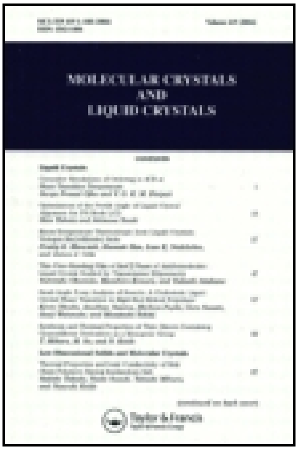

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Conformation and Electronic Properties of Helical Cis-Polyacetylene

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CONFORMATION AND ELECTRONIC PROPERTIES OF HELICAL *CIS*–POLYACETYLENE

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Abstract Recent experimental evidence indicates that *cis*–polyacetylene may exist in a helical conformation in addition to the well–known planar form. We report electronic structure calculations which demonstrate that planar *cis*–polyacetylene is indeed marginally unstable towards helix formation, but that the potential energy curve is essentially flat over a wide range of single–bond twist angles. This result is consistent with the fact that both the planar and the helical isomers are found experimentally. We employ a tight–binding model to investigate the band structure changes associated with helix formation.

INTRODUCTION

Polyacetylene is an electroactive polymer whose unique conduction properties depend on its conjugated π–electron system. The planarity of polyacetylene as usually prepared[1] appears established,[2] and therefore it is surprising that recent experimental evidence[3] indicates that *cis*–polyacetylene, when crystallized from solution rather than being synthesized as a thin film *in situ*, apparently exists in a helical conformation. We have investigated the stability of the helical polymer chain and its electronic structure, and report some of our results here.

CHAIN GEOMETRY

We have performed a series of quantum mechanical MNDO calculations on chain segments up to 24 carbon atoms in length to determine the stability of the proposed helical structure for *cis*–polyacetylene. Preliminary results of these calculations have been reported elsewhere.[4] We find that, as the single carbon–carbon bonds are twisted in a concerted fashion while the other geometric parameters are allowed to relax, the energy lowering due to decreased (1,4) hydrogen–hydrogen repulsion roughly balances the energy increase due to decreased delocalization of the π electrons. The resulting potential energy surface is essentially flat over an extremely wide range of single–bond twist angles. There is a small local energy *maximum* at the conventional planar *cis* conformation, and the minimum lies at a twist angle of ±53°. Further

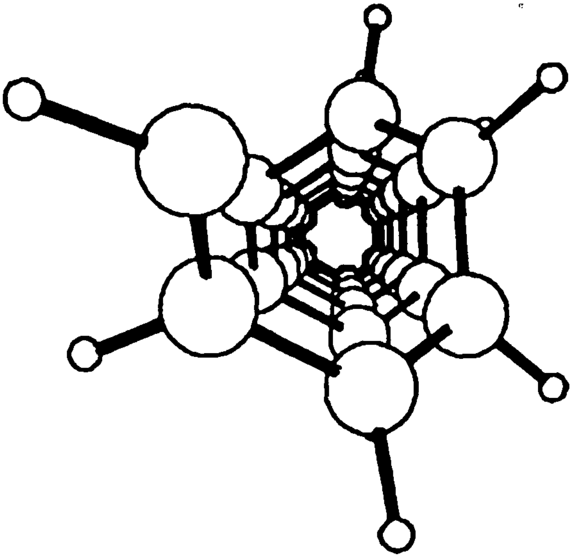

FIGURE 1. A segment of 2*3/1 helical polyacetylene, viewed along the helix axis.

twisting of the single bonds has no significant effect on the energy until an angle of approximately ±120° is reached, as measured from the planar conformation. At that point, repulsion between successive turns of the helix causes the energy to rise sharply.

In the crystalline phase, a tightly coiled helix is preferred in order to minimize interstitial volume. Our results therefore imply that crystalline helical polyacetylene should adopt a twist angle near the edge of the flat region of the potential energy curve, in the vicinity of 120°. In fact, we have found that at a twist angle of 102°, the chain forms a perfect 2*3/1 helix with high translational symmetry (two carbon atoms per motif, three motifs and one helix turn per translational period) whose repeat distance closely matches the experimental unit cell length[3] of 4.84 A. (See figure 1.) Our results are therefore consistent with the observed helical structure. At the same time, our calculations show that the planar and helical isomers are so nearly isoenergetic that the planar conformation could easily be preferred due to interchain steric effects when the polymer is prepared as a thin film, hence also accounting for the results of Baughman et al.[2]

ELECTRONIC STRUCTURE

The electronic structure of helical polyacetylene was investigated by employing a linear–combination–of–atomic–orbitals (LCAO) tight–binding model for the isolated infinite chain. The orbital interaction parameters were obtained by fitting to an accurate *ab initio* band structure of planar *trans*–polyacetylene.[5] A comparison of the *ab initio* and parameterized band structures is shown in figure 2. The same model also reproduces the band structure of planar *cis*–polyacetylene accurately.

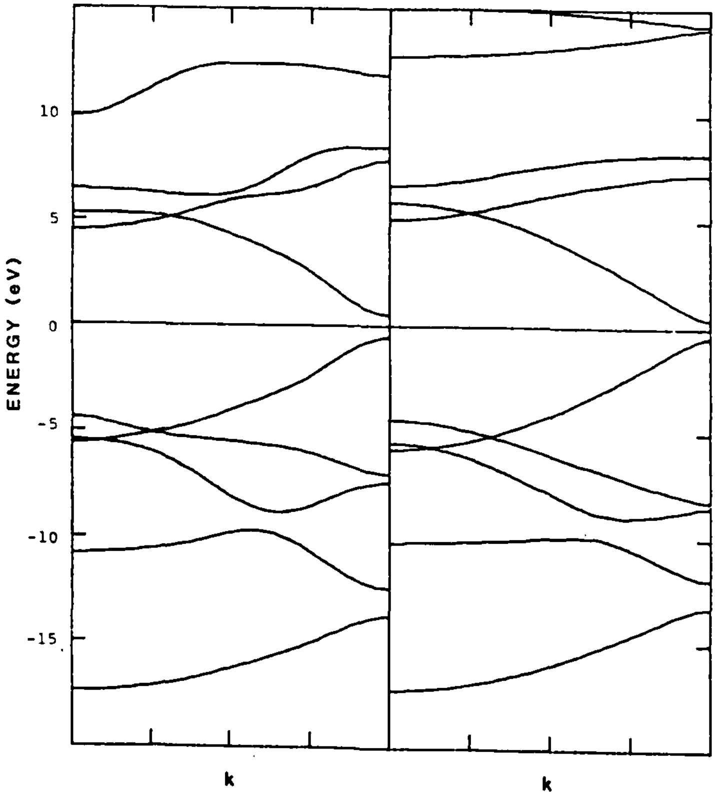

FIGURE 2. Band structures of *trans*–polyacetylene. On the left is the accurate *ab initio* Xα band structure of Mintmire and White.[5] The tight–binding fit is shown on the right.

Figure 3 shows the band structure and density of states for planar and helical *cis*–polyacetylene. The helix geometry used for this calculation is the 2*3/1 structure described above. The most noticeable change in the band structure upon helix formation is the large increase in band gap, from 1.5 eV for planar *cis*–polyacetylene to 4.3 eV for the helical isomer. This is a consequence of the decrease of π overlap across single carbon–carbon bonds as these bonds are twisted, which breaks

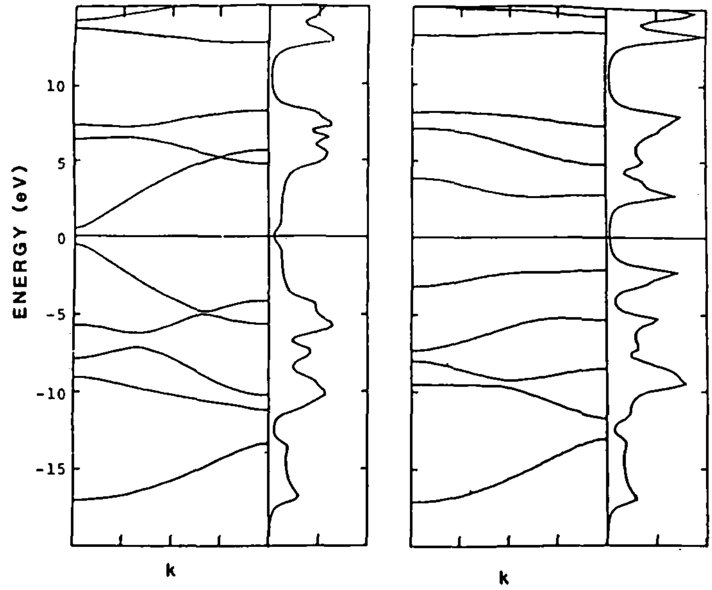

FIGURE 3. Band structure and density of states for planar *cis* (left) and helical (right) polyacetylene, as calculated from our tight–binding model.

the delocalization of the π system and causes the bands to flatten. Interaction with the σ orbitals still affects the position of the π bands and hence the size of the gap, as can be demonstrated by comparing the tight–binding results to a simple π–band–only model. As shown in figure 4, the latter model predicts a band gap in excess of 6 eV at a twist angle of 90°. Since tight–binding calculations for semiconductors typically underestimate band gaps while the π–band–only model represents an overestimate, we conclude that the band gap for single chains of helical polyacetylene should be in the vicinity of 5 eV. The band gap could be narrowed by interchain interactions neglected in the present tight–binding calculation, and studies including these effects are currently

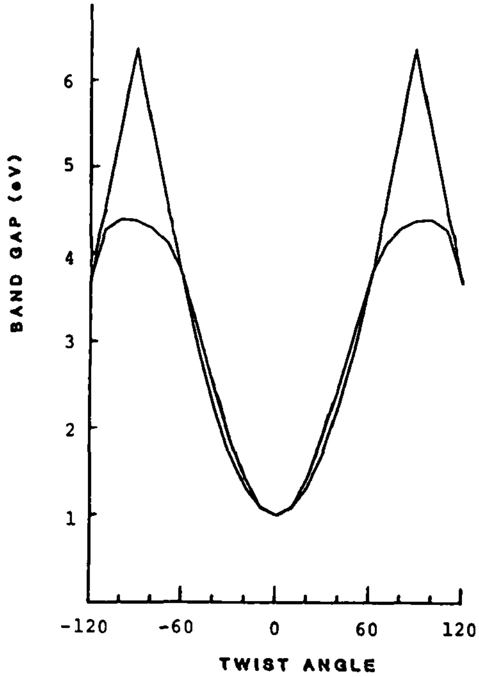

FIGURE 4. Band gap versus twist angle for helical polyacetylene. The upper curve is the result of a single–band model which includes only the π orbitals, while the lower curve is obtained from our full tight–binding model.

underway. Other qualitative changes in the density of states are apparent in figure 3. It should therefore be possible to readily distinguish between planar and helical polyacetylene on the basis of e.g. UPS spectroscopy.

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