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Computer Modeling of the Structure of Large Molecules: III.[1] Local Excitations in the Structure of 2D C_{60}(XII) and C_{60}(VIII) Polymers

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Abstract — The quantum-chemical PM3 method was used to determine the structure of excited poly-C_{60}(XII) and poly-C_{60}(VIII) macromolecules containing diradical defects formed by cleavage of interpolyhedral C–C bonds and degradation of intrapolyhedral C=C bond. The relative energies of such excitations are estimated. The atomic free valences F_A hybridization coefficients of valence-active atomic orbitals contributing maximum $F_a \approx F_A$ to the F_A value are calculated. The valent isomerism of the C_{60}(XII) dodecaradical is discussed. The calculations are performed using the GAMESS computer program and a new SDIAG algorithm for diagonalization of large dense symmetric matrices.
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Fullerite consisting of C_{60} buckminsterfullerene molecules is known to undergo photochemical oligomerization if the photon energy is higher than 1.7 eV (39 kcal mol^{-1}) and polymerization at sufficiently high pressures and temperatures [1–3]. Structure of a two-dimensional (2D) polybuckminsterfullerene(VIII) has been studied by us in [4]. In the present work we used the same procedure for determinining the geometric parameters, symmetry (D_{3d}), and vibration frequencies of a C_{420} cluster, the buckminsterfullerene heptamer (Fig. 1a), which is a model of the metastable (under ambient conditions) rhombohedral phase of polymeric C_{60}(XII).[2]

Heating of the polymer to 650 K results in its decomposition into monomers [1]. At lower temperatures, local defects may arise due to cleavage of single interpolyhedral bonds and degradation of double intrapolyhedral bonds. We performed a quantum-chemical investigation of diradical structural defects of this type in the C_{420} (Fig. 1) and C_{540} (Fig. 2) clusters which model the macromolecules (monolayers) of poly-C_{60}(XII) and poly-C_{60}(VIII), respectively. The calculations were performed at the semiempirical PM3 level using the GAMESS computer program [7] and SDIAG algorithm [4, 8, 9].

The diradicals formed by thermal excitation of an olefin or cleavage of a four-membered ring have been considered in [10, 11]. In the absence of magnetic field, the diradical states are considered as fourfold degenerate (or quasi-degenerate) electronic states with practically coinciding equilibrium nuclear configurations described by the same formula [10, 11]. The four orthonormal wave functions of the diradical state can be transformed into singlet and triplet wave functions. In this study we calculated the equilibrium structure of the diradical in the ROHF approximation, fixing spin quantum numbers M_S = S = 1.

The diradical free valence distribution between atoms $F2$ is described by the free valence indices F_A (denoted as D_A in [12]). By maximization of the orbital contribution F_a to the atomic free valence $F_A = \Sigma_a F_a$ we determined the hybridization coefficients of valence-active atomic orbitals and the max$F_a \approx F_A$ value (see table).

The F_A indices indicate that the electron excitation is localized in the vicinity of the atoms marked by points in the figures. If single bridging bonds between polyhedra are cleaved, the free valence of the ·C atom (F_A 0.61–0.71) is localized on a single valence-active AO consisting mainly of $2p$ orbitals (96% in the dimer, 98% in the polymer). On degradation of a double bond [(*) in poly-C_{60}(VIII), see Fig. 2] the free

[1] For communication II, see [1].

[2] The lattice constant 9.12 Å obtained by us is less than the ealyer published values: 9.20 Å [2], 9.22 Å [3], 9.17 Å [5] and 9.19 Å [6].

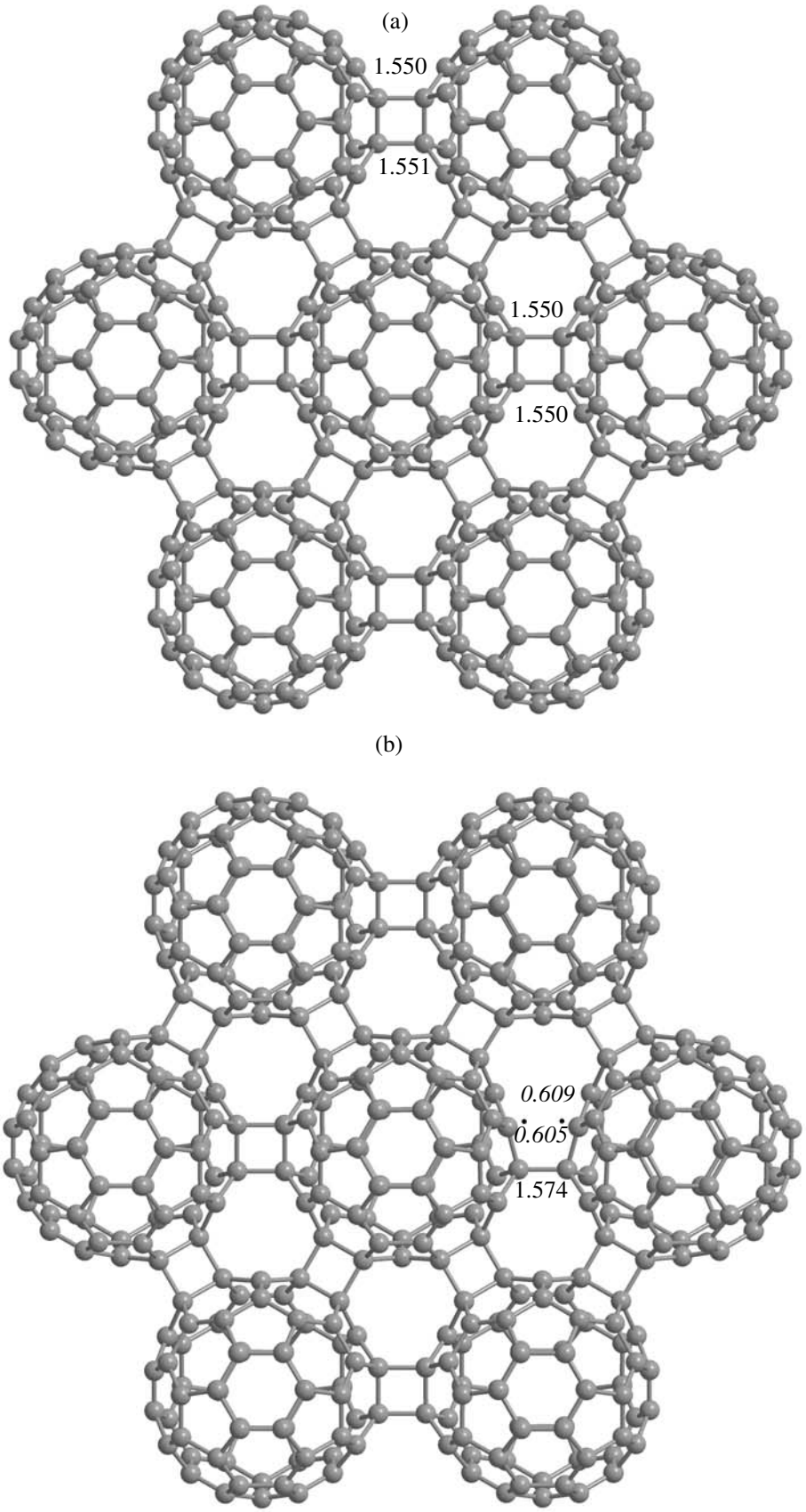

Fig. 1. Cluster C_{420} modeling the poly-C_{60}(XII) macromolecule in the (a) ground and (b) excited states.

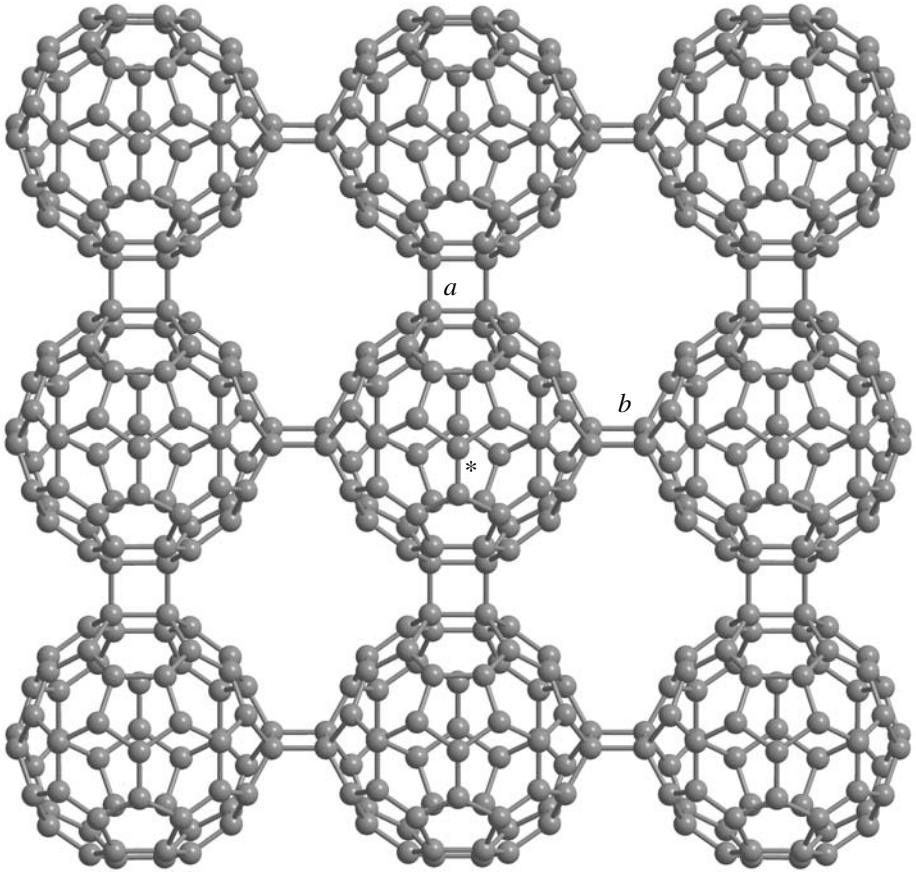

Fig. 2. Cluster C_{540} modeling the poly-C_{60}(VIII) macromolecule in the ground state.

valence is localized to a greater extent (F_A 0.76), and valence-active AOs of the arising ·C–C· defect are *p*-type by 91%. Because of the curved surface of the buckminsterfullerene fragment, they are not parallel and form a 26° angle to one another and a 77° angle to the ·C–C· bond line.

The equilibrium bond lengths and lattice constants (*a* 9.016 Å and *b* 9.085 Å) in an ideal polymer modeled by the C_{540} cluster (Fig. 3a) do not differ from that obtained earlier by modeling with the C_{1500} cluster [4]. The calculated energy of the double bond degradation "*" C=C (1.379 Å) $\longrightarrow$ ·C–C· (1.494 Å, Figs. 2 and 3b) is lower by 1 kcal mol^{-1} than in the free buckminsterfullerene (39 and 40 kcal mol^{-1}, respectively). The cleavage energies of single bridging bonds of the "*a*" and "*b*" type (see Figs. 2, 3c, and 3d) are higher: 57 and 53 kcal mol^{-1}, respectively. In the "*a*" case, the valence-unsaturated carbon atoms ·C are less distant (2.304 Å) than in the "*b*" case (2.386 Å).

The cleavage of one of the twelve equivalent bridging bonds formed by the central polyhedron (Fig. 1)

Free valence indices maxF_a and hybridization coefficients of the valence-active AOs of excited dimer $(C_{60})_2$ and central polyhedron in excited heptamer $(C_{60})_7$ and nonamer $(C_{60})_9$

Cluster	Defect	max F_a	2*s*	$2p_x$	$2p_y$	$2p_z$
$(C_{60})_2$	·C–C–C–C·	0.705	0.193	0.876	–0.441	0.000
$(C_{60})_7$	·C–C–C–C·	0.609	0.133	0.959	0.229	0.107
$(C_{60})_9$	·C–C–C–C· (*a*)	0.659	0.137	–0.266	0.954	0.000
$(C_{60})_9$	·C–C–C–C· (*b*)	0.673	0.162	0.941	0.000	0.297
$(C_{60})_9$	·C–C· (*)	0.762	0.295	0.000	±0.216	0.931

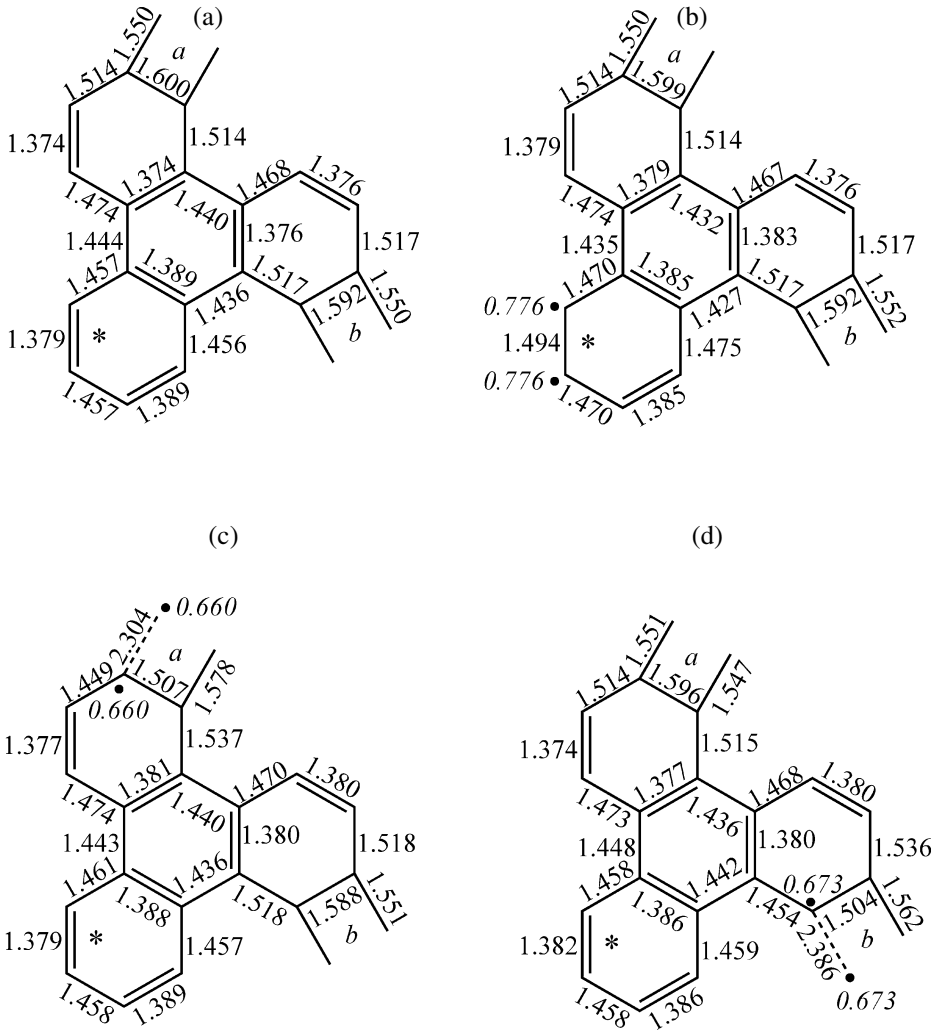

Fig. 3. Free valences of atoms and internuclear distances (Å) characterizing the equilibrium structure of (a) ideal poly-C_{60}(VIII), (b) vicinity of degrading double bond, and (c, d) vicinity of cleaved bridging bond.

requires 55 kcal mol^{-1} (or 53 kcal mol^{-1} with zero-point vibration correction). These values are much higher than the average energy of single bridging bond in the cluster: 16.6 kcal mol^{-1} per each of 24 bonds. The length of the neighboring bridging bond increases by 0.024 Å as a result of the considered electron excitation, the distance between the C atoms becomes 2.294 Å, and the cluster symmetry is lost completely. The absence of imaginary frequencies in the vibration spectra of the ground and excited states provide evidence showing the equilibrium geometry to the C_{420} cluster corresponds to the energy minimum.

The valence state of the dodecaradical C_{60}(XII) in the polymer differs significantly from its valence state in the hexakisadducts like $C_{60}[Pt(PEt_3)_2]_6$ [13] and $C_{60}[C(CO_2(CH_2)_{10}OC_6H_4C_6H_4CN)_2]_6$ [14]. In the dodecaradical which comprises the rhombohedral phase of the polymer, the free valences are located equatorially, and the valence state is characterized by a D_{3d} symmetry point group. In the hexakisadducts, the valance-active atoms of the dodecaradical are distributed uniformly over the C_{60}(XII) polyhedron surface. In an analogous hypothetical symmetrical dodecahydrobuckminsterfullerene [8], the polyhedron belongs to a T_h point group.

The two C_{60}(XII) isomers can be compared with two different exited states of the free buckminsterfullerene molecule with the spin multiplicity 2S + 1 = 13 and with the corresponding localization of free valences. According to calculations, the energy of the free dodecaradical C_{60}(XII, T_h) is much lower than that of the free dodecaradical C_{60}(XII, D_{3d}), by 10.3 kcal mol^{-1} 1without account for nuclear relaxa-

tion, by 15.1 kcal mol^{-1} with account for geometry changes (compared to *symm*-$C_{60}H12$), and by 14.0 kcal mol^{-1} with account for zero-point vibrations. The relatively highe energy of the C_{60}(XII, D_{3d}) state together with the steric factor and strain of the four-membered rings, on the one hand, and the fact that the cleagave energy of a single bridging bond is three times the average energy of bridging bonds, on the other hand, explain the metastability of the rhombohedral phase of the polymeric buckminsterfullerene under ambient conditions.

However, such estimation of the energy of valence state neglects the electron exchange between radicals, which results in that the number of electrons in each of them is indefinite. The valence state is not a "pure" state and cannot be described by a wave function. Although the average number of electrons (360, including 120 core electrons) coincides with the number of electrons in the free dodecaradical, the dispersion of the number of electrons in the onedeterminant approximation is half the valence [15, 16], and rms deviation of the number of electrons from the average value in any dodecaradical equals $(12/2)^{1/2} = 2.45$.

Unlike the corresponding diradical defects in the 2*D* polymers, cleavage of one bridging bond in the dimer $(C_{60})_2$, shown on Fig. 4a, turns one polyhedron relatively to another by 180° around the second bridging bond (Fig. 4b). Therewith, the internuclear distance between the valence-unsaturated carbon atoms increases to 3.95 Å, while the calculated energy of the excited state decreases to 45.5 kcal mol^{-1} (44.1 kcal mol^{-1} with zero-point vibration correction). This energy is higher than necessary to cleave the dimer into monomers (36.3 kcal mol^{-1} with zero-point vibration correction).

Thus, the cleavage energy of a single C–C bridging bond depends on the distance between the ·C atoms. The fact that the radical centers are impossible to separate effectively in the rigid structure of the 2D polymer retards its decomposition into monomers at not too high temperatures. On the other hand, the stability of the 2D polymer toward transformation to a 3D polymer is provided by remoteness of diradical defects formed by double-bond degradation in neighboring monolayers. Cross-linking of the polymer layers by bis-single bonds is impossible, when valence-active atoms of one excited macromolecule $(C_{60})_n$ reside in the bunker between polyhedra of a neighboring macromolecule. The source of the $(C_{60})_2$ dimers that are present, together with C_{60} monomers, in the thermolysis product of polybuckminsterfullerene can be not only the decomposing polymer, but also buckminsterfullerene diradicals, because the energy of double-bond degradation is lower than the energies of cleavage of separate bridging bonds, even if it is higher than the average energy.

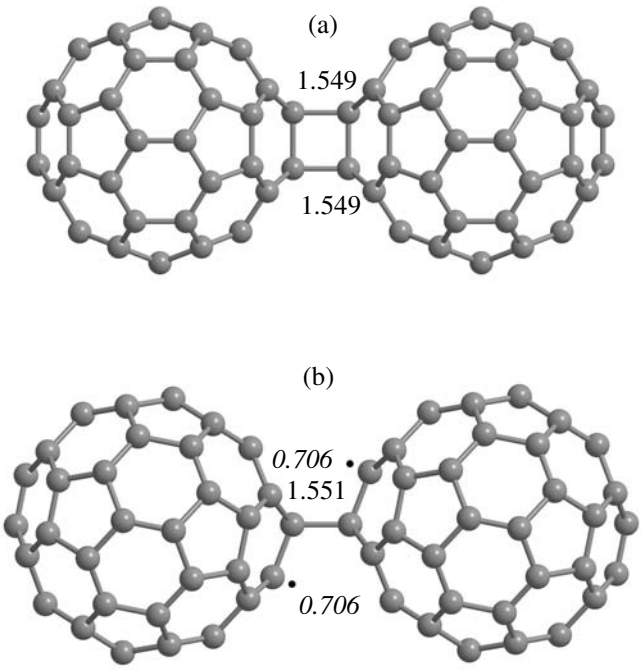

Fig. 4. Equilibrium structure of the $(C_{60})_2$ dimer and the diradical formed by cleavage of one single bridging bond (projection on the tetra-atomic ring plane).

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