

The Pariser-Parr-Pople model for trans-polyenes. I. Ab initio and semiempirical study of the bond alternation in trans-butadiene. Foerner, Wolfgang

Abstract

Ab initio investigations of the bond alternation in butadiene are presented. The at. basis sets applied range from minimal to split valence plus polarization quality. With the latter one the Hartree-Fock limit for the bond alternation is reached. Correlation is considered on Moeller-Plesset many-body perturbation theory of second order (MP2), linear coupled cluster doubles (L-CCD) and coupled cluster doubles (CCD) level. For the smaller basis sets it is shown that for the bond alternation π - π correlations are essential while the effects of r - σ and σ - π correlations are, though large, nearly independent of bond alternation. On MP2 level the variation of σ - π correlation with bond alternation is surprisingly large. This is discussed as an artifact of MP2. Comparative Su-Schrieffer-Heeger (SSH) and PPP (PPP) calcns. show that these models in their usual parametrizations cannot reproduce the ab initio results.