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Tight-binding total-energy method applied to polyacetylene

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We apply the tight-binding total-energy method to the study of energetic, structural, and elastic properties of different polyacetylene isomers. Our results show good agreement with experimental and *ab initio* theoretical results, suggesting that this simpler method can be useful in the study of conjugated polymers.

I. INTRODUCTION

The discovery[1] in 1977 that polyacetylene (PA) can be doped up to high degrees of conductivity initiated an era of extremely active research on this and related materials with attractive electrical and/or optical properties, so-called conjugated polymers. Because of its simplicity, the PA chain, particularly the *trans*-PA (TPA) configuration, has been the subject of most theoretical and experimental investigations. It is the prototype of all quasi-one-dimensional conducting polymers and, therefore, the benchmark for testing novel calculation techniques in organic polymers.

The role of electron-lattice interaction and disorder in affecting the structural, electronic, and optical properties of conjugated polymers cannot be overemphasized. In this regard, we can find two lines of theoretical study on structural and electronic properties in conjugate polymers: (i) simple models to explain the electronic structure and conductivity properties where these effects are introduced in a simplified form by fitting experimental data[2] and (ii) *ab initio* calculations for small molecules or perfectly periodic chains where disorder cannot be included due to computational difficulties.[3]

In this work we introduce an alternative technique known as the tight-binding total-energy (TBTE) method. The TBTE method, first introduced long ago by Chadi,[4] has become increasingly popular in the last ten years as an intermediate description between classical potentials and fully quantum-mechanical *ab initio* methods to describe structural and dynamical properties of semiconductors. It consists in separating the total energy into electronic and repulsive contributions. The electronic part (E_{ele}) is calculated by adding the occupied eigenvalues of a tight-binding Hamiltonian and therefore incorporates a quantum-mechanical description of bonding. The repulsive part (E_{rep}) is usually a two-body functional which takes into account in an empirical way the core-core and overlap repulsions, as well as the double counting of the electronic energy in E_{ele}.

Although originally developed for semiconductors, the TBTE method has been extended by Wang *et al.* to describe carbon nanostructures[5] and more recently by Horsfield *et al.* for hydrocarbons.[6] In this work we explore the possibility of using the TBTE method within the parametrization proposed by Horsfield *et al.* to describe energetic, structural, and elastic properties of conjugated polymers, more specifically PA. Our focus will be on comparing the TBTE predictions with existing experimental or theoretical results.

II. METHOD

In the TBTE method the total energy is written as

$$E_{tot}=E_{ele}+E_{rep}, \tag{1}$$

where E_{ele} is the sum of electronic eigenvalues over all occupied states, and E_{rep} is a short-range repulsive energy. For hydrocarbons,[6] the electronic eigenvalues are obtained by solving the tight-binding Hamiltonian H_{TB} including sp^3 orbitals for the C atoms and s orbitals for the H atoms. The σ bonding is therefore included explicitly in the model, contrary to most TB descriptions of conjugated polymers which retain only the π electrons.[7]

The off-diagonal elements of H_{TB} are described by a set sp^3 of two-center hopping parameters, $V_{ss\sigma}(r)$, $V_{sp\sigma}(r)$, $V_{pp\sigma}(r)$, and $V_{pp\pi}(r)$. Electron-lattice coupling is built into the model through the dependence of these matrix elements on the interatomic separation r, $V_\mu(r)=V_\mu(r_0)h(r)$, where the scaling function $h(r)$ is given by

$$h(r)=\left(\frac{r_0}{r}\right)^n e^{n[-(r/r_c)^{n_c}+(r_0/r_c)^{n_c}]}. \tag{2}$$

On-site elements of H_{TB} are the atomic orbital energies $\epsilon_{i\alpha}$, where i denotes the atom type (C or H) and $\alpha=s$ or p. In systems containing only carbon and hydrogen, very little charge transfer takes place. Therefore it is reasonable to impose local charge neutrality (LCN) self-consistently through shifts in the on-site energies $(\epsilon_{i\alpha})\rightarrow\epsilon'_{i\alpha}=\epsilon_{i\alpha}+\Delta\epsilon_i$. The shifts depend only on the site and not on the orbital (thus all the orbitals on one site shift together). LCN is achieved when the number of electrons on each site equals the number of valence electrons of each atomic species (4 for C and 1 for H).

The repulsive energy is modeled by

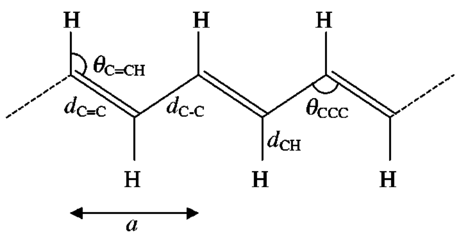
$$E_{rep}=\sum_i \mathcal{F}\left(\sum_j \phi(r_{ij})\right) \tag{3}$$

where $\phi(r_{ij})$ is the pairwise repulsive interaction between atoms i and j,

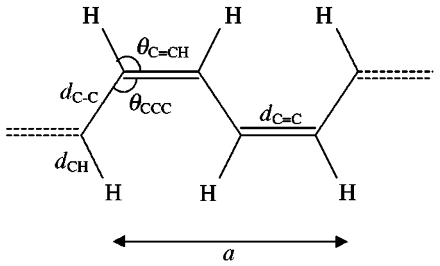
$$\phi(r)=\phi_0\left(\frac{d_0}{r}\right)^m e^{m[-(r/d_c)^{m_c}+(d_0/d_c)^{m_c}]} \tag{4}$$

and $\mathcal{F}(x)$ is an embedding function expressed as a fourth-order polynomial with argument $x=\Sigma_j\phi(r_{ij})$,

(a) *Trans*



(b) *Cis-transoid*



(b) *Trans-cisoid*

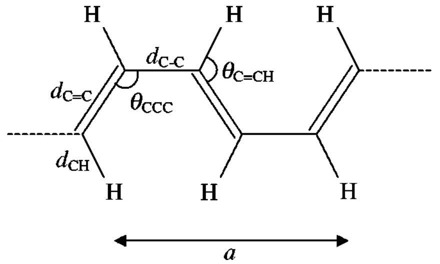


FIG. 1. Geometry and definition of structural parameters for (a) *trans*- polyacetylene (TPA), (b) *cis-transoid* polyacetylene (Ct-PA), and (c) *trans-cisoid* polyacetylene (Tc-PA).

$$\mathcal{F}\left(\sum_j \phi(r_{ij})\right)=\sum_{i=1}^{4} A_i\left(\sum_j \phi(r_{ij})\right)^i. \tag{5}$$

The functions $h(r)$ and $\phi(r)$ go smoothly to zero beyond some designated cutoff distance r_{cut}, a particularly desirable feature for eventual molecular dynamics applications. This is accomplished by replacing the tails of these functions, between r_1 and r_{cut}, by a third-order polynomial with the functional form

$$t(r)=B_0+B_1(r-r_1)+B_2(r-r_1)^2+B_3(r-r_1)^3, \tag{6}$$

where the coefficients are given by $B_0=f(r_1)$, $B_1=f'(r_1)$, $B_2=-2(B_1/\Delta)-3(B_0/\Delta^2)$, $B_3=(B_1/\Delta^2)+2(B_0/\Delta^3)$, $\Delta=(r_{cut}-r_1)$, and $f(r)$ is the replaced function [$h(r)$ or $\phi(r)$]. The full set of numerical parameters is given in Ref. 6.

III. RESULTS AND DISCUSSION

We focus initially on the energetics and geometry of the different polyacetylene isomers, namely, *trans* [TPA, Fig. 1(a)], *cis-transoid* [Ct-PA, Fig. 1(b)], and *trans-cisoid* [Tc-PA, Fig. 1(c)]. Supercells with periodic boundary conditions along the chain axis are used. Equilibrium energy and lattice constant a are obtained for each of the three isomers by the position of the minimum in the total energy vs lattice constant plot, shown in Fig. 2, for supercells with 10 C_2H_2 units. All atomic coordinates are fully relaxed for each lattice constant. We find $a_0=2.444$ Å for TPA, $a_0=4.263$ Å for Ct-PA, and $a_0=4.304$ Å for Tc-PA. These values are in excellent agreement with the experimental lattice constants: 2.46 Å for TPA,[8] and 4.38 Å for *cis*-PA.[9]

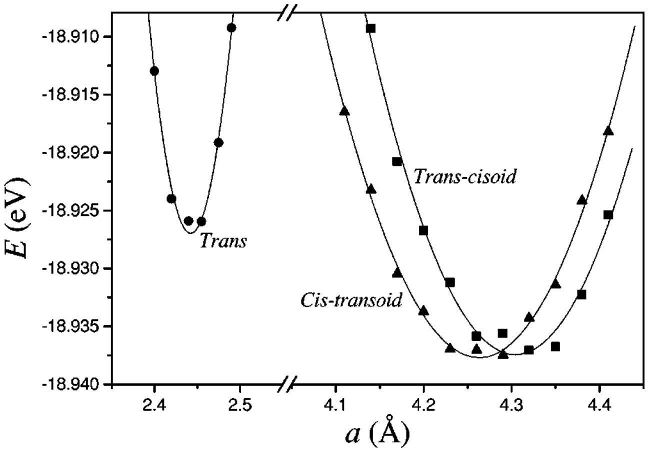


FIG. 2. Total energy vs lattice constant for TPA (circles), Ct-PA (triangles), and Tc-PA (squares).

Experimentally, the polymerization process generally leads to the formation of *cis*-PA, and TPA is obtained by heating the sample, indicating that the *trans* isomer is the thermodynamically stable form.[10] Earlier theoretical calculations[11] were controversial with respect to the relative stability of *cis*- and *trans*-PA. However, more recent *ab initio* calculations[3,12,13] seem to correctly indicate TPA to be the stable isomer, with a *cis-trans* energy difference of roughly 0.1 eV per C_2H_2.[14] This is a very small energy difference and we do not expect the TBTE method to be reliable in capturing it. In fact, our results show that the Ct and Tc isomers are basically degenerate in energy, and both have lower energy than TPA, by only 0.01 eV per C_2H_2 unit, which is again beyond the reliability of the present method.

We present in Tables I, II, and III, other structural parameters for TPA, Ct-PA, and Tc-PA, respectively, along with available experimental and *ab initio* theoretical results. In general, the agreement is quite good. For the case of TPA, an important parameter is the dimerization (Peierls) distortion

TABLE I. Structural parameters for TPA. *Ab initio* results correspond to the B3LYP exchange-correlation functional and 6-31G^* basis set. Lengths in Å and angles in degrees.

Parameter	Experiment (Refs. 8,15)	*Ab initio* (Ref. 3)	This work
a_0	2.46	2.474	2.444
$d_{C=C}$	1.36	1.369	1.384
d_{C-C}	1.44	1.426	1.432
d_{C-H}		1.091	1.075
θ_{CCC}		124.5	120.2
$\theta_{C=CH}$		118.3	119.4
u	0.03	0.032	0.028

TABLE II. Structural parameters for Ct-PA. *Ab initio* results correspond to the B3LYP exchange-correlation functional and 6-31G^* basis set. Lengths in Å and angles in degrees.

Parameter	Experiment (Refs. 9,15)	*Ab initio* (Ref. 3)	This work
a_0	4.38	4.443	4.263
$d_{C=C}$	1.37	1.369	1.382
d_{C-C}		1.435	1.425
d_{C-H}		1.087	1.073
θ_{CCC}		126.7	121.1
$\theta_{C=CH}$		116.4	118.9

TABLE III. Structural parameters for Tc-PA. *Ab initio* results correspond to the B3LYP exchange-correlation functional and 3-21G basis set. Lengths in Å and angles in degrees.

Parameter	Experiment (Refs. 9,15)	*Ab initio* (Ref. 3)	This work
a_0	4.38	4.507	4.304
$d_{C=C}$	1.37	1.373	1.376
d_{C-C}		1.429	1.433
d_{C-H}		1.087	1.074
θ_{CCC}		126.9	122.1
$\theta_{C=CH}$		117.9	117.8

along the chain axis, u, which is responsible for the opening of an energy gap at the Fermi level. This parameter is very sensitive to a careful treatment of electronic correlation and k-space sampling.[3] It is therefore surprising that our simple tight-binding approach with a relatively small supercell can describe it so well (see Table I). In fact, increasing our supercell size to 50 C_2H_2 (which effectively improves the k-point sampling) decreases u to 0.015 Å. The energy gap in our calculation is 0.41 eV, to be compared to the experimental value 1.8 eV.

From the plots in Fig. 2, one can calculate Young's moduli for the different isomers, defined as

$$Y = \frac{a_0}{A} \left. \frac{d^2E}{da_x^2} \right|_{a_0}, \qquad (7)$$

were a_0 is the equilibrium lattice constant and A is the cross-sectional area for the polymer. We adopt, for the three isomers, the experimental value for TPA, $A = 15.52$ Å^2.[8] Our results are $Y_{TPA} = 389$ GPa, $Y_{Ct\text{-}PA} = 161$ GPa, and $Y_{Tc\text{-}PA} = 172$ GPa. Experimental measurements of the Young's modulus are usually much lower than theoretical results due to misorientation effects. Cao *et al.*[16] have performed measurements of Y_{TPA} for different draw ratios and obtained an extrapolated value of 290 ± 40 GPa for perfectly oriented TPA. Using spectroscopically determined force constants, Hong and Kertesz[17] have obtained $Y_{TPA} = 373$ GPa, $Y_{Ct\text{-}PA} = 170$ GPa, and $Y_{Tc\text{-}PA} = 188$ GPa. The same authors have calculated $Y_{TPA} = 591$ GPa, $Y_{Ct\text{-}PA} = 309$ GPa, and $Y_{Tc\text{-}PA} = 325$ GPa using a modified neglect of differential overlap method. Our results are in excellent agreement with the spectroscopically determined values, which Hong and Kertesz suggest to be the most reliable. In particular, the large difference between *cis* and *trans* Young's moduli, which can be explained in simple geometrical terms,[17] and the small difference between $Y_{Ct\text{-}PA}$ and $Y_{Tc\text{-}PA}$ are well reproduced.

IV. CONCLUSIONS

We have presented a systematic study of the applicability of the TBTE model introduced in Ref. 6 to the different PA isomers. The calculated properties at (geometric structural parameters) and near (Young's moduli) equilibrium are in very good agreement with experiment and with previous *ab initio* calculations, confirming the reliability of the TBTE method for these properties. For electronic-structure-related properties, such as the Peierls gap and eventually soliton-related properties, the present parametrization leads to relatively poor results. This is not surprising, since the original parameters were fitted to describe only total energy and geometric data, and not electronic transitions. But one could in principle modify these parameters for situations when a more quantitative description of the band gap is needed.

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