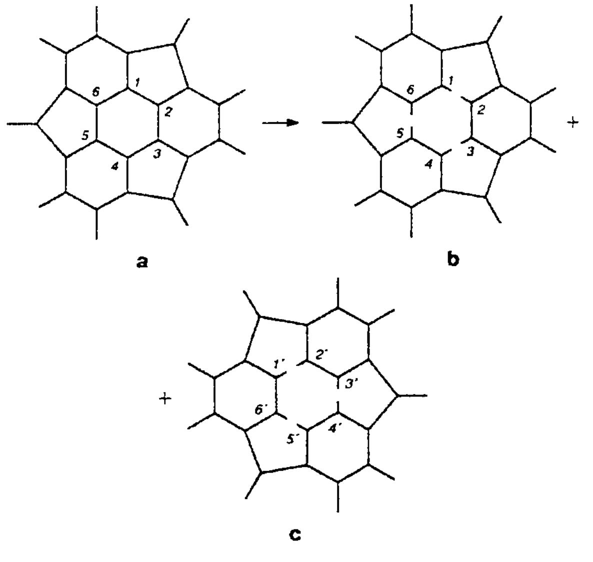


and *1—3'* are formed. In addition, let us form the bonds *1—1'* and *2—2'*. As a result, dimer **2** is obtained (see Fig. 1) whose carbon atoms *1*, *2*, *1'*, and *2'* in the four-membered ring are sp^3-hybridized, and the remaining 116 carbon atoms have three neighbors each. The cyclobutane ring and eight adjacent unsaturated six-membered rings form a skeleton structure, which consists of 28 carbon atoms and in which π-conjugation between two monomers is disrupted.

If four carbon atoms (*1*, *2*, *1'*, and *2'*) of the strained four-membered (cyclobutane) ring are "removed" and two remaining C_{58} fragments are linked directly through the bonds *6—4'*, *3—5'*, *5—3'*, and *4—6'*, the C_{116} dimer is formed (see Fig. 1, structure **3**), all C atoms of which are sp^2-hybridized. This structure is the most stable of the C_{116} clusters reported in Ref. 6. However, even in this structure, a rather strained bracelet-like fragment, which is formed by four eight-membered rings, occurs at the juncture of two monomers. As a result, the conjugation between monomeric fragments of system **3** should be insignificant.

The family of stable dumbbell-like dimers of C_{60} fullerene consists not only of the clusters reported previously.[5,8] For example, a more stable dumbbell-like dimer of C_{60} fullerene (see Fig. 1, structure **4**), which has D_{3d} symmetry, was reported in Ref. 14. In this dimer, all 120 atoms are sp^2-hybridized. The scheme of formation of cluster **4** can be represented as follows.[15] In one six-membered ring of C_{60} fullerene (Scheme 2, **a**, **b**), the bonds *1—2*, *3—4*, and *5—6* are broken, and the atoms *1—6*, which possess free valences, form six new bonds with atoms of another analogously transformed monomer, which is rotated by 60° about the three-fold symmetry axis common to both monomers (Scheme 2, **c**). As a result, the bonds *1—2'*, *6—1'*, *2—3'*, *3—4'*, *4—5'*, and *5—6'* are formed. Therefore, a "bracelet" formed by six seven-membered rings (see also the published data[16] on an analogous structure of the C_{108} cluster) occurs at the juncture of two monomers. By repeating the above-described procedure, dimers **1—4** can be completed to trimers **5—8**, respectively (Fig. 2). These modes of bonding of polyhedral carbon clusters can be used also for constructing rather extended crimped polymer structures.[16]

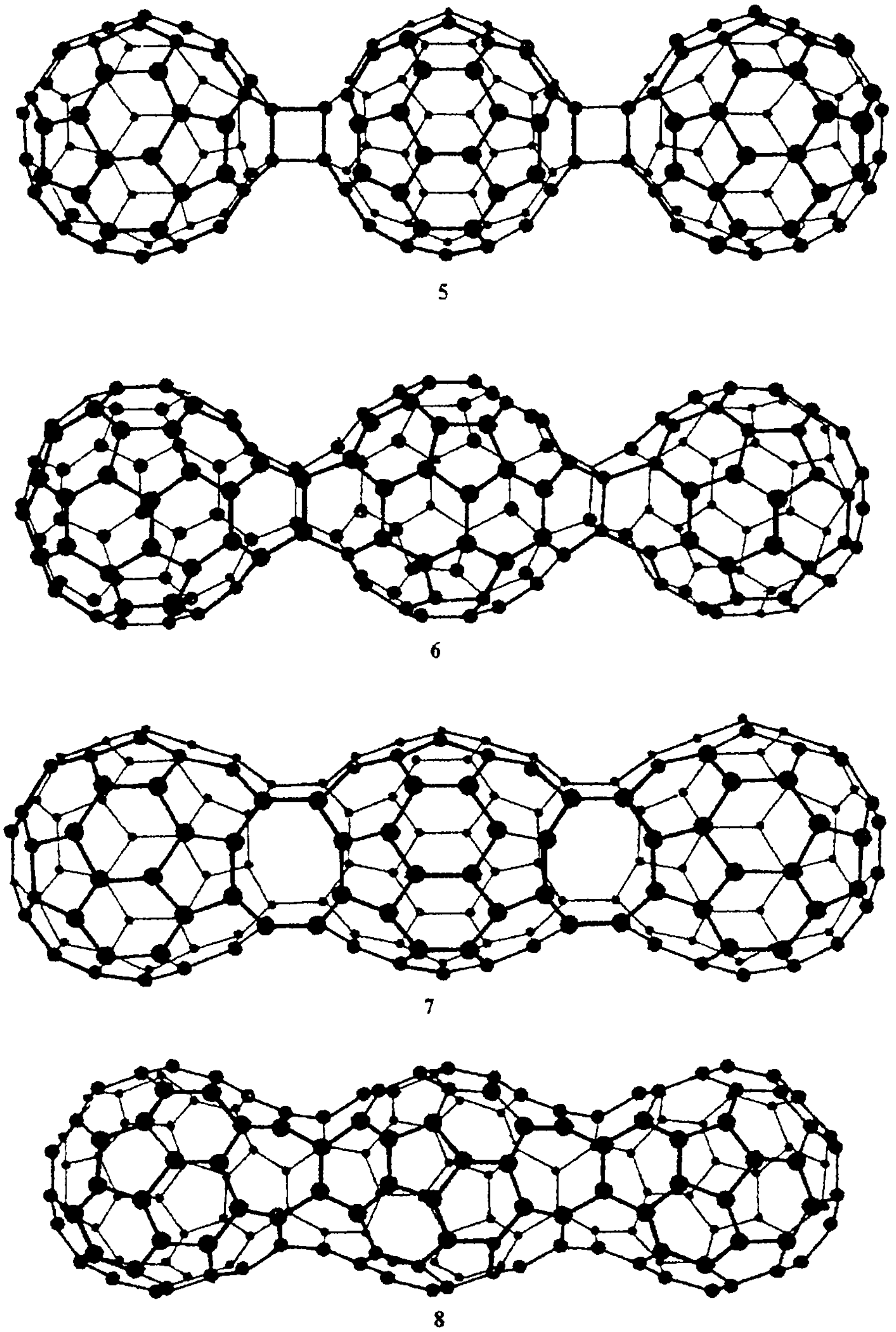
Scheme 2



The calculated energy characteristics of trimers **5—8** are given in Table 1. In this table, the corresponding parameters of dimers **1—4** obtained previously[7,8,14] are given for comparison. In addition, to study the structure of linkages between monomers in more detail, we carried out calculations of two skeleton hydrocarbon molecules, namely, $C_{60}H_{20}$ (**9**) (Fig. 3) and $C_{72}H_{24}$ (**10**) (Fig. 4), all C atoms of which are sp^2-hybridized. The carbon skeletons of these molecules model the fragments of clusters **3** and **4** at the juncture of two spheroidal monomers. Molecule **9** (D_{2h} symmetry) consists of two identical fragments formed by a *cata*-condensed system (bracelet-like) from alternating five- and six-membered rings, which are linked to each other through a "bracelet" formed by four eight-membered rings. Molecule **10** contains two identical condensed polycyclic systems (bracelet-like), which are linked to each other through a "bracelet" formed by six condensed seven-membered rings. Molecules **9** and **10** are also of interest as examples of skeleton conjugated hydrocarbons whose atoms are located on the surface similar to a hyperboloid

Table 1. Characteristics of clusters **1—8** and molecules **9** and **10** calculated by the MNDO/PM3 and AM1 methods (in parentheses): heats of formation (ΔH_f), specific heats of formation ($\Delta H_f \cdot n^{-1}$), energies of HOMO (E_{HOMO}), and $\delta E = E_{LUMO} - E_{HOMO}$

Cluster	Symmetry	ΔH_f	$\Delta H_f \cdot n^{-1}$	$-E_{HOMO}$ /eV	Symmetry of HOMO	δE /eV
		kcal mol^{-1}				
C_{120} (**1**)	D_{2h}	1586.5 (1913.6)[7]	13.22 (15.95)[7]	9.28 (9.48)[7]	b_{2u}	6.53 (6.52)[7]
C_{120} (**2**)	D_{2h}	1552.7 (1865.1)	12.94 (15.54)	9.11 (9.24)	b_{2g}	6.18 (6.23)
C_{116} (**3**)	D_{2h}	1539.3 (1827.6)	13.27 (15.76)	8.89 (9.04)	b_{2u}	5.66 (5.73)
C_{120} (**4**)	D_{3d}	1491.8 (1779.9)	12.43 (14.83)	9.21 (9.35)	e_g	6.26 (6.34)
C_{180} (**5**)	D_{2h}	2363.4	13.13	9.23	b_{2u}	6.529
C_{180} (**6**)	D_{2h}	2293.8	12.74	9.05	b_{3u}	6.07
C_{172} (**7**)	D_{2h}	2270.5	13.20	8.77	b_{3g}	5.58
C_{180} (**8**)	D_{3d}	2167.4	12.04	9.15	e_u	6.17
$C_{60}H_{20}$ (**9**)	D_{2h}	671.5	—	7.01	b_{2g}	3.69
$C_{72}H_{24}$ (**10**)	D_{3d}	521.0	—	7.09	e_g	6.80
C_{60} (**11**)	I_h	811.7 (973.3)	13.53 (16.22)	9.48 (9.64)	h	6.60 (6.70)



5

6

7

8

Fig. 2. Structures of trimers 5—8.

of one sheet. The results of calculations of electronic structures of these systems are given in Table 1.

Energy characteristics. From the data of Table 1 it follows that the heats of formation of I_h-C_{60} fullerene (**11**) calculated by the MNDO/PM3 and AM1 methods differ substantially from the experimental value (ΔH_f = 545 kcal mol^{-1}).[17] The value of ΔH_f calculated by the MNDO/PM3 method is closer to the experimental value. The values of heats of formation of dimers also depend on the method of calculation. However, in spite of the differences of degree in the results of calculations of dimers, both methods lead to analogous tendencies for a change in the energy characteristics of these clusters. For example, the energy of dimerization $\Delta E_2 = 2\Delta H_f(C_{60}) - \Delta H_f(C_{120})$ of C_{60} fullerene increases in the series **1** → **2** → **4** (according to AM1 calculations, ΔE_2 is

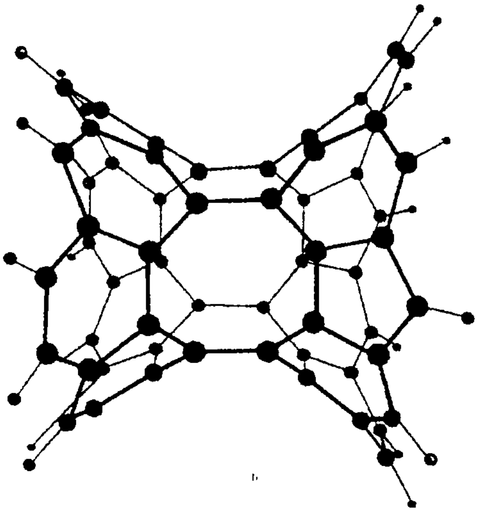


Fig. 3. Structure of the $C_{60}H_{20}$ molecule (**9**), which models the linkage fragment of two C_{58} fullerenes in clusters **3** and **7**.

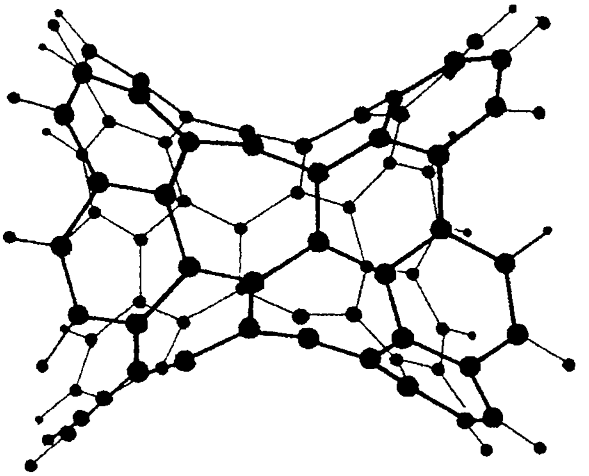


Fig. 4. Structure of the $C_{72}H_{24}$ molecule (**10**), which models the linkage fragment of two C_{60} fullerenes in clusters **4** and **8**.

33.1, 81.5, and 166.7 kcal mol^{-1}, respectively; and according to MNDO/PM3 calculations, ΔE_2 is 37.0, 70.7, and 131.6 kcal mol^{-1}, respectively).

The ionization potentials determined from the energies of HOMOs depend only slightly on the approximation used and have similar values. Therefore, trimers **5**—**8** were calculated only by the MNDO/PM3 method. It was established that the stability of the C_{180} clusters, which is characterized by the value of $\Delta E_3 = 3E(C_{60}) - E(C_{180})$, increases in the series **5** → **6** → **8** (71.1, 141.3, and 267.7 kcal mol^{-1}, respectively). In addition, in these trimers the value of the energy gap δE between the energy levels of unoccupied and occupied MOs is larger than 5.5 eV, which is indicative of the kinetic stability of the clusters under study. Note also that among systems **1**—**4**, dimer **3**, which contains two C_{58} clusters, has the highest specific heat of formation $\Delta H_f \cdot n^{-1}$ (per one atom). Of structures **5**—**8**, pseudo-trimer **7**, which consists of two C_{58} fragments and one C_{56} fragment, has the highest specific heat of formation. Moreover, the gain in energy due to formation of trimers from C_{60} fullerenes is approximately twice as large as in the case of dimers.

Geometric characteristics. The structures of the fragments that link monomers are of most interest. In going from dimers to trimers, these fragments change only slightly. Therefore, the view of their structures can be obtained from the results of calculations of either dimers and trimers or of the model hydrocarbon molecules $C_{60}H_{20}$ (**9**, see Fig. 3) and $C_{72}H_{24}$ (**10**, see Fig. 4). In cluster **1**, the bond lengths in the cyclobutane fragment, which links two monomers, alternate and are equal to 1.546 and 1.603 Å (AM1)[7] and 1.549 and 1.598 Å (MNDO/PM3), respectively.[14] Two of four C—C bonds in this ring, which belong to the monomers, are substantially elongated compared to the single bond owing to the strain of the ring. Cluster **2** also contains the cyclobutane fragment, all atoms of which are shared by both monomers of fullerene. The bond lengths in this ring alternate and are 1.547 and 1.629 Å (AM1)[7] and 1.543 and 1.620 Å (MNDO/PM3),[14] respectively. Two bonds opposite to the five-membered rings are substantially longer than the single bonds.

Let us use the results of calculations of hydrocarbon molecules **9** and **10**, which demonstrate that these molecules are stable and have closed electron shells, to describe more complex structures of linkages in dimers **3** and **4** and trimers **7** and **8**. Molecule **9** contains four eight-membered rings. All the rings adopt a boat conformation. In these rings, the bonds between the atoms of two monomers are shorter (1.39 Å) than the remaining bonds (1.411—1.423 Å), which correspond to normal aromatic bonds. The torsion angles in the eight-membered rings are ~133°. Molecule **10** contains six seven-membered rings. All the rings adopt a boat conformation, which is distorted with respect to the *2*—*7* and *3*—*6* lines (see Fig. 4). The dihedral angles in these rings are 157.7° and 131.8°, respectively. The bond lengths vary from

Table 2. Linear sizes (l_x, l_y, and l_z) of clusters **1**—**8** along the *x*, *y*, and *z* coordinate axes

Cluster	l_x	l_y	l_z
		Å	
1	6.94	6.97	16.03
2	6.77	7.12	15.68
3	6.80	7.06	14.89
4	6.93	6.93	15.11
5	6.89	6.97	25.10
6	6.57	7.22	24.41
7	6.60	7.18	22.84
8	6.85	6.85	23.73

Table 3. Coordinates (Å) of symmetrically nonequivalent atoms in clusters **5**—**8**

Number of the atom	*x*	*y*	*z*	Number of the atom	*x*	*y*	*z*	Number of the atom	*x*	*y*	*z*	Number of the atom	*x*	*y*	*z*
Cluster **5**				Cluster **6**				Cluster **7**				Cluster **8**			
1	0.690	3.488	0.000	*1*	0.000	3.612	0.688	*1*	0.689	3.297	0.000	*1*	0.000	3.398	0.664
2	1.414	3.030	1.181	*2*	1.169	3.139	1.417	*2*	1.383	2.886	1.192	*2*	0.000	2.903	1.975
3	0.726	2.591	2.305	*3*	0.740	2.489	2.627	*3*	0.719	2.480	2.348	*3*	1.259	2.367	2.280
4	1.171	1.440	3.059	*4*	1.416	1.403	3.152	*4*	1.491	1.643	3.299	*4*	1.397	1.602	3.699
5	0.000	0.803	3.787	*5*	0.810	0.771	4.365	*5*	2.628	2.248	0.724	*5*	2.276	2.642	0.215
6	2.582	2.303	0.729	*6*	2.256	2.629	0.730	*6*	3.099	1.156	1.407	*6*	2.305	2.168	1.580
7	2.984	1.176	1.425	*7*	2.855	1.398	1.192	*7*	2.365	0.684	2.601				
8	2.259	0.737	2.061	*8*	2.398	0.732	2.339	*8*	3.589	0.000	0.696				
9	3.429	0.691	0.691	*9*	3.283	0.682	0.000								

1.37 Å to 1.46 Å. The seven-membered rings that link monomer fragments are nonplanar, which results in a partial disruption of conjugation between the monomers. This may affect substantially the conducting properties of the corresponding polymer chains.

The linear sizes of clusters **1**—**8** are given in Table 2. This table lists the largest distances between the carbon atoms along three directions: along the *z* axis, which coincides with the longitudinal symmetry axis of the cluster, and along the *x* and *y* axes (the direction of the *x* axis corresponds to the smallest diameter of the cluster in the (*x*, *y*) section; in the dimers, the (*x*, *y*) section passes through the center of one monomer, and in the trimers, this section passes through the center of the inner fragment). Table 2 demonstrates that the sizes of the C_{120} and C_{180} clusters under study along the *z* axis decrease in the series **1** → **2** → **4** and **4** → **6** → **8**, respectively. In going from dimers to trimers, the cross sections of the clusters change only slightly (no more than 0.2 Å).

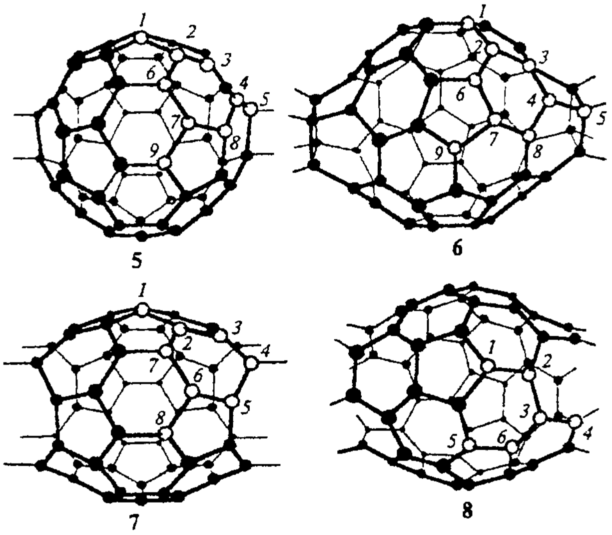


Fig. 5. Numbering scheme of nonequivalent atoms of the inner fragments of trimers **5**—**8**.

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To summarize, in this work we calculated the geometric and energy characteristic of three C_{180} clusters (trimers of C_{60}) and one C_{172} cluster (pseudo-trimer formed by two C_{58} clusters and one C_{56} cluster) with the most natural structures of linkages. The geometries of the inner monomers of trimers **5**—**8** can be used for modeling structures of repeating units and estimating the lengths of translations of the corresponding quasi-one-dimensional macromolecular forms of carbon, which consist of polyhedral fragments. The coordinates of nonequivalent atoms of the inner fragments of trimers **5**—**8** (Fig. 5) are given in Table 3. It is of interest to compare the electronic spectra of these crimped quasi-one-dimensional macromolecules and their doped forms with those of regular carbon tubulenes with similar diameters. We plan to carry out this comparison and to publish the results elsewhere.

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