Molecular and electronic structure of some bowl-shaped unsaturated hydrocarbon molecular systems, possible precursors of C_{60} fullerene

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The AM1 calculations of hydrocarbon molecules $C_{20}H_{10}$ (**1**) and $C_{30}H_{10}$ (**2**) and anions $C_{20}H_{15}^-$ (**3**) and $C_{30}H_{15}^-$ (**4**) have been performed with the full energy optimization of the geometric parameters. The chosen topology of the carbon framework of the studied compounds is identical to the topology of the corresponding carbon fragments of C_{60} fullerene. Analysis of the structure of the frontier orbitals of systems **1**—**4** demonstrated that the tendency of the $C_{20}H_{10}$ molecule to form sandwich π-complexes of the η^5-type with transition metal atoms is small; however, this tendency is significantly larger than that of $C_{30}H_{10}$. Moreover, the exclusion of the five-membered cycle of bowl-shaped unsaturated hydrocarbon molecules and anions from the conjugated system (as a result of the conversion of five framing C atoms to saturated carbon centers) favors the stabilization of their η^5-type π-complexes with $M(C_5H_5)$ species. The stability of these complexes must approach the stability of classical sandwich complexes of the ferrocene type. The results obtained have been extrapolated to polyhedral C_{60} and C_{70} carbon clusters.

Key words: fullerene fragments, polyhedral clusters, η^5-π-complexes; AM1 method.

The polyhedral clusters of carbon C_{60} predicted in the early 1970s in a number of theoretical works[1,2] were first found in 1985, when graphite was vaporized under the action of a laser beam.[3] At present, C_{60} fullerene as well as the polyhedral molecular carbon forms with a larger number of atoms are obtained mainly by the electric arc method.[4] Chemical methods for the synthesis of polyhedral carbon clusters remain to be developed.[5,6]

In this connection, it is of interest to model the geometric and electronic structure of hydrocarbon bowl-shaped molecules with carbon frameworks structurally close to the cores of polyhedral carbon cluster fragments.[7,8] These molecules might be precursors of C_{60} and C_{70} clusters and other fullerenes in the chemical synthesis of these compounds. Moreover, the characteristics of the above-mentioned molecules may be used in theoretical modeling of the chemical properties of some derivatives of C_{60}, *e.g.*, the $C_{60}H_5^{\cdot}$ radical.

The molecule of corannulene $C_{20}H_{10}$ (**1**) (Fig. 1, Table 1), which was synthesized[9] in the early 1970s, is the simplest example of an unsaturated hydrocarbon system with a carbon framework similar to the framework of the "polar bowls" (with respect to the five-fold symmetry axis) of the C_{60} and C_{70} clusters. Molecule **1** has C_{5v} symmetry and, despite the presence of pericondensed cycles, tends to bowl—bowl type inversion. The potential barrier to this rearrangement is ~11—12 kcal mol^{-1} (see Ref. 10).

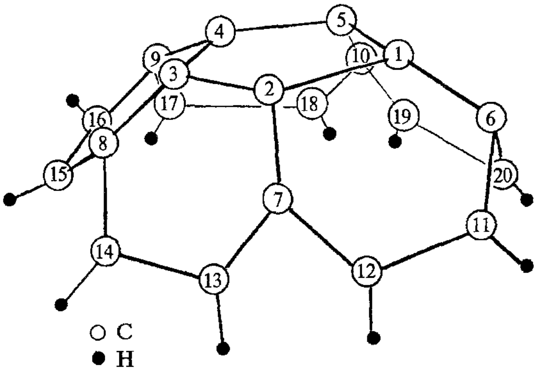

Fig. 1. Optimized geometry of the $C_{20}H_{10}$ molecule (see Table 1). The z axis is perpendicular to the C(1)...C(5) plane.

Table 1. Bond lengths (d), Wiberg bond indices (W), and principal bond angles (φ) in the $C_{20}H_{10}$ molecule

Bond	d/Å	W/au	Angle	φ/deg
C(1)—C(2)	1.436	1.141	C(1)-C(2)-C(7)	128.8
C(1)—C(6)	1.384	1.424	C(1)-C(6)-C(11)	114.1
C(6)—C(11)	1.441	1.157	C(6)-C(11)-C(12)	122.6
C(11)—C(12)	1.382	1.665	C(1)-C(6)-C(7)-C(11)	171.0

Note. The angle between the C(1)—C(6) bond and the plane of the C(1)...C(5) ring (α) is 157.1°.

The synthesis of the $C_{22}H_{14}$ molecule, which differs from corannulene by the presence of the C_2H_4 group closing two *peri*-vertices to form a new five-membered cycle, has also been reported.[10] It was noted that, unlike **1**, the $C_{22}H_{14}$ molecule is structurally rigid. The poten-

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tial barrier to the bowl—bowl type inversion is no less than 26 kcal mol^{-1}.

In this work, we report the results of the AM1 calculations of the hydrocarbon systems $C_{20}H_{10}$ (**1**), $C_{30}H_{10}$ (**2**), $C_{20}H_{15}^-$ (**3**), and $C_{30}H_{15}^-$ (**4**). The carbon frameworks of compounds **2** and **4** are topologically equivalent to the carbon framework of one of the halves of the C_{60} cluster. Anion **4** models the fragment of the $C_{60}H_5^-$ cluster containing the cyclopentadienyl anion separated from the common conjugated system by five saturated CH vertices framing this anion.

Molecule 1. Corannulene has been studied by different quantum-chemical methods (see, *e.g.*, Refs. 8, 11, 12); however, the results of the calculations reported in the above-mentioned works are not comprehensive. In particular, there is no analysis of the structure of the frontier MOs, though it is of interest for estimating the reactivity of molecule **1** and predicting the possibility of the existence of its stable η^5-π-complexes with compounds of transition metals.

The calculated values of selected bond lengths, bond angles, and Wiberg bond indices in molecule **1** are given in Fig. 1 and Table 1. It can be seen that the bond lengths of the six-membered cycle alternate; the value of the alternation is approximately 0.05—0.06 Å. The energy of the highest occupied MO ($E_{\rm HOMO}$) is −8.92 eV, and the energy of the lowest unoccupied MO ($E_{\rm LUMO}$) is approximately −0.9 eV. The calculated heat of formation of molecule **1** is 159 kcal mol^{-1}.

When performing the calculations for molecule **1**, we assumed that the z axis of the coordinate system is perpendicular to the plane of the five-membered cycle. This made it possible to estimate the contributions of the $2p_z$-AOs of the atoms of the C(1)...C(5) five-membered cycle to the corresponding MOs. We analyzed the structure of the five highest occupied MOs and established that three of them can be assigned to π-type MOs (with respect to the plane of the five-membered cycle). The highest occupied energy level is doubly degenerate; its MO is a σ-type MO and belongs to the e_2 irreducible representation of the C_{5v} group. The contribution of the electrons occupying these MOs to the population of each of the $2p_z$-AOs is small (0.074) (the contribution of an electron occupying the MO to the AO population is the square of the corresponding coefficient).

The energetically closest occupied π-type MOs belong to the two-dimensional e_1 representation. Their energies differ from $E_{\rm HOMO}$ by only 0.1 eV. The populations of the $2p_z$-AOs of the C(1)—C(5) atoms determined by these MOs are 0.36. Finally, the fifth π-type frontier orbital has a_1 symmetry and substantially lower energy (by approximately 2 eV). The populations of the $2p_z$-AOs from this MO are 0.136.

Therefore, the total contribution of the π-type MOs to the population of each of the $2p_z$-AOs of the C(1)—C(5) atoms is only 0.246, *i.e.*, substantially smaller than the contributions of π-MOs to the population of the $2p_z$-AOs in the cyclopentadienyl anion (1.200) and even in the cyclopentadienyl radical (1.000). Apparently, this indicates that the sandwich η^5-π-complexes of corannulene, if they exist, should be substantially less stable than the classical sandwich complexes of ferrocene.

Molecule 2. Optimization of the structure of molecule **2** was performed with the retention of its C_{5v} symmetry. A local minimum was found on the corresponding potential energy surface. It was established that the position of this local minimum is retained after removal of the symmetry conditions.

The atomic numbering scheme, bond lengths, bond angles, and bond indices are given in Fig. 2 and Table 2. Similarly to corannulene, the alternation of bond lengths is observed in the six-membered cycles of molecule **2**, although in the C(1)...C(5) five-membered cycle, these bonds are equalized. In each of the remaining five-membered cycles, the bonds are not equivalent, which results in slight differences in their lengths. In molecule **2**, $E_{\rm HOMO}$ = −8.71 eV, and $E_{\rm LUMO}$ =

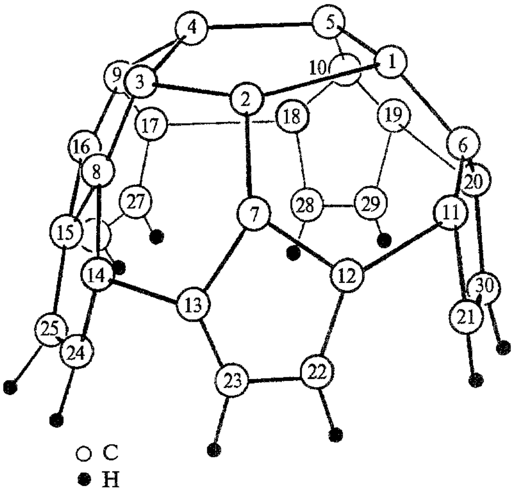

Fig. 2. Optimized geometry of the $C_{30}H_{10}$ molecule (see Table 2).

Table 2. Bond lengths (*d*), Wiberg bond indices (*W*), and principal bond angles (φ) in the $C_{30}H_{10}$ molecule

Bond	*d*/Å	*W* /au	Angle	φ/deg
C(1)—C(2)	1.453	1.100	C(1)-C(2)-C(7)	118.7
C(1)—C(6)	1.371	1.499	C(1)-C(6)-C(11)	122.5
C(6)—C(11)	1.468	1.102	C(6)-C(11)-C(12)	118.4
C(11)—C(12)	1.371	1.593	C(13)-C(7)-C(12)	108.5
C(12)—C(22)	1.477	1.027	C(7)-C(12)-C(22)	104.2
C(22)—C(23)	1.370	1.829	C(12)-C(22)-C(23)	110.1
			C(1)-C(6)-C(7)-C(11)	−173.3
			C(7)-C(13)-C(12)-C(22)	163.1

Note: α = 144.8°.

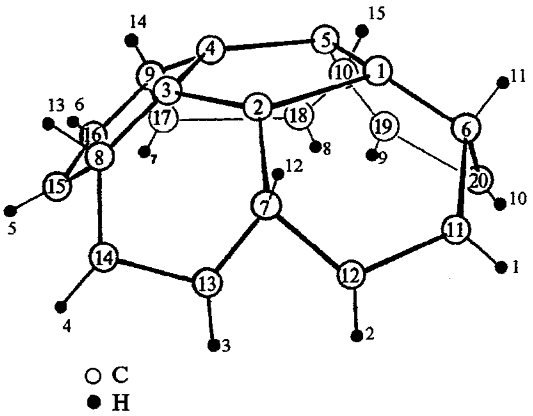

Fig. 3. Optimized geometry of the $C_{20}H_{15}^-$ anion (see Table 3).

Table 3. Bond lengths (d), Wiberg bond indices (W), and principal bond angles (φ) in the $C_{20}H_{15}^-$ anion

Bond	d/Å	W /au	Angle	φ/deg
C(1)—C(2)	1.419	1.347	C(1)-C(2)-C(7)	123.4
C(1)—C(6)	1.474	0.987	C(1)-C(6)-C(11)	111.1
C(6)—C(11)	1.496	0.971	C(6)-C(11)-C(12)	124.6
C(11)—C(12)	1.340	1.925	C(13)-C(7)-C(12)	115.3
			C(1)-C(6)-C(7)-C(11)	−167.8

Note: α = 159.3°.

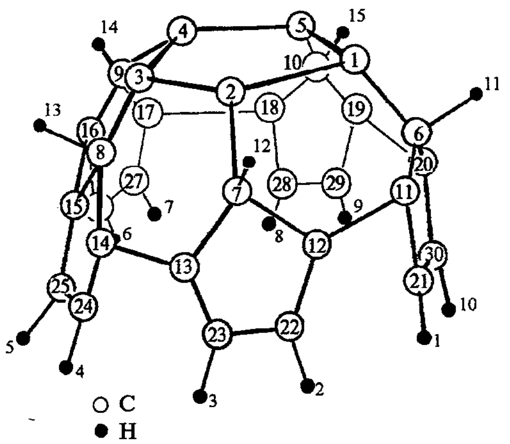

Fig. 4. Optimized geometry of the $C_{30}H_{15}^-$ anion (see Table 4).

Table 4. Bond lengths (d), Wiberg bond indices (W), and principal bond angles (φ) in the $C_{30}H_{15}^-$ anion

Bond	d/Å	W /au	Angle	φ/deg
C(1)—C(2)	1.416	1.344	C(1)-C(2)-C(7)	123.3
C(1)—C(6)	1.462	0.989	C(1)-C(6)-C(11)	110.5
C(6)—C(11)	1.537	0.947	C(6)-C(11)-C(12)	123.1
C(11)—C(12)	1.343	1.791	C(12)-C(7)-C(13)	101.2
C(12)—C(22)	1.470	1.026	C(7)-C(12)-C(22)	105.1
C(22)—C(23)	1.363	1.831	C(12)-C(22)-C(23)	110.2
			C(1)-C(6)-C(7)-C(11)	−157.8
			C(7)-C(12)-C(13)-C(22)	152.1

Note: α = 158.9°.

−1.63 eV. The effective charges on all of the C atoms are close to zero. A small negative charge (−0.1) is located on each of the peripheral C atoms. The heat of formation of molecule **2** is 394.8 kcal mol^{-1}.

Analysis of the structure of the five highest occupied MOs demonstrated that these MOs include the nonzero contributions from the 2p_z-AOs of the C(1)...C(5) five-membered cycle. However, these contributions are substantially smaller than in the case of corannulene. Thus, for example, the contribution of the electrons occupying the a_1 orbital to the population of the 2p_z-AO is only 0.028. The HOMOs belong to the e_1 irreducible representation; the corresponding contribution to the population of each of the 2p_z-AOs is also small (no more than 0.014).

Therefore, in the transition form corannulene to molecule **2**, which has a carbon framework topologically equivalent to the framework of one of the halves of C_{60} fullerene, a substantial decrease in the population of the 2p_z-AOs of the C(1)—C(5) atoms in the frontier orbitals is observed. Clearly, this should affect the ability of molecule **2** to form sandwich η^5-π-complexes with transition metal atoms coordinated to the upper five-membered cycle. Therefore, it should be expected that the existence of η^5-π-complexes is even less probable for C_{60} and C_{70} clusters than in the case of corannulene.

Anions 3 and 4. Formally, these systems may be formed from molecules **1** and **2**, respectively, as a result of the addition of five H atoms (to the positions adjacent to the atoms of the five-membered C(1)...C(5) cycle) and subsequent reduction. The calculated structural characteristics of anion **3** are presented in Fig. 3 and Table 3. Note that the bond lengths in the five-membered cycle are close to those in the corannulene molecule. The bond lengths at the saturated C atoms differ little from the mean length of a single C—C bond.

Analysis of the structure of the highest occupied MOs demonstrated that these orbitals consist mainly of the 2p_z-AOs of the C(1)...C(5) five-membered cycle, and their populations are substantially larger than those of the corresponding AOs in molecule **1**. Thus, the contribution of the HOMO to the population of each of the 2p_z-AOs belonging to the e_1 irreducible representation is 0.656, while the contribution of the a_1 MO is 0.24.

The structure and principal geometric parameters of anion **4** are given in Fig. 4 and Table 4. As in the case of anion **3**, the geometry of the C(1)...C(5) five-membered cycle is changed only slightly. Analysis of the electron density distribution demonstrated that negative charges close to −0.9 are located on the atoms of this five-membered cycle. The highest occupied MOs consist mainly of the $2p_z$-AOs of the atoms of the upper five-membered cycle, and their structures differ little from the structure of the HOMO of anion **3**. The contribution of these MOs to the population of the $2p_z$-AO is 0.658; the similar contribution of the a_1 orbital is ~0.26.

Therefore, the addition of five H atoms to the C atoms adjacent to the C(1)...C(5) five-membered cycle favors the formation of the anion containing a structurally separated five-membered cycle with an electronic structure similar to that of the cyclopentadienyl anion. Hence, the polyhedral radicals of the cyclopentadienyl type obtained as a result of the addition of monovalent groups to five C atoms framing the central five-membered cycle of molecules **1** and **2** should approach the cyclopentadienyl radical in their ability to form π-complexes with transition metal atoms. Evidently, these conclusions can be extended to the $X_5C_{60}^{\cdot}$ and $X_5C_{70}^{\cdot}$ radicals.

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