INTER-RING AND HEXYL CHAIN TORSIONAL POTENTIALS IN POLY (3-HEXYLTHIOPHENE) OLIGOMERS: SCALING WITH THE LENGTH OF THE CONJUGTED POLYMER BACKBONE

RAM S. BHATTA, DAVID S. PERRY, *Department of Chemistry, The University of Akron, OH 44325-3601*; YENENEH YIMER AND MESFIN TSIGE, *Department of Polymer Science, The University of Akron, OH 44325-3909*.

Density functional theory calculations are presented for the equilibrium structures and torsional potentials for isolated Poly (3-Hexylthiophene) (P3HT) oligomers up to 12 monomer units (up to 302 atoms). Calculations were performed at B3LYP/6-31++G(d,p) treating both the backbone of thiophene rings and the hexyl chains explicitly. One-dimensional inter-ring torsional potentials were calculated by rotating backbone around the central inter-ring bond and hexyl torsional potentials were calculated rotating n-hexyl group adjacent to the central inter-ring bond for each oligomer. The torsional and electronic properties change significantly for oligomers with 2 to 8 units but reach asymptotic values for a 10 unit P3HT chain, thereby suggesting the 10 unit long oligomer as a molecular model for the extended polymer. For P3HT oligomers having 10 or more units, all the rings and the hexyl groups are approximately coplanar except for one hexyl group at head end. The principal interaction that promotes the coplanarity of the hexyl groups is the attraction of the proximal methylene hydrogens to the sulfur on the adjacent thiophene ring. The cis conformation of the backbone is about 2kT higher than the trans minimum at room temperature. The gauche conformation of the hexyl group is within about half kT of the planar minimum. Therefore conformational polymorphisms of both types will likely be significant in the heterogeneous environment of photovoltaic devices.