Bonding, Electron Densities and Vibration Frequencies of [3]-, [4]-, [5]- and [6]-Radialenes; a B3LYP Density Functional Study

Muthana Shanshal and Rehab M. Kubba

Department of Chemistry, College of Science, University of Baghdad, Jadiriya, Baghdad, Iraq

Reprint requests to Prof. M. S.; E-mail: mshanshal2003@yahoo.com

Z. Naturforsch. 61a, 95 – 98 (2006); received October 26, 2005

B3LYP density functional treatment is reported for the [3]- to [6]-radialene. For the first two molecules the corresponding $D_{nh}$ symmetry resulted from the treatment. For the [5]-radialene, the completely planar $D_{5h}$ structure was found energetically a non-minimal configuration showing two imaginary vibrations. An almost planar $C_{1}$ structure of [5]-radialene emerged as the stable species. As for [6]-radialene, the planar $D_{6h}$ structure proved to be a non-minimal structure too, showing three imaginary vibrations. The $D_{3d}$ chair form was most stable, followed by a twisted boat form of the molecule. The chair form of [6]-radialene was more stable than the twist boat form by 0.9 kcal/mol. Variation of the bond lengths, of $A_{1g}$ ($\nu_{CC}$ and $\nu_{CH}$) vibration frequencies as well as of the total ($\rho^{tot}$) and $\sigma$ ($\rho^{\sigma}$) electron densities for the four molecules, compared with those of ethylene, is discussed. To explain the results, a bonding model for the radialene rings is suggested, which assumes an sp hybridization of the ring atoms in [3]- and [4]-radialenes going over to sp$^{2}$ hybridization in [5]- and [6]-radialenes.

Key words: Radialene; Frequency; Geometry; Density.