

Helical versus planar *cis*-polyacetylene

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An established quantum chemical self-consistent-field method, the modified neglect of diatomic overlap approach, is used to study the equilibrium geometry of *cis*-polyacetylene. This study was stimulated by very recent experimental results suggesting the existence of helical *cis*-polyacetylene. For a single chain of this material we do find that the planar structure is unstable towards formation of a helical conformation. Owing to a remarkable flatness in the potential-energy surface over a wide range of carbon-carbon single-bond twist angles, the results account for the experimentally implied existence of both planar and helical  $2\frac{1}{3}$  *cis*-polyacetylene.

The planarity of *cis*-polyacetylene prepared by the Shirakawa technique<sup>1</sup> appears established,<sup>2</sup> with each chain in the film adopting the conformation shown in Fig. 1(a). Bates and Baker,<sup>3</sup> however, using novel techniques, very recently obtained single crystals of this material that yield x-ray and electron diffraction data that they propose can be best interpreted in terms of the  $2\frac{1}{3}$  helical structure<sup>4</sup> shown in Fig. 1(b). These authors further suggest that the equilibrium conformation of single chains of *cis*-polyacetylene in solution is helical, but that in films prepared by the Shirakawa technique immediate solidification prevents the attainment of this more stable configuration. Cernia and D'Ilario<sup>5</sup> have also recently suggested that isolated *cis*-polyacetylene chains are helical. Their conclusions, however, based as they are on classical potential-energy calculations, depend strongly on details of their as-

sumed conjugation barrier height for rotation around a C-C single bond. Unfortunately, this barrier is neither well known<sup>5</sup> nor well defined.<sup>6</sup>

Here we present results of the first self-consistent-field total-energy cluster calculations directed toward determining the conformation of isolated *cis*-polyacetylene chains. Consistent with Refs. 3 and 5, our results imply that single *cis* chains do prefer a helical ground state. We find, however, that the total energy of the system is remarkably flat over an extremely broad range ( $-120^\circ$  to  $+120^\circ$ ) of twist angles around the C-C single bond. Our results naturally account for both the helical structure reported by Bates and Baker and the planar structure of Baughman *et al.*

To arrive at our conclusions we used the self-consistent-field total energy method developed by Dewar and co-workers.<sup>7</sup> This approach includes, quantum mechanically, electron-nucleus and electron-electron interactions between all *s* and *p* valence electrons. The carbon core electrons are assumed frozen and treated as part of the nuclear potential. All Coulomb and exchange integrals involving diatomic overlap distributions are neglected in the electronic Hamiltonian  $H_{el}$ . The remaining one- and two-electron integrals defining  $H_{el}$  are parametrized using an established prescription.<sup>7</sup> For example, the one-center two-electron repulsion integrals are obtained from atomic data while the two-center two-electron repulsion integrals are obtained from multipole-multipole expansions. These expansions have the correct limiting behavior at small and large atomic separations. An optimal (Hartree-Fock) single-determinant linear-combination-of-atomic-orbitals wave function is used to compute the electronic energy from  $H_{el}$ . This result is then added to the effective nuclear-nuclear repulsive energy to determine self-consistently the total system energy at a particular geometry. The entire method, termed MNDO (MNDO stands for modified neglect of diatomic overlap) is detailed in the literature.<sup>7</sup> This method has enjoyed great success in predicting the geometries of a host of organic molecules.<sup>8</sup>

The explicit results reported below are for a twelve-carbon-atom chain,  $C_{12}H_{14}$ . This cluster size was chosen as a compromise between computational feasibility and our desire to minimize end effects. To see if any of our conclusions were seriously affected by the choice of chain length, additional calculations were performed for a ten-

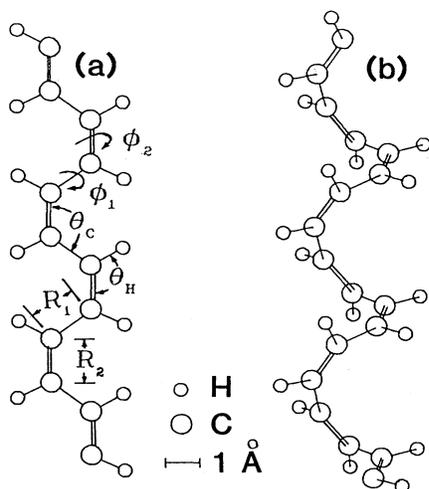


FIG. 1. *cis*-transoid polyacetylene (a) in the commonly assumed planar structure and (b) an oblique view of the  $2\frac{1}{3}$  helical structure suggested in Ref. 3. The configurational parameters optimized in this work are displayed in (a). Note the twist angles  $\phi_1$  and  $\phi_2$  are measured from the plane formed by the carbon-carbon bond that is twisted and the preceding C atom in the chain before twisting from the planar structure.

atom chain,  $C_{10}H_{12}$ . This  $C_{10}H_{12}$  study yielded essentially the same results as the  $C_{12}H_{14}$  calculations. As a further check on the results, all reported energies were calculated including a minimal configuration interaction (CI) that allows mixing between the Hartree-Fock ground state and the lowest-lying double excitation of the system. The CI had no significant effect on any of our calculated relative energies. This result indicates that the single-determinant Hartree-Fock wave function is adequate for computing the electronic contribution to the total energy from the MNDO Hamiltonian.

Throughout our calculations all C-H bond lengths were fixed at 1.08 Å. Also, each C-H bond was constrained to lie in the plane formed by the carbon atom participating in the bond and its two nearest-neighbor carbon atoms along the chain. To model the configuration of the infinite polymer chain more accurately, all carbon-carbon double bonds were required to have equal lengths, as were all the carbon-carbon single bonds. Similarly, identical rotation angles were applied to each type of bond for nonplanar configurations. With these restrictions, there are six parameters that determine the configuration of the system, namely, the C-C (single) bond length  $R_1$ ; the C=C (double) bond length  $R_2$ ; the C=C-C bond angle  $\theta_C$ ; the C=C-H bond angle  $\theta_H$ ; the angle for twisting around C-C single bond,  $\phi_1$ ; and the angle for twisting around the C=C double bond,  $\phi_2$ . (For the planar *cis-transoid* isomer,  $\phi_1 = \phi_2 = 0^\circ$ .) These parameters are defined pictorially in Fig. 1(a).

With the exception of  $\phi_1$ , good initial estimates of all the configurational parameters can be made by analogy with small  $sp^2$  hydrocarbon molecules. With use of these starting parameter estimates, calculations were performed yielding an equilibrium geometry for *cis*-polyacetylene defined by  $\phi_1^0 = \pm 53^\circ$ ,  $\phi_2^0 = 0^\circ$ ,  $\theta_C^0 = 127^\circ$ ,  $\theta_H^0 = 119^\circ$ ,  $R_1^0 = 1.47$  Å, and  $R_2^0 = 1.35$  Å. Because  $\phi_1^0 = \pm 53^\circ$  and not  $0^\circ$ , these results indicate that isolated *cis*-polyacetylene chains prefer a helical geometry.

When the other parameters are optimized, we see from Fig. 2 that the system potential energy as a function of  $\phi_1$  is remarkably flat, changing no more than 0.010 eV per CH unit over an extremely broad range of twist angles  $\phi_1$  ( $-120^\circ \leq \phi_1 \leq 120^\circ$ ). Along this path the other parameters do not vary much from their optimized values at  $\phi_1^0 = \pm 53^\circ$ . The angle  $\phi_2$  remains at  $0^\circ$  and  $(R_1 + R_2)/2$  changes by only 0.001 Å. In addition,  $\theta_H$  and  $\theta_C$  change by no more than  $2.0^\circ$  and  $2.5^\circ$ , respectively. The degree of dimerization,  $(R_1 - R_2)/2$ , does vary somewhat, reaching its maximum value of 0.063 Å at  $\phi_1 = \pm 90^\circ$ , where the  $\pi$  overlap across the single bonds is zero and its minimum value of 0.054 Å at  $\phi_1 = 0^\circ$  where the chain is planar. Further calculations showed that the path of Fig. 2 follows a narrow valley in the potential-energy hypersurface. This valley is bound on all ten sides by steep rises in the system energy per CH unit.

The flat region shown in Fig. 2 results primarily from a balance between conjugation and steric effects. As  $\phi_1$  approaches  $0^\circ$ , the hydrogen atoms associated with third neighboring carbon atoms along the chain begin to repel. The resultant increase in the system energy, however, is largely compensated by energy lowering of the  $\pi$  electrons due to their increasing delocalization along the chain. Similar effects occur as  $\phi_1$  approaches  $\pm 130^\circ$  and the chain becomes more tightly twisted. In these cases the Coulomb

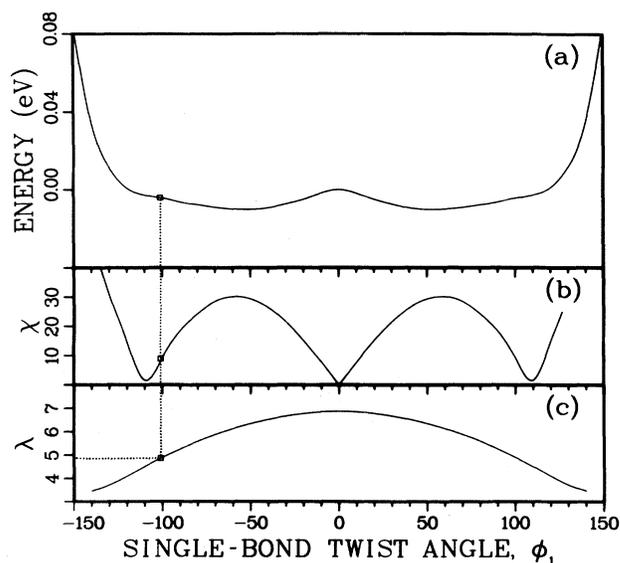


FIG. 2. (a) The energy per CH unit as a function of  $\phi_1$  with all other configurational parameters optimized. The energy is measured with respect to its value at  $\phi_1 = 0^\circ$ . (b) Angle of inclination,  $\chi$ , between the  $n$ th and  $(n+6)$ th C-C bonds, in degrees. (c) The distance  $\lambda$  between the  $n$ th and  $(n+6)$ th C atoms, in angstroms. The dotted line corresponds to the chain-unit cell length reported in Ref. 3.

repulsion between successive turns in the chain eventually dominates and the energy rises sharply.

Often a polymer chain's local geometry in a crystal is rather accurately determined from the configuration of the corresponding isolated chain.<sup>9</sup> By contrast, Fig. 2 implies that environment and history likely determine the chain's local geometry in crystalline *cis*-polyacetylene. Although the shape of this curve shows that our predicted value of  $\phi_1$  must be viewed with caution, this same shape naturally accounts for the chain-unit cell length reported by Bates and Baker. This follows if we assume that the chains in their crystalline sample (arranged on a hexagonal lattice with  $a = 5.12$  Å) twist so as to minimize the interstitial volume, and do this while not significantly increasing the energy of the chain per unit length. We see then from Fig. 2 that upon crystallization  $\phi_1$  should lie close to the edge of the flat region of the potential surface. As shown in Fig. 2, Bates and Baker's reported unit cell length ( $c = 4.84$  Å) does correspond to a value of  $\phi_1$  near the edges of this region. In addition, we also see from Fig. 2 that the resulting helix is very close to a perfect  $2\frac{1}{3}/1$  helix with an angle of misalignment between the  $n$ th and  $(n+6)$ th C=C bond of only  $9^\circ$ . Furthermore, by allowing small changes in  $\phi_2$  we have found a perfect  $2\frac{1}{3}/1$  helix with a chain-unit cell length of 4.84 Å that is only 0.008 eV/CH higher in energy than the equilibrium isolated chain configuration. The parameters characterizing this  $2\frac{1}{3}/1$  helix are

$$R_1 = 1.47 \text{ \AA}, \quad R_2 = 1.35 \text{ \AA}, \quad \theta_C = 129^\circ, \\ \phi_1 = \pm 102^\circ, \quad \text{and} \quad \phi_2 = \mp 2^\circ.$$

Helical polyacetylene in the crystalline state should adopt

such a configuration, with high translational symmetry along the helix axis.<sup>10</sup>

For films obtained by the Shirakawa technique, Bates and Baker argue that the immediate solidification that occurs after preparation dictates a crystal structure based on planar *cis* chains. Our results support this picture. The optimized completely planar chain has an energy per C-H unit only 0.002-eV higher than that found for the perfect 2\*3/1 helix described above. In addition we have found an almost planar structure with  $\phi_1 = \pm 10^\circ$  that has the same energy as this helix. So, once the planar structure is prepared, this structure is easily stabilized by interchain steric effects provided the chains are closely packed. This should occur in films prepared by the Shirakawa technique. The herringbone chain packing structure reported by Baughman *et al.* implies that any attempt to twist an individual chain will bring the hydrogen atoms on this and neighboring chains closer together than their van der Waals radii and hence cause a sharp energy increase.

We have presented the first quantum chemical results that indicate that single *cis*-polyacetylene chains have a helical, not planar, ground state. On the other hand, the calculations show that the chain energy is remarkably flat over a wide range of C-C single-bond twist angles. Although the reported planar and helical structures of crystalline *cis*-polyacetylene are dramatically different, our results account for both these configurations.

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<sup>4</sup>This notation is described by B. Wunderlich, *Macromolecular Physics* (Academic, New York, 1973), Vol. 1, p. 72. For *cis*-polyacetylene a 2\*3/1 helix denotes two CH units per motif and three motifs and one helical turn per translational identity period *c*.

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