

Correlated ab initio and density functional calculations on small model molecules for the unit cell of polyparaphenylene in its aromatic and quinoidal forms: equilibrium geometries and vibrational spectra. Forner, Wolfgang; Utz, Wolfram

Abstract

The density functional theory (DFT) was applied to biphenylene (BP) and terphenylene (TP), and also MP2 (Moller-Plesset perturbation theory of 2nd order) to BP. Further, the corresponding model molecules for the quinoidal B phase were studied. These are the molecules of interest because they are oligomers of polyparaphenylene (PP) in its aromatic (A-phase) and quinoidal (B-phase) form. This polymer is of importance because of its blue light emission. In BP and TP, DFT turned out to yield reliable structures, which as far as the important torsional angle between the rings is concerned, is even better than MP2. Also the vibrational spectra are in fair agreement with experimental ones. In BP, restricted Hartree Fock (RHF), DFT and experimental IR spectra all show 2 very intense absorptions around 700 cm^{-1} , while MP2 gives only one intense absorption band in this region. DFT also reproduces the position of these 2 lines rather well. Superposition of the vibrational IR spectra of TP and of the B-phase model molecule reveals that features could be detected in the spectra of the doped polymer which would indicate B-phase, and therefore the presence of bipolarons in the doped material. Further, this might lead the way to an experimental estimate of the width of such bipolarons, if present at all.