Theoretical study of bipolaron dynamics in polyparaphenylene: II. Density functional theory (DFT) calculations on neutral dimers and semiempirical Hueckel-type calculations on neutral and charged model chains. Foerner, Wolfgang

Abstract

We have derived earlier the rather lengthy formalism for time simulations in poly(p-phenylene), treating the rings as semirigid rotors. To this end the Euler-Lagrange formalism had to be used. As a first step we intended to parametrize the simplified Hueckel-type hamiltonian on the basis of d. functional theory (DFT) calcns. on some dimeric model systems. The results of this attempt are reported here. However, calcns. on much longer chains, contg. up to 200 rings, show a clear tendency of our model to favor the quinoid B-phase structure over the arom. one. Further, in doubly charged chains, the charge tends to remain unsepd. and to be completely delocalized over virtually the complete part of the chain, that is in B-phase conformation. The bipolaron width turns out to be extremely small, of about 10 rings in a chain having 200 rings. This is rather unexpected and interpreted as a shortcoming of the Hueckel-type nature of the hamiltonian. The reason is that in the Hueckel-type model the two electrons, taken away to charge the chain, are from the same orbital, and thus charge sepn. is more difficult, leading, in this case, only to a delocalization, keeping the bipolaron small. We assume, that in line with Prof. Paldus' work, the inclusion of direct electron-electron interactions in the form of a PPP (PPP) type model could overcome this difficulty. The treatment has to be done, probably, in an open shell form to make possible spin sepn., if necessary. Care has to be taken for spin contaminations in such treatments and possibly even the explicit inclusion of electron correlation might be necessary. In this paper we report our model which was derived in detail in a previous paper. Then we discuss the parametrization attempts and our results on longer chains. In conclusion our suggestion is that a PPP type model must be used at least to allow for bipolaron calcns. and confinement of the two like charges. Such calcns. would be the content of a forthcoming paper.