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SCF-MO STUDIES OF THE ROTATIONAL POTENTIAL ENERGY SURFACE OF *trans-cisoidal* POLYACETYLENE

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ABSTRACT

Molecular Hartree-Fock calculations have been performed on *trans-cisoidal* polyacetylene to study the effect of simultaneous rotation about two successive single bonds on the energy of this polymer. A potential energy surface mapped out for this molecule shows that the all-*trans* conformation corresponding to the simultaneous rotations of all single bonds by 180° is the lowest energy state for this polymer.

INTRODUCTION

Polyacetylene can exist in three isomeric conformations. These are the *trans,* the *cis-transoidal* (CT), and the *trans-cisoidal* (TC). Theoretical studies have shown [1] that when a rotation of 180° occurs about a single bond in the TC form, it exhibits a segment of *trans* configuration at that point. Due to steric hinderances, such production of *trans* polyacetylene is not possible starting from the CT conformation. Moreover, formation of the *trans* from the CT with rotations about the double bonds is also not easy because this would require rotations about the double bonds and these rotations are expensive in terms of energy. Thus, *cis-trans* isomerization can occur between the TC and the *trans* only. It is suggested that during the changes of conformations, "kinks" could be introduced in the polymer which would provide the mechanism for electrical conduction. Therefore, the TC-*trans* isomerization requires detailed study.

Rao et al. [1] have already studied this problem for a single bond rotation. However, bond–bond interactions [2], known to be important, have not been considered in their work. In the present work we have studied a TC chain of polyacetylene with simultaneous rotations about two successive single bonds to produce a rotational potential energy surface which can provide important information about the ground states of these chains as well as the possible steric hinderance effects when the polymer folds back upon itself.

METHOD

We present a schematic model of TC polyacetylene in Fig. 1. This chain has been curtailed at a length of 10 carbon atoms in the backbone. We have already demonstrated [3] that this molecule can be used to study the electronic structure of polyacetylene suitably as this shows the bond alternation expected due to Peierls instability. Moreover, with these 10 carbon atoms the bond rotations happen at the center of the chain and are not affected by the finite length of the chain. We have considered the rotations ϕ_1 and ϕ_2 about two successive single bonds C_4–C_5 and C_6–C_7 in the middle of the chain. Rotation about the double bond has been neglected because it is energetically expensive. This limited model used in our study has one extra hydrogen atom added to each of the end carbon atoms to remove dangling bonds. The values of the bond lengths and angles have been obtained using suitable optimization procedures. These compare well with those available from experiments [1].

The theoretical method used here is the *ab initio* self-consistent field molecular orbital (SCF-MO) [4, 5] method where the molecular orbitals (MO) are obtained as linear combinations of atomic orbitals. Here, the atomic orbitals are represented by

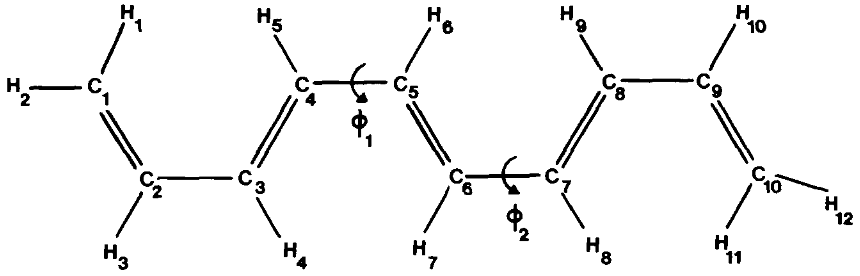

FIG. 1. Segment of the *trans-cisoidal* polyacetylene molecule studied in this work.

combinations of Cartesian Gaussian functions. This enables one to perform analytic calculations of the integrals and to decrease numerical inaccuracies as well as to decrease the computation time. The total energy of a given conformation is then calculated self-consistently.

A modified STO-3G [3, 6] basis set has been used in the present calculations where extra polarization functions (2s and 2p functions of the STO-3G type with optimized scale factors of 1.20) have been added at some of the hydrogen atom sites. These hydrogens are number 4, 6, 7, and 9 as shown in Fig. 1. Only these hydrogen atoms interact while the rotations ϕ_1 and ϕ_2 take place. Therefore, to simulate the detailed effects connected with the bond rotations, it is sufficient to modify these hydrogens only. It has already been demonstrated [6] that with only this modification, one can suitably represent the situation in polyacetylene. With these basis sets, the *GAUSSIAN 82* program [7] was used to compute the total energies of the chain for various values of ϕ_1 and ϕ_2. The sampling grid for the angles was chosen with a mesh size of 10°. Near points of special interest (e.g., near potential maximum or minimum), a finer grid was employed. Since the potential did not have any wild oscillations, this was considered to be sufficient.

RESULTS AND DISCUSSIONS

Under experimental conditions, polymer chains are expected to fold back upon themselves. This is dependent upon temperature and other experimental environments. Rotations about single bonds occur with relative ease in conjugated molecules upon warming up. Previously we had calculated the potential energies for TC [1] and CT [6] for a rotation about one single bond. We also had showed [3] that for the CT conformation the rotational potential energy surface was quite different from what one would expect to obtain if one did not consider the effect of bond–bond interaction. Thus suitable representation of the effects of steric hindrance is important. In the case of CT it was observed that instead of a tight 2*3/1 helix, a much extended super-helix was the ground state. Now we have studied the bond–bond interaction for the TC to determine whether this interaction influences the minima in the potential in this case also.

For a detailed study of the results we present the contour map of the rotational potential energy surface in Fig. 2. The same surface is schematically presented in three-dimensions in Fig. 3 for easier visualization. One notices that for rotations of $\phi_1 = 180°$ and $\phi_2 = 180°$ (represented as the [180,180] state), one obtains the lowest energy state. We have plotted the figures with this conformation as the reference. It is easily seen that the planar TC is not the state that is energetically favored.

Our previous potential [1] for TC with a single bond rotation had showed two minima. The deep minimum was at a rotational angle of 180° while a shallow

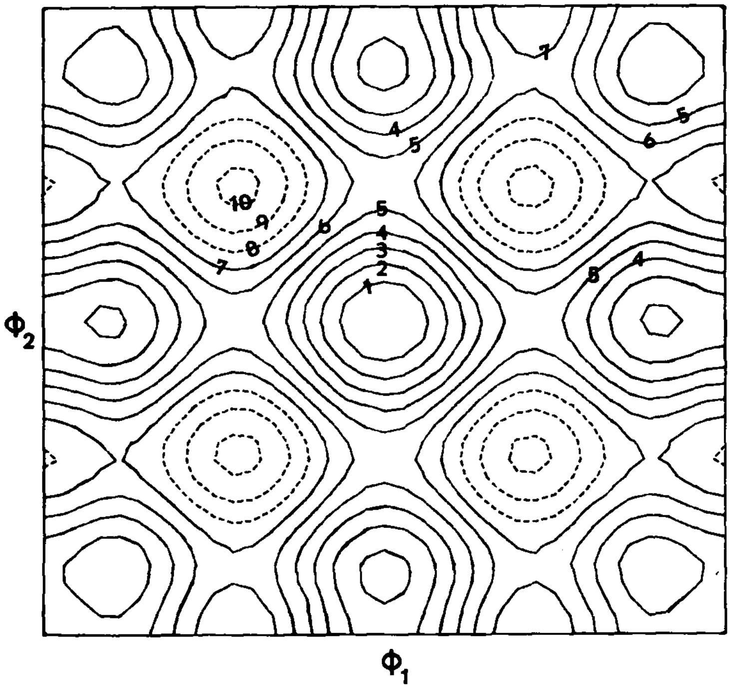

FIG. 2. Potential energy surface contour for the *trans-cisoidal* molecule with simultaneous rotations ϕ_1 and ϕ_2. The energy values of the contours are given in kilocalories. These are the energies with respect to the [180,180] state. Angles are as shown in Fig. 3.

minimum occurred at an angle close to 40°. The previous conformation corresponded to the *trans* and the later one represented a *gauche* state. The later state left the polymer bent out-of-plane. In the present case, it is noticed that in addition to the minimum corresponding to the [180,180] position, there are also minima at [40,180] and its symmetric equivalent [180,40] as well as at [40,40] and [320,320]. In these positions the energy is close to ground state. However, the minima are very localized while in the case of [180,180] the minimum is rather extended.

The observation of the maxima also leads to a similar pattern. In the single bond rotation [1], the maximum occurred at about 100°. In the present case the maxima occur at [0,100], [100,100], [0,260], and their symmetric counterparts. Note that in each case the maximum occurs at a rotational angle of 100° from the planar TC state (i.e., ϕ = 0 or 360°).

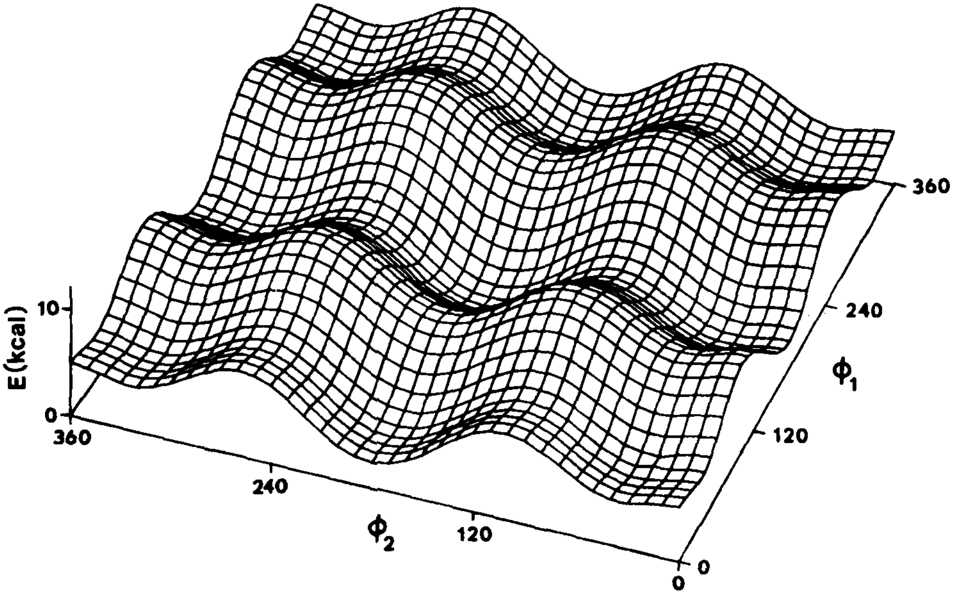

FIG. 3. Three-dimensional plot of the potential energy surface represented in Fig. 2.

We had noticed that the effect of simultaneous rotation about two successive bonds was not additive in the case of the CT conformation. However, in the present case the energies are changed in an additive manner. This has to be expected because the relative distances among the neighboring hydrogen atoms change when the rotations occur simultaneously. That pushes the conformation toward an all-*trans* form. Still, some possibility exists for the chain to be in a *gauche* state. This is because there are localized minima at non-*trans* positions (e.g., [40,180]). Even though localized, the relative energies in these cases are close to zero, and that should provide finite probability for the polymer to "lock" into some of these minima.

The near-additivity of the rotational energies can be explained by observing the changes in the interactions created by the rotations. When one has the planar TC (for [0,0]), the interactions between H_4 and H_7 as well as that between H_6 and H_9 are close to repulsive. Therefore, when one of the angles begins to increase, the repulsion decreases and there is a lowering of energy. However, when the angle passes the 40° mark, any further increase in angle begins to break the charge-sharing occurring in the hydrogen pairs, and this leads to an increase in energy. After passing 100°, this bond is essentially broken. Therefore, a further increase in energy does not take place. On the other hand, the conjugation available in the *trans* conformation is responsible for the lowering of energy. This adds up in the two cases of hydrogen pairs mentioned. Unlike the case of CT [3], there is no steric hindrance produced by simultaneous rotations. Therefore, the additive effects are noticeable.

A summary of the values of the relative energies from different points in the potential energy surface is given in Table 1. These, in addition to Figs. 2 and 3, indicate that besides favoring an all-*trans* conformation, TC may also exist in a helical form if the chain stays in all the *gauche* angles. The most likely conformation would be a chain of *trans* polymer with some segments of *gauche*. Again, this would depend upon the experimental temperature and other conditions. A Monte Carlo calculation is under way to examine this by using the potential energy surface generated by the present calculations.

CONCLUSIONS

Ab initio theoretical calculations have been performed to examine the interactions between successive single bonds in the case of *trans-cisoidal* polyacetylene. The potential energy surface shows deep minima for rotations of 180° and its multiples, indicating that an all-*trans* conformation is its ground state. There are local minima corresponding to rotations of 40° off the planar TC, providing the possibility for the chain to stay in off-planar configurations also. This could lead to mixtures of *trans*

TABLE 1. Relative Energy Values at Some Interesting Points of Rotation

Position	Relative energy, kcal
[0,0]	5.0276
[0,40]	4.1983
[0,100]	8.1155
[0,180]	2.5027
[0,260]	8.1155
[0,320]	4.1983
[0,360]	5.0276
[40,40]	3.2204
[40,100]	6.9622
[40,180]	1.8270
[100,100]	10.2786
[100,180]	5.4729
[180,180]	0.0

and *gauche* segments in a chain as well as an all-*gauche* helix. In the case of the TC, the bond rotations are mostly additive, showing negligible bond–bond interaction. This is in contrast with the case of CT where this interaction is important.

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