On some carbon clusters containing sp^2- and sp^3-hybridized atoms

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A new class of thread-like carbon clusters consisting of dodecahedra and containing sp^2- and sp^3-hybridized atoms is described. Molecular and electronic structures of the simplest representative of this class (the C_{102} cluster) and of the polyhedral $C_{90}H_{12}$ hydrocarbon molecule, whose carbon framework is identical to the toroidal fragment of the C_{102} cluster, have been calculated by the MNDO and MNDO-PM3 methods.

Key words: fullerenes; carbon clusters; quantum-chemical methods, MNDO, MNDO-PM3.

Experimental detection of giant carbon molecules such as C_{60} and C_{70} fullerenes and tubulenes gave impetus to intensive studies of their physicochemical properties and resulted in a great number of works in the field of molecular design and prediction of the properties of new carbon materials.[1–3] In particular, it has been demonstrated that the C_{60} and C_{70} clusters consist of three-coordinate carbon atoms. These atoms are located on closed convex surfaces and are involved in formation of extended conjugated π-electron systems, which stabilize these spheroidal molecules. It was also suggested that higher fullerenes have hollow polyhedral structures as well.[3]

With a rather large number of atoms, the formation of carbon clusters containing atoms with different coordination numbers is not ruled out. These systems may have the structures of "filled" polyhedra. Although the occurrence of filled clusters is, apparently, more probable for other Group IV elements, for example, for silicon,[4,5] it is of interest to search for stable structures consisting of carbon atoms with coordination numbers of three and four. In this work, a family of clusters consisting of sp^2- and sp^3-hybridized carbon atoms is described, and the results of quantum-chemical calculations of the simplest representatives of the structures considered (the C_{102} fullerene and the $C_{90}H_{12}$ molecule, whose carbon framework is identical to the toroidal fragment of the C_{102} cluster) are examined.

One of the C_{90} isomers is the suitable system containing sp^2- and sp^3-hybridized carbon atoms. The structure of this isomer can be described as follows: six pentagonal dodecahedra are fused in pairs *via* shared five-membered faces so that the toroidal C_{90} cluster (**1**) with D_{6h} symmetry (Fig. 1) is formed.

This cluster consists of 30 sp^3- and 60 sp^2-hybridized carbon atoms. The formal analysis of the Kekule's structures of cluster **1** and the results of the MNDO calculations demonstrated that this system should contain at least 12 radical centers and it should exhibit a high reactivity. Cluster **1** can be stabilized by saturating the free valences of all its radical centers in one of two ways. The first way consists in attaching hydrogen atoms to all these centers with the formation of the $C_{90}H_{12}$ hydrocarbon molecule (**2**) (or attaching monovalent groups, which results in substituted derivatives of compound **2**). The second method consists of adding two "caps," *i.e.*, six-membered carbon cycles, to the C_{90} cluster from above and below; these caps are located parallel to the equatorial plane of the cluster; as a result, the C_{102} cluster (**3**) with D_{6h} symmetry is formed (Fig. 2).

Thread-like structures can also be built of C_{90} clusters. To do this, let us take several clusters **1** and stack then as dishes turning each next layer of clusters with respect to the previous one by 30° (in this case, dodecahedra of the upper layer are brought into the cavities between two adjacent dodecahedra of the lower layer) and taking pairs of coinciding atoms as one atom. In this way, a however large thread-like (stacked) structure **4**,

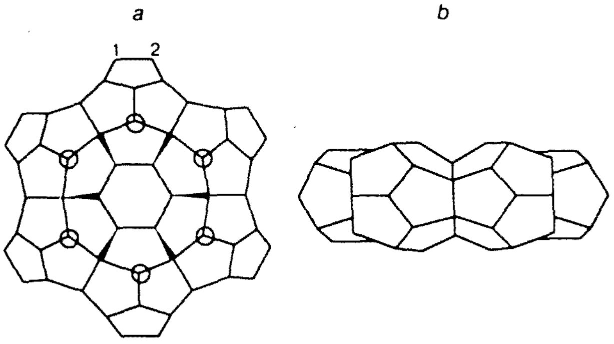

Fig. 1. Structure of the hypothetical C_{90} cluster **1** with D_{6h} symmetry: *a*, top view; *b*, side view; radical centers are represented by circles.

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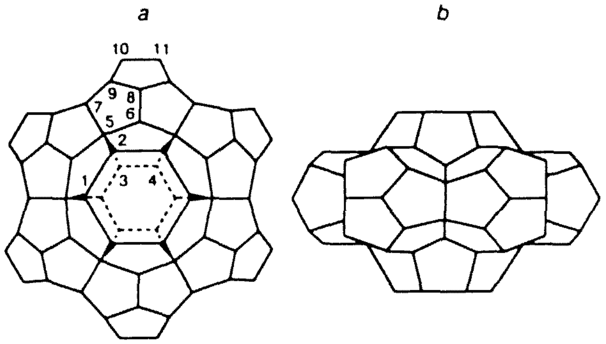

Fig. 2. Structure of the C_{102} cluster with D_{6h} symmetry: *a*, top view; *b*, side view.

Table 1. Enthalpies of formations (kcal mol^{-1}) of the C_{60}, C_{102}, and $C_{90}H_{12}$ molecules

Method	C_{60}	C_{102}	$C_{90}H_{12}$
MNDO	879	2450.5	1953.7
MNDO-PM3	812	2240.8	1761.4
Experiment	545	—	—

Table 2. Bond lengths (Å) and orders of the bonds in the C_{102} and $C_{90}H_{12}$ molecules (the MNDO-PM3 method)*

C—C bond	Bond length	Order
C(1)—C(2)	1.421 (2.332)	1.38 (0)
C(2)—C(6)	1.545 (1.110)	0.95 (0.96)
C(3)—C(4)	1.559 (1.565)	0.95 (0.96)
C(3)—C(5)	1.548 (1.573)	0.96 (0.95)
C(5)—C(6)	1.555 (1.555)	0.95 (0.96)
C(5)—C(7)	1.560 (1.592)	0.94 (0.94)
C(6)—C(8)	1.546 (1.517)	0.95 (0.96)
C(7)—C(9)	1.481 (1.491)	0.97 (0.96)
C(7)—C(12)**	1.569 (1.567)	0.94 (0.95)
C(8)—C(9)	1.424 (1.412)	1.35 (1.36)
C(9)—C(10)	1.449 (1.445)	1.21 (1.20)
C(10)—C(11)	1.446 (1.458)	1.22 (1.22)

* Values for $C_{90}H_{12}$ are given in parentheses.

** Atoms 7 and 12 are located symmetrically with respect to the equatorial plane.

consisting predominantly of sp^3-hybridized carbon atoms, can be built. The sp^2-hybridized atoms, for example, the C(1) and C(2) atoms (see Fig. 1), are located on the lateral surface of cluster **4**, each dodecahedra having eight such atoms. These atoms form a conjugated system.

As with the C_{90} cluster, in the case of the finite structure of the above-described type, six-membered cycles are added to this structure from above and below for saturating free valences of the atoms of the terminal fragments with the formation of cluster **5** of the general formula $C_{102+54n}$, n = 1, 2,... The shortest distances from the inner atoms in systems **4** and **5** to the principal symmetry axis are close to the values of the single bonds. Therefore, in these clusters cylindrical cavities of sufficiently large sizes are absent. However, the C_{24} clusters of the barrelene type with D_{6h} symmetry form cavities in which atoms (or ions) of light elements can be located.

The simplest representative of the above-described family, cluster **3** (Fig. 2), contains 42 sp^3- and 60 sp^2-hybridized atoms; hydrocarbon molecule **2** consists of 42 sp^3- and 48 sp^2-hybridized carbon atoms. The calculations of the C_{102} and $C_{90}H_{12}$ molecules were performed by the MNDO[6] and MNDO-PM3[7] methods using the GAMESS program package[8] adapted to the DEC ALPHA AXP/3000 work station (Model 400). Analysis of the energy levels in the C_{102} and $C_{90}H_{12}$ molecules demonstrated that their frontier molecular orbitals are nondegenerate and have negative energies (ε_{HOMO} = −9.44 eV and ε_{LUMO} = −3.45 eV (C_{102}); ε_{HOMO} = −9.14 eV and ε_{LUMO} = −3.19 eV ($C_{90}H_{12}$)). Therefore, each system mentioned above has a closed electron shell and a rather large energy gap separating the HOMO and LUMO. Hence, the C_{102} and $C_{90}H_{12}$ molecules are, apparently, kinetically stable. However, the calculations demonstrated that the C_{102} cluster should be less stable than the molecule of fullerene by ~9 kcal mol^{-1} (per one carbon atom).

As is seen from Table 1, both methods (MNDO and MNDO-PM3) overestimate the enthalpy of formation (ΔH_f) of the C_{60} cluster by a factor of ~1.5; however, the value of ΔH_f calculated by the MNDO-PM3 method is 67 kcal mol^{-1} lower, *i.e.*, this value is closer to that experimentally determined. Therefore, only the results of the calculations of the C_{102} and $C_{90}H_{12}$ molecules obtained by the MNDO-PM3 method are given in Table 2.

Note that the C_{102} and $C_{90}H_{12}$ structures are slightly strained. This is predominantly reflected in the properties of some C—C bonds, which appear to be longer (by ~0.02—0.03 Å) than those in the unstrained hydrocarbon systems. The C(1)—C(2) and C(8)—C(9) bonds in the C_{102} cluster (Fig. 2) are virtually identical to those in graphite (1.42 Å).[9] The diameter of the C_{102} cluster (taking into account the van der Waals radii) is 14 Å, and the thickness is 9 Å. In the C_{102} and $C_{90}H_{12}$ molecules, a nonuniform charge distribution on the carbon atoms occurs: the differences in the charges are

Table 3. Effective charges (a.u.) on atoms in the C_{102} and $C_{90}H_{12}$ molecules (the MNDO-PM3 method)*

C atom	Charge	C atom	Charge
1	0 (0.1)	7	−0.02 (−0.02)
3	0.01 (0.01)	8	−0.17 (−0.24)
5	−0.11 (−0.05)	9	0.17 (0.16)
6	0.14 (0.03)	10	−0.16 (−0.16)

* Values for $C_{90}H_{12}$ are given in parentheses.

0.4 a.u. In the C_{102} cluster, the largest negative charges are located on the C(8) and C(10) atoms, whereas the largest positive charges are located on the C(9) atoms (Fig. 2). The calculations of the C_{102} and $C_{90}H_{12}$ systems by the MNDO and MNDO-PM3 methods demonstrated that although the charges on the atoms are virtually the same, the bond lengths and the formation enthalpies determined by the MNDO method are larger than those calculated in the MNDO-PM3 approximation. In conclusion, note that the above-described thread-like structures may also occur with atoms of other Group IV elements, in particular, silicon.

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References

1. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. E. Curl, and R. E. Smaley, *Nature*, 1985, **318**, 162.
2. H. W. Kroto, A. W. Allaf, and S. P. Balm, *Chem. Rev.*, 1991, **91**, 1213.
3. I. V. Stankevich, *Chem. Rev.*, 1994, **20**, 1.
4. E. Kaxiras, *Chem. Phys. Lett.*, 1989, **163**, 323.
5. D. W. Brenner, B. I. Dunlap, J. A. Harrison, J. W. Mintmire, R. C. Mowrey, D. H. Robertson, and C. T. White, *Phys. Rev. B*, 1991, **44**, 3479.
6. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.
7. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209.
8. M. Schmidt, K. K. Balridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupius, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
9. A Wells, *Structural Inorganic Chemistry*, vol. 3, Clarendon Press, Oxford, 1986.

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