The discovery that doping can increase the conductivity of polyacetylene and some other conjugated polymers to near metallic levels has focused much attention on these organic systems. Of particular interest are the changes in the polymer electronic and geometric structures upon doping. In this note, we present a theoretical study of the amount of charge transferred to the polymer chain, (ii) the bond length and bond order alternation in the chain, and (iii) the band structure (and band gap) in the one-electron picture.

The key result of our calculations is that, at surprisingly small degrees of charge transfer, there are major changes in the polymer electronic and geometric structures upon doping. In this note, we present a theoretical study of the effect of an alkali metal, Li, acting as a dopant on (i) the amount of charge transferred to the polymer chain, (ii) the bond length and bond order alternation in the chain, and (iii) the band structure (and band gap) in the one-electron picture.

The key result of our calculations is that, at surprisingly small degrees of charge transfer, there are major changes...
TABLE I: RHFR Geometry Optimization Results (in au) on trans-(CH)$_x$, Using a Christoffersen Basis Set

<table>
<thead>
<tr>
<th></th>
<th>alternating chain</th>
<th>equal bond-lengths chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{C-C}$</td>
<td>2.555</td>
<td>2.589</td>
</tr>
<tr>
<td>$R_{C-C}$</td>
<td>2.623</td>
<td>2.589</td>
</tr>
<tr>
<td>C-C-C angle, deg</td>
<td>119.0</td>
<td>119.0</td>
</tr>
<tr>
<td>total energy</td>
<td>-65.835103</td>
<td>-65.833870</td>
</tr>
</tbody>
</table>

$^a$ 1 au (length) = 0.52917 Å. 1 au (energy) = 27.2 eV.

in the nuclear geometry of the chain and hence in its electronic structure. This casts serious doubts on the appropriateness of rigid band structure models in theoretical studies of dopant polymer interactions. In fact, our results are consistent with the theoretical concepts based on solitons for describing doped (CH)$_x$.

We have performed ab initio crystal orbital calculations at the restricted Hartree–Fock–Roothaan (RHRF) level on infinite single chains of trans-polyacetylene, (CH)$_x$ with and without Li atoms at a variety of distances from the chain. In the case of doped systems, we present our data (C$_x$H$_{y}$Li)$_z$, which represents a doping level of 33%. The reasons for our choice of this concentration are that (a) it is close to the experimentally achieved concentration of 30%; (b) the unit cell, which is as large as we can handle on our computer, has the freedom for structural changes; (c) the RHRF method can only easily handle closed-shell systems. Because of the size of the unit cell, we have used a subminimal Christoffersen basis set which has proved to give reliable results in conformational studies of polyacetylene as well as other cases.

Long-range Coulombic interactions which are expected to be of particular importance in this charge-transfer system have been properly taken into account through a multipole based technique for lattice summation.

The focus of this study involves ground-state properties, namely, the charge transfer and the geometry changes in the chain that occur on doping. We do not address quantitatively the questions related to metallic or optical properties which require going beyond the one-electron picture.

The geometry of our system is as follows:

As a first step, we have optimized the “single” and “double” bond lengths and the C–C–C angle of the undoped chain (i.e., $R_{Li-C} = \infty$) while keeping the CH distance fixed at 2.04 au and the C–C–H angle as 180°–1/2(3C–C–C angle). The results are given in Table I. As expected, we find the alternating chain to be most stable, in agreement with previous RHFR extended basis set geometry optimization by Karpfen and Petkov (KP). The degree of alternation (C–C bond length difference) $\Delta r = R_{C-C} - R_{C-C}$ short we find is rather low (0.068 au), less than half that found by KP, which can be understood from our use of the Christoffersen basis which is known to give rather short C–C single bonds. However, our overall results for undoped polyacetylene, and in particular the potential curve (Figure 1a), agree well with the more extended calculations of KP. Note that the optimized C–C distance for the equal bond length case is exactly midway between the single and double bond lengths in the lowest energy configuration.

In the doped chains, each Li is positioned equidistant from three carbon atoms in analogy with the structure found in the lithium intercalated graphite compound. The two lithium atoms are placed one above and one below the plane of the chain. We have considered three lithium–carbon distances, $R_{Li-C}$, and optimized the energy by allowing the difference between single and double bond lengths ($\Delta r$) to vary again keeping the CH distances fixed, and the C–C–H angle as 180°–1/2(C–C–C angle). The range of lithium–carbon distances is chosen to be in accord with crystal packing calculations, which show that the interchain carbon–carbon distance (in the cis polymer)
The most important feature of our results is that the bond alternation persists although it is less than the lowest energy configuration. Thus even with a small degree of charge transfer by Li atoms is that even a small degree of charge transfer dramatically alters the chain geometry, and, as a consequence, its electronic structure. We suggest that these results imply strong electron-phonon coupling (even in the undoped chain). This will tend to localize optical excitations, and have substantial effects on transport properties.

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(17) Note that in the three-dimensional structure of the doped system there will be other effects (other Li atoms and other chains) which will influence the dispersion in the Li bands. Clearly, at a 30% doping level the average Li-Li separation will be less than 5 Å. However, we believe that the major effect on the dispersion in the Li bands will be in k directions perpendicular to the chain direction.