A p-electron conjugation in fullerenes and carbon nanotubes

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Properties of fullerenes and nanotubes are considerably determinel by conjugated p-electron system. If the p_Z-AO axes coincide with a perpendiculars to a core plane in a hydrocarbon conjugated molecules then in fullerenes and nanotubes the p_Z-AO axes coincide with a normals to spherical and cylindrical surfaces, respectively. Therefore π– and σ–electron systems are not orthogonal in these molecules. This fact bears witness about a distinction of π - conjugation in a plane molecules from ρ-conjugation [1] in fullerenes and nanotubes.

For an investigation of ρ-conjugation peculiarities we made calculations of the two groups of molecules with ab initio Hartry-Fock method in 3-21G basis set: 1) cis- and trans-polyenes and 2) polyacenes and polyphenes. In every group was examined the following location of carbon atoms: a) open on a plane (linear), b) cycled on a cylindrical surface (cyclic), c) cycled on an one-side Mobius surface (mobius). A double C-C bond number n is equal n=6-16 in the first group, a hexagon number m – m=6-16 in the second group.

As distinctive characteristics of p-electron conjugation the value of the band gap is used. The carried out calculations show:

1) The value ΔE for all types of cis-polyenes decreases monotonously asymptotically with an increase of n (n is even for a security of a chosen structure), for all types of cis-polyenes there is $\Delta E_{lin} < \Delta E_{mob} < \Delta E_{cyc}$.

2) The value ΔE for linear trans-polyenes decreases monotonously asymptotically with an increase of n, ΔE_{cyc} oscillates asymptotically with an increase of n, what a maxima of amplitude reaches when n is odd, ΔE_{mob} oscillates also asymptotically with an increase of n though oscillations have enough rather a complicated character.

3) The value ΔE for linear polyphenes decreases monotonously asymptotically with an increase of m (m is even for a security of a chosen structure), for cyclic and mobius polyphenes ΔE increases monotto asymptotically with an increase of m. Fof all types of polyphenes there is $\Delta E_{cyc} < \Delta E_{lin} < \Delta E_{mob}$.

4) The value ΔE for linear polyacenes decreases m monotonously asymptotically with an increase of m, ΔE_{cyc} oscillates asymptotically with an increase of m, maxima of amplitude are reached when n is odd, ΔE_{mob} also oscillates asymptotically with an increase of m though oscillations have rather a complicated character.

Thus, ρ-conjugation of carbon atoms situated on non-linear surfaces has a peculiarities distinguishing from π-conjugation of a plane hydrocarbon molecules.

[1] D.A. Bochvar, E.G. Galpern, *Dokl. Akad. Nauk SSSR* **209**, 610 (1973).