# Lack of a *trans-cisoid* phase in *cis*-polyacetylene

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By an *ab initio* calculation based on the local-density approximation of density-functional theory, the possible geometries of *cis*-polyacetylene are determined. While the stable *cis-transoid* structure is confirmed, the ''metastable'' *trans-cisoid* phase is not found in our first-principles calculation. Further calculations indicate that the electronic band gap in *cis*-polyacetylene is contributed almost equally by the Peierls dimerization and the nonequivalence of its two kinds of bonds. This fact is shown to account for the nonexistence of the *trans-cisoid* phase in *cis*-polyacetylene. [S0163-1829(98)04802-4]

Polyacetylene (abbreviated as PA),[1] a prototype of conducting polymers, has been studied extensively due to its promising electric, magnetic, and optical properties.[2] As a planar molecule, in principle, PA has four possible structures, i.e., *trans-transoid*, *cis-transoid*, *trans-cisoid*, and *cis-cisoid*.[3] Among these four configurations *cis-cisoid* cannot be realized due to geometric constraints. The *trans-transoid* (simply called *trans*-PA) is known to be the most stable phase and has twofold degenerate ground state due to the symmetry of its single and double bonds exchange.[4] However, *cis*-PA (simply for both *cis-transoid* and *trans-cisoid*) is not degenerate due to the nonequivalence of its neighboring bonds. While the *cis-transoid* PA is observed to be topologically stable, the *trans-cisoid* PA is thought to be a metastable phase,[5–7] but it is not confirmed by experimental measurements.[8,9] Although there have been a lot of works concerning the two phases of *cis*-PA,[10–12] specifically concerning the energetics among the *cis-trans* isomers by *ab initio* crystal calculations,[13,14] the result obtained seems to be still in poor agreement with observation.

*Ab initio* methods based on density-functional theory (DFT) are by now common and well established tools for studying structural properties of materials, which are usually not easily obtained from experiments. The plane-wave pseudopotential method and local-density approximation (LDA) to DFT have provided a simple framework whose accuracy and predictive power have been convincingly demonstrated in a large variety of systems. The calculations of energetics and geometries in semiconductors are well within the reach of DFT. There have been a lot of studies on the *trans*-PA chain by this method.[15–20] In this paper, we present the result of our *ab initio* calculation on a *cis*-PA chain based on the local-density approximation (LDA) of density-functional theory. We computed, as the first trial, the total energies of *cis*-PA with relaxed and constrained geometries. While the stable *cis-transoid* structure is confirmed, the

''metastable'' *trans-cisoid* phase is not found in our calculation. Further calculations indicate that the electronic band gap of the *cis-transoid* configuration is contributed almost equally by the Peierls dimerization and the nonequivalency of its two kinds of bonds. This fact is shown to account for the nonexistence of the *trans-cisoid* phase in *cis*-PA.

The present numerical calculations have been performed using the local-density functional theory[21,22] and the norm-conserving pseudopotential method.[23,24] The Kohn-Sham equations were solved iteratively in terms of a plane-wave basis. The electron density is the only information transmitted from one step to the other of the iteration. The total energy of the system is directly minimized by using the
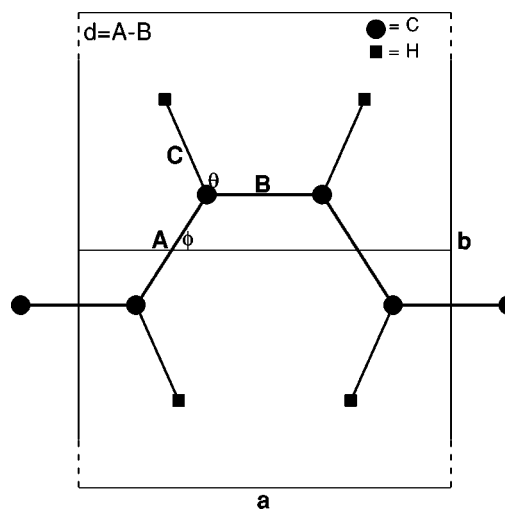


FIG. 1. Schematic structure of *cis*-polyacetylene. A positive (negative) $d$ (as defined in text) corresponds to the *cis-transoid* (*trans-cisoid*) structure. The optimized geometry is at the *cis-transoid* phase with the dimerization $d = 0.047$ Å and the angle $\phi = 53.93°$.
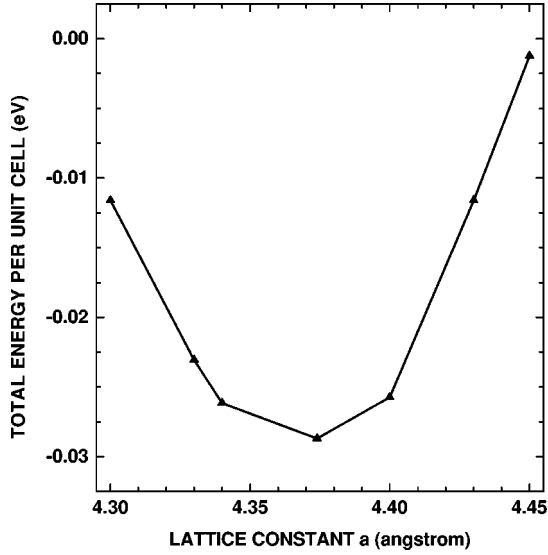
FIG. 2. Total energy per unit cell with optimized geometry for different lattice constants. The optimized lattice constant $a = 4.37$ Å.
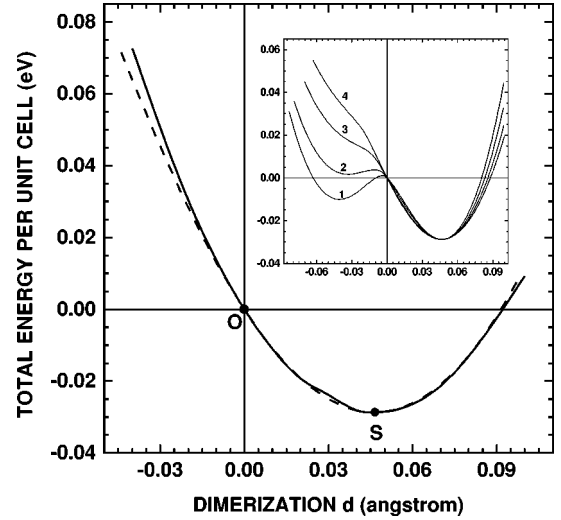


FIG. 3. Total energy vs dimerization in *cis*-polyacetylene. The solid line is for the *ab initio* calculation and the dashed line for the model result with $\eta = 0.5$ and $\lambda = 0.25$. The optimized *cis-transoid* structure is indicated by point S and the undimerized case by point O. The lines 1–4 in the inset are the model results for $\eta = 0.05$, 0.1, 0.2, and 0.3, respectively.

conjugate-gradient technique.[25] We employed the nonlocal norm-conserving pseudopotential[26] for carbon, particularly constructed to optimize the softness of the pseudopotential and thus minimize the size of the basis set needed to represent it. In the case of hydrogen we used the true $1/r$ potential.

The calculations were performed on a single *cis*-PA chain in a supercell $a \times b \times c$ with periodic boundary conditions. The method of special **k** points[27] was used to perform the integrations in **k** space over the first Brillouin zone. As shown in Fig. 1, $a$ is the lattice constant and $b$ and $c$ serve as the in-plane and out-plane interchain distances, respectively. While $a$ will be optimized $b$ and $c$ will be chosen to be large enough so that the interaction between chains can be neglected. The dimerization $d$ is defined as the bond-length difference between the two kinds of carbon-carbon bonds, i.e., the *trans*-bond $A$ which makes an angle $\phi$ with the chain axis and the *cis*-bond $B$ parallel to the chain. These two kinds of bonds are clearly not equivalent. Each point in the $d - \phi$ phase plane defines a configuration of the carbon backbone. A *positive* $d$ corresponds to the *cis-transoid* phase and a *negative* $d$ to the *trans-cisoid* one.

First, we calculated the total energies for a fixed geometry with different interchain distances ($b$ and $c$), plane-wave cutoff energies ($E_{cut}$), and the **k**-point numbers ($N_k$) to get appropriate parameters by the reach of a convergence of the total energies. In the following calculations, we take these values[28] as $b = 10$ Å, $c = 7$ Å, $E_{cut} = 50$ Ry, and $N_k = 5$ **k** points (along the chain direction), which give a very good convergence for the total energy and geometry of the ground state. The choice of **k** points in the integration over the first Brillouin zone is made very carefully. In the one-dimensional Brillouin zone, we have tested three different $k$ meshes,[17] i.e., a regular mesh including the boundaries, a regular mesh including only interior points, and a nonregular Gaussian mesh. Unlike the case of *trans*-PA, the geometry of *cis*-PA, specifically its dimerization, is insensitive to the $k$ mesh. It is less than 10% for the difference of dimerization between 5 $k$-point regular mesh and 20 $k$-point nonregular

Gaussian mesh. In this work, we take the regular mesh of 9 $k$'s including the boundaries $k = \pm \pi/a$ (these two points with a half weight), the number of independent $k$ points ($N_k$) is five due to the symmetry. Now, we can determine the lattice constant $a$ by comparing total energies of corresponding optimized structures for different lattice constants. During the optimization processes the constraint of $C_{2h}$ symmetry is taken. Figure 2 shows the total energy per unit cell as a function of the lattice constant $a$. The minimum is found at $a = 4.37$ Å.[29] The optimized geometry has the CC bond lengths $A = 1.406$ Å and $B = 1.359$ Å, which corresponds to dimerization $d = 0.047$ Å and $\phi = 53.93°$, the carbon-hydrogen bond length $C = 1.099$ Å, and the CCH angle $\theta = 116.80°$. It is mentioned here that the optimized geometries for different lattice constants are all of the *cis-transoid* configuration, i.e., the dimerization $d$ is always positive.

To search for all possible geometries in *cis*-PA, we restrict the dimerization $d$ to optimize these geometries. For each $d$, we vary the angle $\phi$ and relax the hydrogens to find an optimized structure and its corresponding total energy. In Fig. 3, we show the total energy as a function of the dimerization $d$. The stable *cis-transoid* structure indicated by point S has values of $d = 0.047$ Å and $\phi = 53.93°$, which is exactly what we have found without the constraint, and the undimerized $d = 0$ by point O has the angle $\phi = 54.25°$. The cohesive energy of the *cis-transoid* PA is 7.2 meV per carbon-hydrogen unit, which is much smaller than the value of 19.2 meV of *trans*-PA.[19] An important fact is that we do not find the so-called ''metastable'' *trans-cisoid* phase, i.e., no local minimum be found. This result is further confirmed by a large-area careful search in the $d - \phi$ phase plane.

To understand the physical reason behind the above facts we found by the *ab initio* calculation, we write down the Su-Schrieffer-Heeger-type model[4] for the nondegenerate polymers[7]

$$H = -\sum_{n,\sigma} \{[t_1 + \alpha(u_{2n} - u_{2n+1})](c^\dagger_{2n+1,\sigma}c_{2n,\sigma} + \text{H.c.})$$

$$+ [t_2 + \alpha(u_{2n+1} - u_{2n+2})](c^\dagger_{2n+2,\sigma}c_{2n+1,\sigma} + \text{H.c.})\}$$

$$+ \tfrac{1}{2}K\sum_l (u_l - u_{l+1})^2 + \tfrac{1}{2}M\sum_l \dot{u}_l^2, \qquad (1)$$

where the transfer integrals are assumed to have different values $t_1$ and $t_2$ corresponding to the alternative nonequivalent bonds, respectively. $\alpha$ is the electron-phonon coupling constant, $K$ is the effective spring constant, and $M$ is the mass of the CH group. In the perfectly dimerized chain, the configuration coordinates $u_l$ are constrained by $u_l = (-1)^l u$. The ground state of the chain has exactly one $\pi$ electron per site on average. The static system energy of the dimerized chain in the Born-Oppenheimer approximation is given by

$$E_t = \frac{4Nt_0}{\pi}\left\{\frac{\Delta_i^2}{4\lambda} - \int_0^{\pi/2} dk\sqrt{\cos^2 k + \Delta^2 \sin^2 k}\right\}, \qquad (2)$$

where $N$ is the number of sites of the chain, $\lambda(\equiv 4\alpha^2/\pi(t_1 + t_2)K)$ is the dimensionless electron-phonon coupling constant, the band-gap order parameter $\Delta = \Delta_i + \Delta_e$ is combined by contributions both from the Peierls dimerization, $\Delta_i(=4\alpha u)$, due to the $\pi$ electrons and the external effect, $\Delta_e(=t_1 - t_2)$, due to the $\sigma$ skeleton. By plotting the energy $E_t$ vs the dimerization $\Delta_i$, as shown in the inset of Fig. 3, we find that a metastable phase only appears in the system with a relatively small quantity $\eta$, which is defined by the ratio $\Delta_e/\Delta$, that is, the percentage of the contribution from the external effect ($E_e$, the band gap of the undimerized PA) in the "total" band gap ($E_g$) of polymers.

For cis-PA, we can *estimate* the value $\eta$ by calculating the electronic energies of the *cis-transoid* configuration at point S and that of the undimerized structure at point O shown in Fig. 3. It is understood that the LDA underestimates the band gap, but the ratio $\eta$ should be not far from the reality, furthermore, an approximated $\eta$ value is enough to display these physical facts. The calculations are made by use of 11 **k** points along the chain axis, the energy levels of *cis-transoid* PA is given in Fig. 4. Our calculation gives that the band gap at S is 0.91 eV, which should correspond to $E_g$. It is expected that the value of $E_g$ we found is a little less than the *half* of the observed value 2.05 eV (Ref. 30) due to the LDA we adopted in this calculation. The obtained gap at O is 0.49 eV, which should correspond to $E_e$, the external contribution since there is no Peierls contribution in the equal bond-length case. Then we have the value $\eta(\approx E_e/E_g)$ is
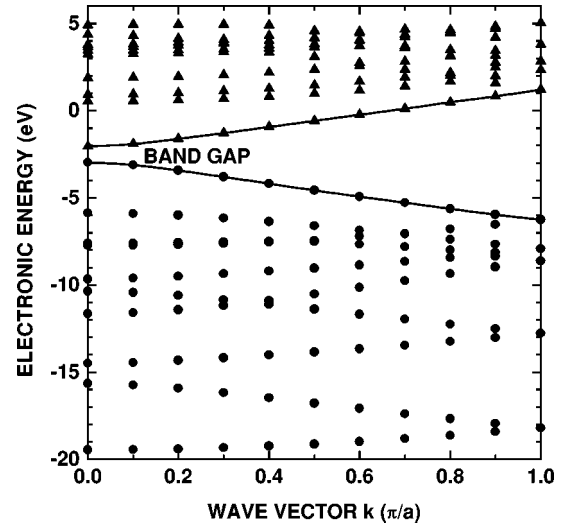


FIG. 4. Electronic energies of *cis*-polyacetylene. The obtained band gap $E_g(\text{S}) = 0.91$ eV for the *cis-transoid* configuration at point S and $E_g(\text{O}) = 0.49$ eV for the undimerized structure at point O.

about 0.5, an unexpected large value. We should mention here that in all previous model considerations,[5–7] this value is taken as a very small one, which makes the metastable phase appear (see the inset of Fig. 3). In Fig. 3, we show the curve from Eq. (2) for $\eta = 0.5$ as a dashed line. The units are scaled by point S, then an excellent agreement between these two curves can be found. This fact implies that it is the large gap due to the external effect, i.e., the nonequivalence between two kinds of bonds that causes the nonexistence of the "metastable" *trans-cisoid* phase.

In summary, the "metastable" *trans-cisoid* phase is not found in the present first-principles calculation. The band gap of the *cis-transoid* polyacetylene is contributed almost equally by the Peierls dimerization and the nonequivalence of its two kinds of bonds, which is shown to account for the nonexistence of the *trans-cisoid* phase in *cis*-polyacetylene.

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[28] The total energy converges for $b \geq 9$ Å, $c \geq 6$ Å, and $E_{cut} \geq 40$ Ry.

[29] Compared with the lattice constant $a = 2.44$ Å (including two hydrogen-carbon units) of *trans*-PA, this value indicates that *cis*-PA is more condensed, at least along the chain axis.

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