

DFT/PBE study of IE, EA, cation and anion structures

of functionally substituted fullerenes.

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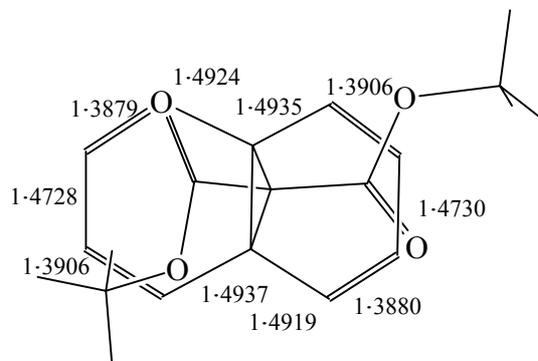
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Molecular structure, ionization energy and electron affinity, geometries and electronic structure of cation and anions radicals, di and trianions of fullerene C₆₀ (1) and methanofullerenes C₆₁H₂ (2), C₆₁H (COOMe) (3), C₆₁ (COOMe)₂ (4), C₆₁(COOEt)₂ (5), C₆₁(COOMe)[P(O)(OMe)₂] (6), C₆₁H [P(S)(OMe)₂] (7), C₆₁[P(S)(OMe)₂]₂ (8), C₆₁H [P(O)(OMe)₂] (9), C₆₁[P(O)(OMe)₂]₂ (10), C₆₁H₂CN (11), C₆₁(COOMe)CN (12) and C₆₁(CN)₂ (13) are studied by DFT/PBE method with TZ2P basis. We found monotony of change of geometrical parameters, IE and EA explored methanofullerenes 2-13. The calculations 2 and 13 ab initio with basis STO 3G up to 6-31G ** and semiempirical methods MNDO, PM3 and AM1 result in the same sequence of the upper occupied orbitals b₂, b₁, a₂, a₁ and lower unoccupied orbitals a₁, b₁, b₂. For compounds 3-12 relevant properties of symmetry of frontal orbitals are conserved approximately. The calculations by a method DFT/PBE show that the model HOMO-LUMO rather approximately features quantities IE and EA, charge distribution, spin densities, lengthening or shortening of single and double bonds in cations, anions and multiply charged ions. In particular conduction of the first and second electrons to the greatest degree lengthening eq1 bonds, the third electron does not affect this bonds.

Alternation and attenuation of change of bond lengths in the conjugate branches cis1-cis2-eq2-tr3 and cis1-cis3-tr4-tr2-tr1 is established. In cations and anion - radicals the polarization effects are developed more intensively, double bond lengths, charges and spin density are alternation. The mechanism of retro-Bingel reaction at the cleave of two C-C bonds between the C(61) atom and fullerene shell accompanied by

electrochemical electron transfer was proposed. For di- and trianions of 6 the transition structures of retro-reaction are localized. The stable conformations 4-6, 10 and their anion of radicals are explored. The difference of EA of conformers are no more than 0.10 eV.



Symmetry and asymmetry of the properties of methanofullerenes 2-13 and their cation and anion structures are explored also. Asymmetric addends C₆₁XY (X, Y = COOMe, COOEt, P(O)(OMe)₂, P(S)(OMe)₂) divide fullerene core on four nonequivalent fragments. According to calculations by method DFT/PBE the most stable conformations of methanofullerenes C₆₁XY are characterized by Coulon interaction of phosphoryl, carbonyl or ester oxygen atoms of with one of carbon atoms of fullerene core and polarization of the appropriate fragment. It creates asymmetry of bonds lengths, charges and spin densities of fullerene core. In cation and anion radicals the asymmetry of fragments is expressed in the greater degree. The asymmetry of four fragments is a consequence of through space interaction of atoms addends with fullerene shell.

Theoretical results are compared to the experimental data. The programs PRIRODA and GAMESS are used.

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