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Computational Modeling of the Structure of Large Molecules: I. Molecule $C_{60}H_{12}$ and Cluster C_{852}

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Abstract—Structural parameters of dodecahydro-Buckminster fullerene $C_{60}H_{12}$ and its derivative, the carbon cluster C_{852} consisting of a central C_{60} dodecaradical and twelve peripheral C_{60} diradicals connected by eighteen –C≡C–C≡C– bridges, are calculated using a PM3 quantum-chemical method. The $C_{60}H_{12}$ molecule and the central fragment of the cluster each contain eight quasiaromatic six-membered rings with bond lengths of 1.38 and 1.43 Å. The calculations we performed using the GAMESS package and an original algorithm for diagonalization of dense symmetric matrices.

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The discovery of fullerenes, stable low-molecular carbon structures, gave rise to attempts to obtain new allotropic modifications of this chemical element. In particular, we suggest the synthesis of crystals consisting of Buckminster fullerene dodecaradicals C_{60} (Fig. 1) connected to a rigid structure by linear carbon bridges $–C_k–$. In this work we consider buta-1,3-diyne-1,4-diyl –C≡C–C≡C– bridges ($k = 4$) which provide auniform angular tension distribution within the 18-membered rings formed. Space between C_{60} polyhedrons can be filled by alloying component molecules.

The cluster C_{852} depicted in Fig. 2 represents a molecular form of pure carbon and simultaneously can be taken as a model of such a hypothetic crystal. This compound formally falls within the realms of general chemistry, but its synthesis should involve organic intermediates, such as the Buckminster-fullerene monoadduct $C_{60}X_2$ and hexaadduct $C_{60}(X_2)_6$.

The equilibrium structural parameters of the $C_{60}H_{12}$ hydrocarbon (Fig. 3) and C_{852} cluster (Fig. 4) were calculated with no symmetry constraints by the PM3 method using the GAMESS program package [1].

Since over the past decade the speed of computations has substantially increased, quantum-chemical calculations of large molecules by semiempirical methods (PM3, AM1, etc.) on a single computer are limited basically by memory resources for multiple diagonalization of the Fock matrix.

To extend the scope for application of a personal computer for quantum-chemical investigations of polyatomic chemical structures, we replaced the diagonalization algorithms in the original version of GAMESS [1] by a new algorithm for transformation of the dense symmetrical matrix to diagonal, developed by one of the authors (Yu.F. Sigolaev). The algorithm is based on the theory described in [2] and developed for overcoming constraints imposed by a

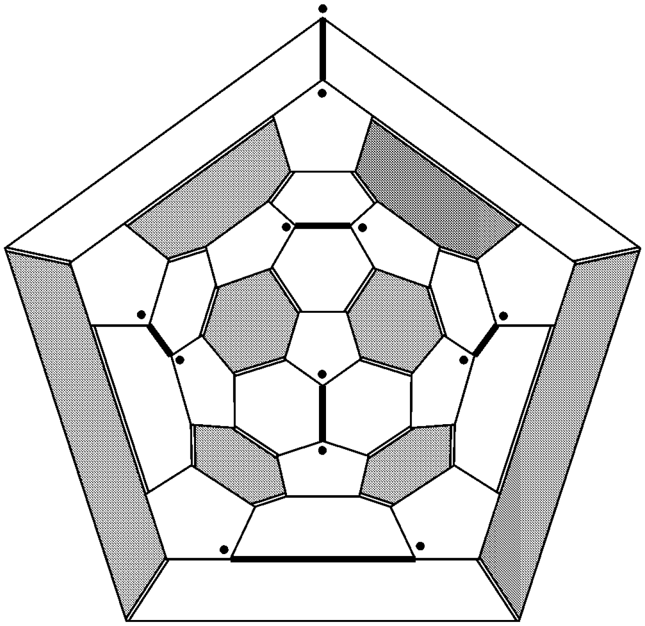

Fig. 1. Structural formula of the dodecaradical corresponding to the hydrocarbon $C_{60}H_{12}$. The single C–C bonds that were the double bonds in the parent C_{60} molecule are printed bold, and the quasi-aromatic six-membered rings are printed gray.

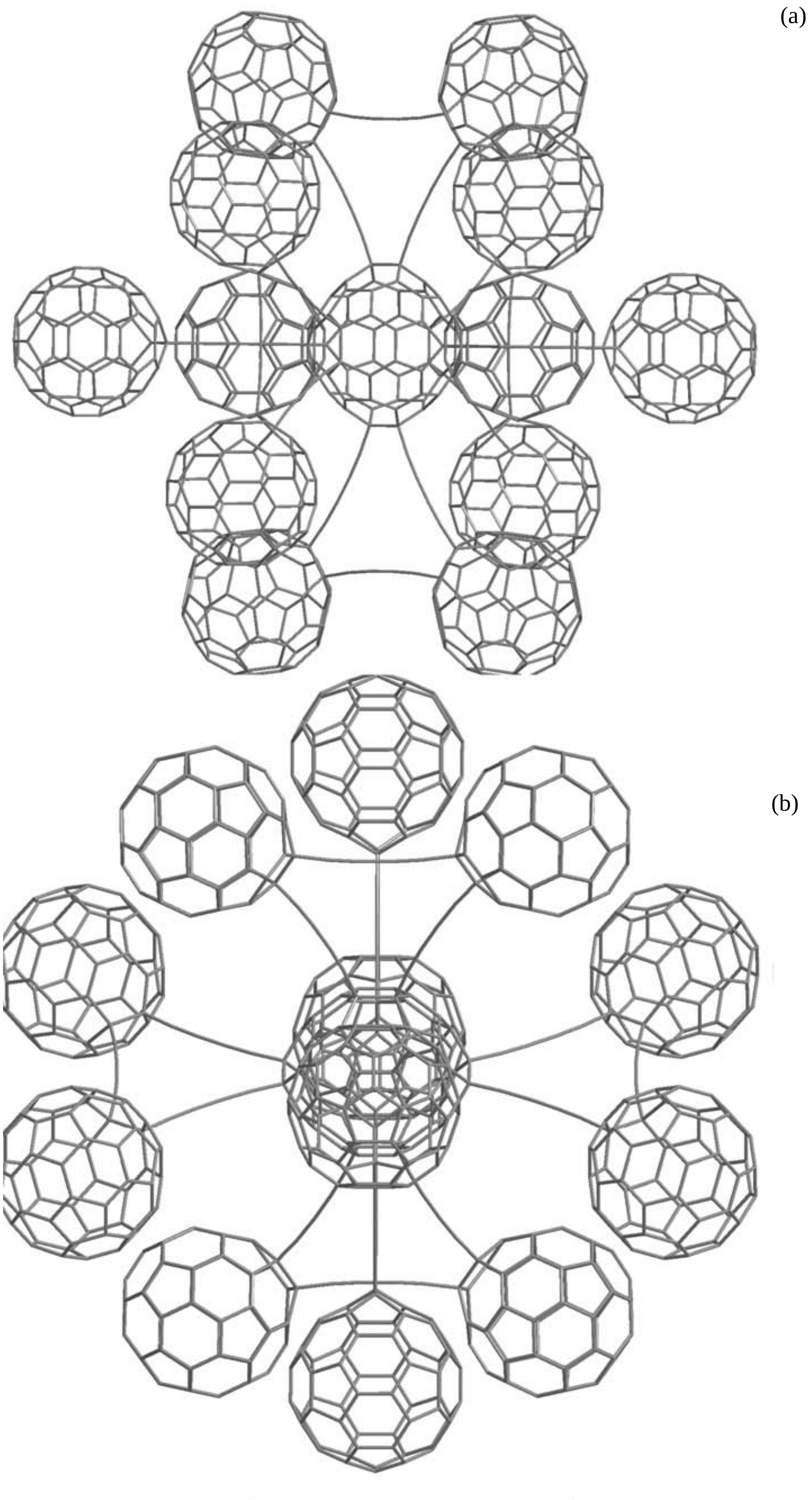

Fig. 2. Equilibrium structure of the C_{852} cluster. General view from two viewpoints (a, b).

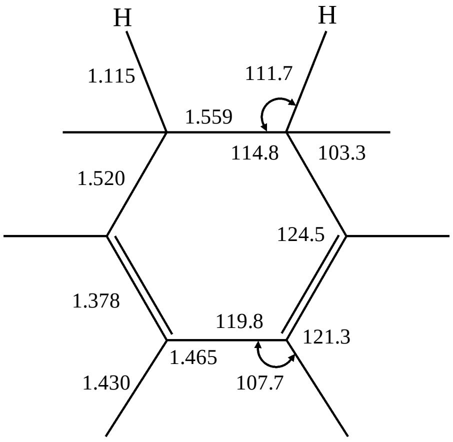

Fig. 3. Equilibrium internuclear distances (Å) and bond angles (deg) characterizing the structure of the $C_{60}H_{12}$ molecule.

32-byte architecture and accounting for the high speed of RAM processing in modern personal computers. Certain ideas of the newly developed algorithm (SDIAG) were adopted from our previous work [3]. Further development made it possible to diagonalize 22000–22000 matrices on a 2-Gb RAM computer, 15000–15000 matrices on a 1-Gb RAM computer, 11500–11500 matrices on a 512-Mb RAM computer, and 7500–7500 matrices on a 256-Mb RAM computer at a previously unattainable speed [4]. To reduce the RAM size, the SDIAG algorithm in the self-consistent field (SCF) procedure in combined with a new algorithm of density matrix calculation, which excludes the necessity of saving the eigenvector matrix of the Fock matrix.

The use of the SDIAG algorithm in the present work reduced the time of one SCF iteration in the calculation of the C_{852} cluster to 33.7 s, of which 26.6 s falls to diagonalization of the Fock matrix. For comparison, one SCF iteration in the known PC GAMESS program [5] takes 49.6 s and uses 6 times more RAM for diagonalization.

Both the $C_{60}H_{12}$ molecule and the central fragment of the cluster contain eight quasiaromatic six-membered rings which are characterized by widely varying calculated bond lengths (1.376–1.378 and 1.430 Å). In the Buckminster fullerene C_{60} molecule, there are, too, two types of carbon–carbon bonds (C=C and C–C). By single-crystal X-ray diffraction at 110 K, the following bond lengths were obtained for C_{60}, Å: C=C 1.340–1.391, C–C 1.378–1.561, average 1.355 and 1.467, respectively [6]. Neutron power diffraction at 5 K gave the following bond lengths, Å: C=C 1.366–1.412, C–C 1.420–1.487, average 1.391 and 1.455 Å, respectively [7]. Gas-phase electron diffraction experiment at 730°C gave average bond lengths of 1.401 and 1.458 Å [8]. According to PM3 calculations, the equilibrium C=C and C–C bond lengths are 1.384 and 1.458 Å.

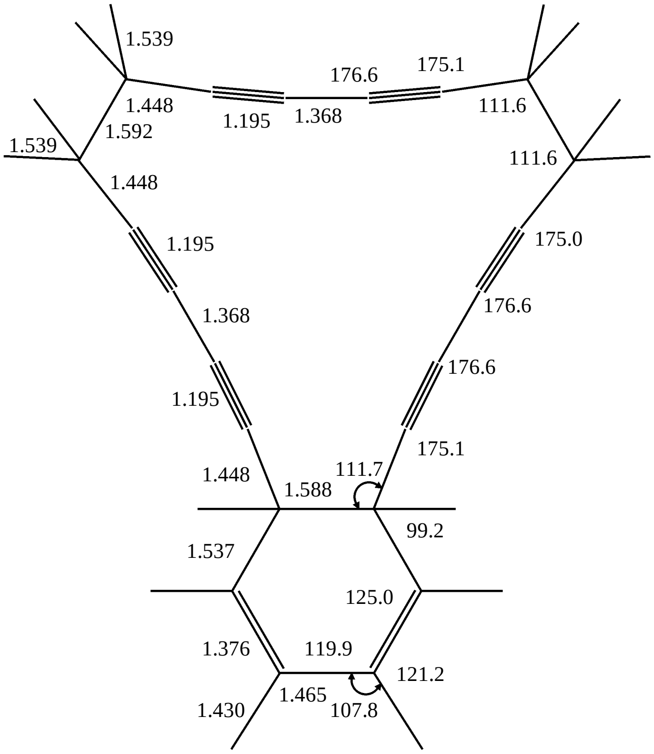

Fig. 4. Equilibrium internuclear distances (Å) and bond angles (deg) characterizing the structure of the C_{852} cluster.

The degradation of six double bonds in Buckminster fullerene upon addition to the latter of six hydrogen molecules is evidenced by their elongation by 0.175 Å (from 1.384 Å in C_{60} to 1.559 Å in $C_{60}H_{12}$). In the central fragment of C_{852}, these bonds become even longer (1.588 Å). The equilibrium molecular geometry of $C_{60}H_{12}$ is consistent with a T_h symmetry group. The Hessian eigenvalues $\nu_7 = \nu_8 = 243$ cm^{-1} correspond to a low-frequency doubly degenerate deformation vibration e_g of the polyhedron.

The four-atomic bridges between polyhedra forming a 18-membered rind are slightly concave. The bond angles deviate from 180° by no more than 5°. Because of the bent bridges, the bond angles formed by the degraded double bonds of the Buckminster fullerene (111.7°) differ as little as 2.2° from tetrahedral (109.47°). The bridge acetylenic fragments are conjugated through a formally single bond (1.368 Å) which is, however, 0.008 Å shorter than short bonds in quasiaromatic rings.

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