**Abstract**

The molecular oxygen interacting properties of polyethylene (PE) chain with three different conformations (PE1, PE1 and PE3) have been explored using ab initio method. The isolated (PE) and complex PE…O2 systems were obtained using HF/6-31G level of theory. In order to understand the structural propensities of the isolated PE chains and their oxygen complexes, comparative analysis on geometrical parameters was carried out. The natural bond orbital analysis (NBO) was employed, to examine the non-bonded inter-actions that are present in the PE…O2 complexes. The calculated occupation numbers of the bond and the antibond orbitals were used, to study the nature of the non-bonded interactions of C-H…O type. The two body analysis was employed to calculate the interaction energies (∆E) of PE systems with the guest molecular oxygen, and the tendencies of ∆E, in the considered PE systems was also explored.