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CROSS-LINKS IN POLYACETYLENE

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Résumé - Nous suggérons que la réticulation consécutive à l'isomérisation cis-trans du polyacétylène peut rendre compte de la présence des électrons non-appariés dans le film trans. Cette idée est confortée et illustrée par des résultats de calculs "self-consistent" de chimie quantique.

Abstract - We suggest that cross-link formation during the cis to trans isomerization of polyacetylene can account for the unpaired electron spins in the trans-film. Results of self-consistent quantum chemical calculations that support and illustrate the basic ideas are reported.

1. Introduction

The cis to trans isomerization of polyacetylene generates mobile free radicals that have been associated with solitons/1/. The fact that these free radicals persist in the trans-film is difficult to understand within an isolated constant chain length framework. Explicitly, within this context one would ultimately expect no more free radicals within the trans-film than in the cis-film. We propose that the generation of these radicals can be considered a natural consequence of assuming that cross-links form during the isomerization process. These concepts will be illustrated by the results of quantum chemical cluster calculations on the modified neglect of diatomic overlap/2/ (MNDO) level. Kuzmany et al./3/ have already noted that cross-links may play a role in the production of spins accompanying the cis-trans conversion.

2. Basic Ideas/Results

Our basic idea is that the cis-polymer contains incipient cross-links that form during the isomerization with the concomitant generation of two neutral soliton-like defects. In general terms, we envision two local minima in the free energy of the film as a function of some local configuration coordinate. One minimum occurs because of the tendency of the chains to remain planar and corresponds to cross-links not being formed. The other minimum arises from the local stability of the cross-link. In this configuration two neutral radicals are assumed to be present in the system. We do not relate the formation of these cross-links with the breaking of any CH bonds, which would be energetically unlikely, but rather with the conversion of an even number of C atoms from three-fold to four-fold coordinated through the formation of interchain C-C tetrahedral bonds. Perhaps the simplest example of such a cross-link with many of the necessary properties is shown in Fig. 1. In Fig. 1a a cross-link does not exist while in Fig. 1b the cross-link is formed and a bi-radical is now assumed to be present.
Figure 1. Newman projections looking down the possible cross-link bond axis. In Configuration (a) no cross-link is formed while in Configuration (b) a cross-link is formed and a neutral bi-radical is now present.

We have performed quantum chemical calculations on the MNDO level for the type of cluster shown in Fig. 1. These calculations were carried out to demonstrate that each of the two configurations sketched in Fig. 1 can correspond to a local minimum in the system energy. Results obtained by varying the C-C bond distance, \( d \), between the two carbon atoms capable of forming the cross-link are shown in Fig. 2 (solid line). These results indicate that direct application of the MNDO approach leads to just one minimum in the cluster energy as a function of \( d \). The vertical line in Fig. 2 corresponds to the C-C distance where the two chains would be planar. Due to Coulomb repulsion between the chains the minimum in the cluster energy occurs at values of \( d \) slightly beyond this line.

Figure 2. MNDO total cluster energy vs. possible C-C cross-link bond distance for a cluster similar to that shown in Fig. 1. The solid (dashed) line is the lowest single determinant singlet (triplet) state energy of the cluster.
The reason a second minimum does not develop in the solid line of Fig. 2 is due to the use of a restricted Hartree-Fock wave function in calculating the total cluster energy. This causes all electrons to be paired and is contrary to the ideas schematically illustrated in Fig. 1b. That the system would actually prefer two largely unpaired electrons in the presence of the cross-link can be seen by examining the lowest triplet state energy of the cluster (Fig. 2 dashed line). These results show a well-defined minimum in the cluster energy when the C-C cross-link is formed (d ≈ 1.52 Å).

**Figure 3.** MNDO results for the ground state singlet energy for the same cluster as studied in Fig. 2 obtained by including the simplest configuration interaction.

We do not want to use the above results to suggest that cross-link formation involves a singlet-triplet transition but rather that the restricted Hartree-Fock wave function used in the MNDO calculation is incapable of describing the configuration shown in Fig. 1b. This problem, however, can be largely rectified by using a two determinant wave function that will allow the Hartree-Fock ground state to optimally mix with the lowest energy double electronic excitation predicted by Hartree-Fock calculation. This procedure, starting as it does from the Hartree-Fock wave functions and being variational, must lead to a calculated total energy that is less than or equal to the previous Hartree-Fock singlet energy. The resultant wave function is still a singlet but for d's where the mixing (λ) turns out to be large, this wave function has the clear interpretation of one corresponding to a bi-radical. Results obtained in this way are shown in Fig. 3. Two well defined minima now occur in the predicted cluster energy and these minima are consistent with Fig. 1. That λ is large in the presence of the cross-link can be seen by noting that our calculated singlet energy is now only slightly greater than the previously determined triplet energy for this range of d's.

We have performed calculations with similar results to those reported in Fig. 3 on more complex clusters using several configurational coordinates. A number of these clusters were found to exhibit a bi-radical cross-linked geometry that lies significantly lower than the uncross-linked case. A detailed description of these results is complicated and will be reported elsewhere. However, these calculations clearly show that cross-linking, and hence spin production, can be a largely irreversible process.
3. Concluding Remarks

The results reported above demonstrate that cross-link formation during the cis to trans conversion of polyacetylene can account for the observed largely irreversible production of unpaired spins that accompanies isomerization. Additional evidence exists for the formation of cross-links during the cis to trans isomerization of polyacetylene. Druy et al./4/ have suggested that the increased embrittlement that is observed with the isomerization of polyacetylene is consistent with cross-link formation. Also, Wegner and coworkers have prepared soluble cis-polyacetylene at low temperature by using Luttinger’s catalyst. However, this material becomes insoluble upon isomerization indicating that cross-links form during the cis to trans conversion.

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References