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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### An Ab Initio Study of the Rotational Potential Energy Surface of Cis-Transoidal Polyacetylene

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**To cite this Article** Darsey, J. A. , Kuehler, J. F. , Kestner, N. R. and Rao, B. K.(1988) 'An Ab Initio Study of the Rotational Potential Energy Surface of Cis-Transoidal Polyacetylene', Journal of Macromolecular Science, Part A, 25: 2, 159 – 169

**To link to this Article:** DOI: 10.1080/00222338808051960

**URL:** <http://dx.doi.org/10.1080/00222338808051960>

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## **AN *ab initio* STUDY OF THE ROTATIONAL POTENTIAL ENERGY SURFACE OF *cis-transoidal* POLYACETYLENE**

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### **ABSTRACT**

*Ab initio* self-consistent field molecular orbital calculations have been performed to obtain the intramolecular rotational potential energy surface for *cis-transoidal* polyacetylene with simultaneous rotations about two successive single bonds. The results indicate the possibility of existence of a "superhelix" instead of a tight  $2\frac{3}{1}$  helix. Using the energy surface obtained, Monte Carlo calculations have been done to obtain the probabilities of the existence of various conformations of this polymer.

## INTRODUCTION

Among all the polymers showing high dc conductivity, polyacetylene is the one which has been the subject of the most extensive study [1]. This polymer is usually obtained by Shirakawa's technique [2-4] as a film with metallic luster which, upon suitable doping, can be almost as conducting as mercury. Depending on the conditions of synthesis, the molecular weight can vary from about 500 to 220 000. These long chains have a tendency to fold back upon themselves to form lamellar structures. Various useful properties [5] of this polymer depend upon the positions of defects in the chain and the chain conformation. These two factors also guide the doping and determine the positions and the amounts of dopants going into the polymer. Therefore, a complete understanding of the molecular configuration and electronic structure is highly desirable.

Polyacetylene can exist in three distinct configurations—*trans*, *trans-cisoidal* (TC), and *cis-transoidal* (CT). Of these, only *trans*-polyacetylene has been studied in detail [6-8]. Even though some limited work has been done on the *cis* forms [9-11], questions still remain about whether these exist in the planar [12] ground state. Theoretical calculations have shown that the intramolecular rotational potential energy of the CT form goes through a minimum [11] for rotations about a single bond. The corresponding angle for CT is about  $117^\circ$  and that for TC is nearly  $42^\circ$ . However, when rotations about many successive single bonds are calculated, the minimum does not occur at the same angles because steric hindrances are expected to arise. In the present study we have generated a potential energy surface for CT with rotations about two successive single bonds and have examined this surface from various points of view.

## METHOD

Figure 1 is the schematic model of CT polyacetylene used in our calculations. This shows the bond alternation expected due to the Peierls instability [13]. We consider here the rotations  $\phi_1$  and  $\phi_2$  about two successive single bonds in the middle of the chain. Rotation about the double bond has been neglected because it is energetically expensive. The length of the polymer has been truncated after 10 carbon atoms for the following reasons: 1) increasing the number of atoms in the backbone results in excessive computation time, 2) it has been reported [9] that the potential energy stabilizes when the chain length reaches eight carbon atoms and does not change when

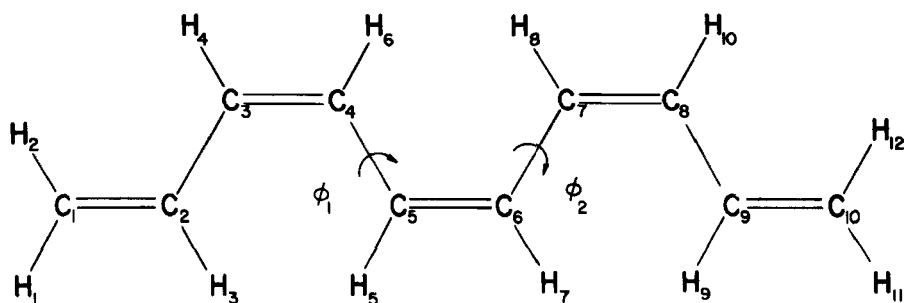


FIG. 1. Segment of the *cis-transoidal* polyacetylene molecule studied in this work.

further carbon atoms are added, 3) with 10 carbon atoms one can completely simulate all the possible interactions and steric hindrances due to the rotations  $\phi_1$  and  $\phi_2$ . One extra hydrogen atom has been added to each end carbon to eliminate dangling bonds. The values of the bond lengths and angles were obtained by suitable optimization procedures. These compare well with those given previously [9] and are very close to available experimental values.

The theoretical method used here is the *ab initio* self-consistent field molecular orbital (SCF-MO) method where the molecular orbitals (MO) are obtained as linear combinations of atomic orbitals. In the present work the atomic orbitals are represented by combinations of Cartesian Gaussian functions. This permits analytic evaluations of the integrals and can decrease numerical inaccuracies. The energy of a given conformation is then calculated self-consistently. More details on this procedure can be found elsewhere [14, 15].

In the present work we use a modified STO-3G [11, 15] basis set in which extra polarization functions have been added at hydrogen atom sites 3, 5, 6, 7, 8, and 9 (Fig. 1), which are the only ones that interact when the rotations  $\phi_1$  and  $\phi_2$  take place. We have already reported evidence [11] that this modification can suitably represent the situation in polyacetylene.

The potential energy surface so generated was used to calculate the *a priori* and conditional probabilities of the molecule to exist in any given configuration. The probability for a molecule to exist in any particular conformation is equal to the statistical weight divided by the sum of all statistical weights for all possible conformations. Details of the calculations of statistical weights and various probabilities are available elsewhere [16, 17].

These probabilities were incorporated into a Monte Carlo program, which

generated numerous representative chains. Various statistical properties were then calculated by averaging over a representative ensemble of chains. In this work we generated 5000 chains from 40 to 200 bonds long. The average square end-to-end distance was calculated for each series of 5000 chains. In addition, the characteristic ratio was calculated for each ensemble of 5000 chains by

$$c_n = \langle r^2 \rangle / nl^2 \quad (1)$$

where  $\langle r^2 \rangle$  is the mean-square end-to-end distance of a given chain averaged over the entire ensemble,  $l$  is the average bond length (the average of the single and double bond of polyacetylene), and  $n$  is the total number of bonds in a given chain. An ensemble of 5000 chains was chosen because a calculation of the characteristic ratio did not vary more than 15% for an ensemble of this size.

## RESULTS AND DISCUSSIONS

In previous works [9, 11] we obtained the potential energies for TC and CT for a rotation about one single bond. For example, a rotation of  $\phi = 117^\circ$  produced the most stable structure for CT, while the planar CT ( $\phi = 0^\circ$ ), though a minimum, was higher in energy. This angle, if propagated throughout the entire chain of polyacetylene, would produce a tightly wound  $2\frac{1}{3}$  helix with a chain unit cell length [11] of 4.43 Å. In the present work we tested whether this conformation would exist by examining the potential energy surface of CT polyacetylene for simultaneous rotations  $\phi_1$  and  $\phi_2$  as shown in Fig. 1.

The potential energy surface obtained from the present *ab initio* SCF calculations is given as a contour plot in Fig. 2. The zero of the potential is chosen as the energy of the planar CT for which  $\phi_1 = 0^\circ$ ,  $\phi_2 = 0^\circ$  (represented as the [0,0] state). Thus, all conformations with negative energies would be favored over a planar configuration. As expected from before [11], minima were found at  $\phi_1 = 0^\circ$ ,  $\phi_2 \cong 120^\circ$  and its symmetric analog [120,0]. When bond-bond interactions are absent (leading to zero steric hindrance), [120, 120] would be a deeper minimum because the minima would be simply additive. This would lead to the formation of a tight helix [11]. However, one can notice that, as  $\phi_1$  approaches  $120^\circ$ , the distance between  $H_3$  and  $H_8$  becomes optimum to give rise to the energy minimum. When one increases this further,  $H_3$  and  $H_8$  come closer and the consequent Pauli repulsion increases the energy. When  $\phi_1$  is at the optimum (i.e.,  $\approx 120^\circ$ ), an increase of  $\phi_2$  from

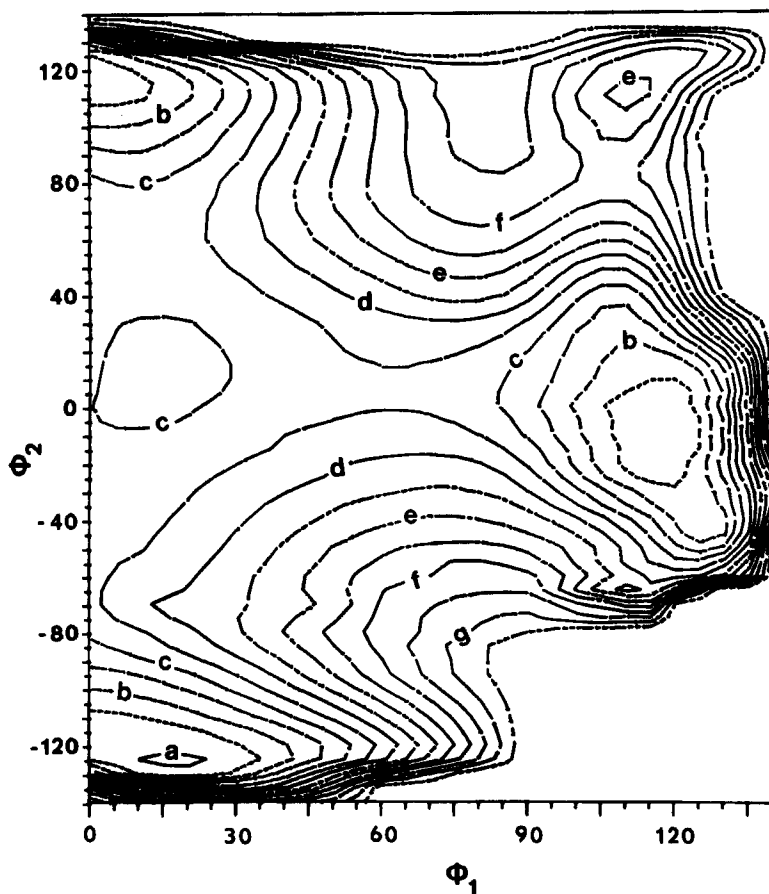


FIG. 2. Potential energy surface contours for the *cis-transoidal* molecule with simultaneous rotations about  $\phi_1$  and  $\phi_2$ . The values of the energies are given in kcal/mol with respect to a reference state of  $\phi_1 = 0, \phi_2 = 0$  as zero. The values of the contours go from -2 to +4 in steps of 0.5 kcal/mol, *a* representing -2 and *g* representing +4.

zero changes the relative distance of  $H_3$  and  $H_8$ , so that they are not at the optimum distance any longer. Consequently, the conformation moves out of the minimum (see Fig. 2).

From the energy map of Fig. 2, additional minimum energy conformations can also be seen. These structures are located at [117,120] and its compli-

TABLE 1. Energies and Conformational Probabilities for Various Conformations

$\phi_1, \phi_2,$ degrees	Energy, hartrees	Relative energy, kcal/mol	Conformational probability, %
0,0	-380.9363497	0.0000000	0.388
0,-120	-380.9392040	-1.7910989	7.420
-120,0	-380.9392040	-1.7910989	7.368
0,120	-380.9392040	-1.7910989	7.224
120,0	-380.9392040	-1.7910989	7.201
110,0	-380.9389825	-1.6521182	5.903
-110,0	-380.9399825	-1.6521182	5.895
0,-110	-380.9399825	-1.6521182	5.856
0,110	-380.9389825	-1.6521182	5.842
30,-120	-380.9387545	-1.5090336	4.786
-120,30	-380.9387545	-1.5090336	4.659
120,-30	-380.9388705	-1.5818247	4.145
-30,120	-380.9388705	-1.5818247	4.145
-30,130	-380.9385604	-1.382234	3.849
130,-30	-380.9385604	-1.3872341	3.815
-130,30	-380.9385604	-1.3872341	3.776
30,-130	-380.9385604	-1.3872341	3.700
-90,0	-380.9369000	-0.3453182	0.669
0,90	-380.9369097	-0.3514050	0.668
0,-90	-380.9369097	-0.3514050	0.647
90,0	-380.9369097	-0.3514050	0.583
110,30	-380.9367608	-0.2579689	0.566
-110,-30	-380.9367608	-0.2579689	0.558

TABLE 1 (continued)

$\phi_1, \phi_2$ , degrees	Energy, hartrees	Relative energy, kcal/mol	Conformational probability, %
30,110	-380.9367608	-0.2579689	0.538
-30,-110	-380.9367608	-0.2579689	0.521
0,130	-380.9364913	-0.0888553	0.445
-130,0	-380.9364913	-0.0888553	0.415
130,0	-380.9364913	-0.0888553	0.351
0,-30	-380.9361829	+0.1046873	0.324
30,30	-380.9361408	+0.1310866	0.320
0,30	-380.9361829	+0.1046873	0.312
-30,0	-380.9361829	+0.1046873	0.309

mentary symmetries such as  $[-117,120]$  etc. The exact value of the minimum is 1.98 kcal/mol above the energy value at  $[0,0]$ . The depth of the potential well at this conformation is also fairly shallow, having a value of only 1.27 kcal/mol. The energy at  $[117,120]$  is 3.85 kcal/mol above the minimum energy structure located at  $[0,117]$ . This high value is responsible for the improbability of this tight helix structure [11]. This energy gain of 3.85 kcal/mol suggests that  $[0,117]$  should be a very prominent structure, and this should favor the formation of a "superhelix."

Table I summarizes the energy values for the 30 "most probable" conformations. The conformational probabilities were calculated by Monte Carlo procedures, as mentioned. The conformations with the highest probability of being formed were found to be those at  $[0,120]$  and its symmetric analogs, i.e.,  $[120,0]$  etc. while that of the  $[117,120]$  state was less than 0.1%. The total for all the high-probability conformations was approximately 30%. These conformations, if propagated to any significant extent, could form what may be called "superhelical" segments. If we include all conformations where the angles  $\phi_1$  and  $\phi_2$  are within  $\pm 10^\circ$  of this "superhelical" state, including all symmetric analogs, the total percent would increase to approximately 60%. It should be noted that no long-range interactions were incorporated into these calculations. It is known that such interactions exist and should increase further the percent of helical structure of the polyacetylene molecule.



It is interesting how the conformational probabilities in Table 1 fall into several distinct groups. First, the most probable conformations i.e., [0,-120], [-120,0], [0,120] and [120,0], are those which, if propagated, would form a "superhelix." These, of course, are the minimum energy structures, as depicted in Fig. 2. The next most probable series of conformations are those which are relatively close to the "superhelix" conformation, i.e., [110,0], [-110,0], [0,-110], and [0,110]. The next eight conformations with probabilities between approximately 3.8 and 4.7% are [30,-120], [-120,30], [120,-30], [-30,120], [-30,120], [130,-30], [-130,30], and [30,-130]. Although these conformations have probabilities about half those which form the "superhelix," they differ by only  $\pm 30^\circ$  from the "superhelical" conformations.

There is a major break at the next series of conformations. The conformational percentage drops from 3.70% for [30,-130] to 0.67% for [-90,0] and [0,90], conformations about 1.6 kcal/mol higher in energy than the minimum energy conformations at [0,-120] or [-120,0]. These latter two conformations along with [0,-90], [30,90], and [90,0] differ in probability by less than 0.1% with values ranging from 0.67 to 0.58%. There were many additional conformations which appeared in the Monte Carlo calculations. However, most were with probabilities below 0.5%, many even below 0.01%. The highest 16 conformations in Table 1 had a total conformational probability of 85.6%. Therefore, all other possible values of  $\phi_1$  and  $\phi_2$  contribute less than 15% to the possible values of  $\phi_1$  and  $\phi_2$ .

Figure 3 is a plot of the characteristic ratio ( $c_n$ , see Eq. 1) of polyacetylene for an increasing number of bonds. The calculations were done on 5000 chains of 20, 40, 60, 80, 100, 120, 160, and 200 bonds, but computational time needed made it impractical to calculate longer chains. The characteristic ratio is seen to be proportional to  $n$ , indicating a very stiff rodlike molecule, as opposed to a very flexible polymer chain for which  $c_n$  approaches a constant value with increasing  $n$ . The chain stiffness is not surprising since the molecule is an alternating single-double bonded chain.

As pointed out before [11], the CT conformation cannot go to a *trans* or a TC form. These latter two are rotational isomeric states of each other, and the percentage of *trans* conformation is much greater at higher temperatures. Therefore, a similar study is under way for the *trans-cisoidal* form of polyacetylene.

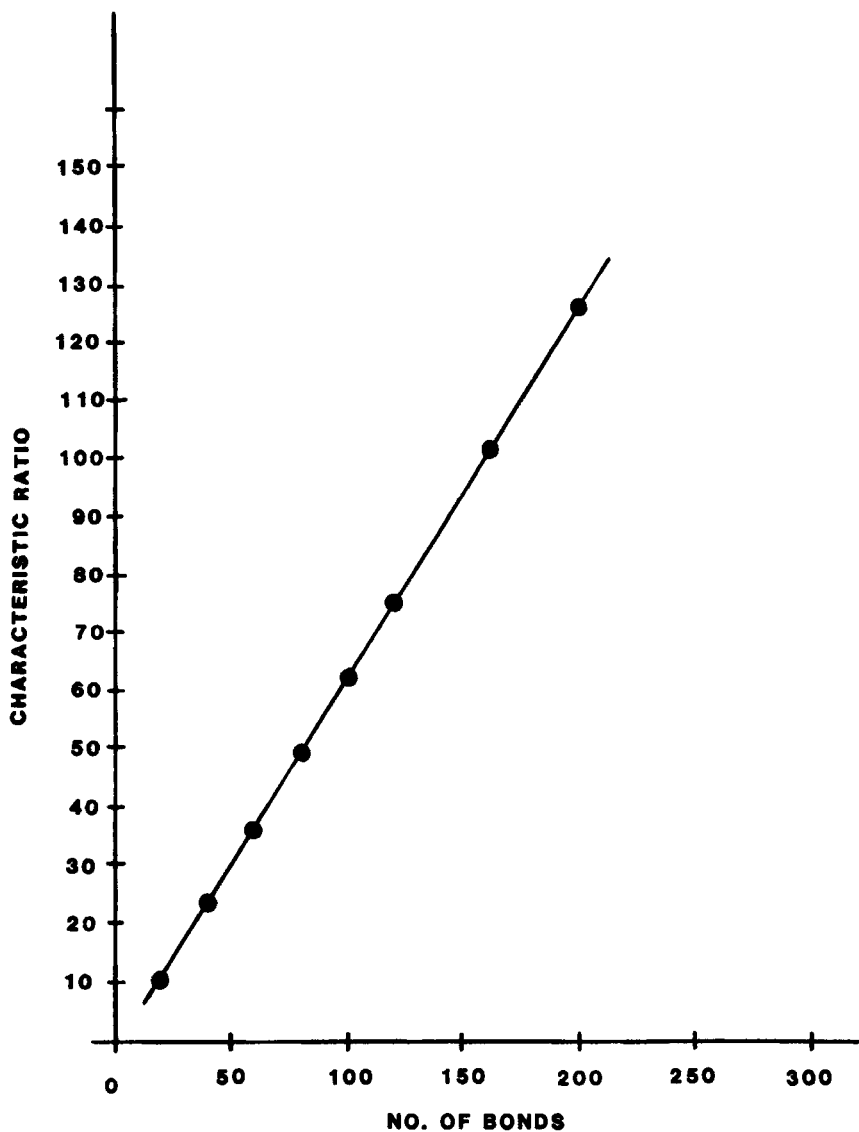


FIG. 3. Plot of the characteristic ratio for various chain lengths.

## CONCLUSIONS

*Ab initio* molecular orbital calculations indicate that several minimum-energy conformations exist for *cis-transoidal* polyacetylene. The structures with the greatest probability of occurring were [0,117] and its symmetric analogs. This conformation propagates to form a "superhelical" segment of the macromolecule.

Another conformation examined closely was [117,120], which on propagation would lead to a "tight" helix. It had an energy 4.85 kcal/mol above the minimum-energy structure, but the depth of its potential-energy well was only 1.27 kcal/mol, and Monte Carlo calculations indicated that its probability of occurring was only 0.1%.

Calculations of the end-to-end distance indicate that *cis-transoidal* polyacetylene is a very stiff molecule, which might well support very long helical segments. Future studies will address long-range interactions to determine how long a "superhelical" segment might be propagated.

## ACKNOWLEDGMENTS

J.A.D. was supported in part by the Center for Energy and Mineral Resources of Texas A&M University and the Organized Research Grant of Tarleton State University. N.R.K. was supported in part by the Department of Energy contract DE-AS05-77ER05399.

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Received May 5, 1987

Revision received August 16, 1987