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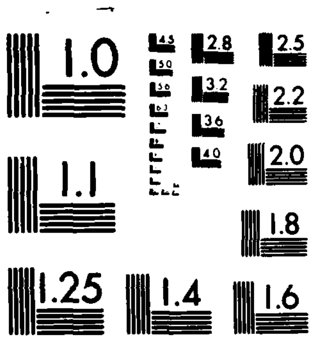

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Nutation NMR Studies of Polyacetylene

by

T. C. Clarke, R. D. Kendrick, and C. S. Yannoni

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San Jose, CA 95193

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Research Report

NUTATION NMR STUDIES OF POLYACETYLENE

T. C. Clarke
R. D. Kendrick
C. S. Yannoni

IBM Research Laboratory
San Jose, California 95193

IBM Research Division
Yorktown Heights, New York • San Jose, California • Zurich, Switzerland

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NUTATION NMR STUDIES OF POLYACETYLENE

T. C. Clarke
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ABSTRACT: Using nutation NMR spectroscopy we have been able to determine directly the carbon-carbon bond lengths in polyacetylene. For trans-polyacetylene we find double and single bond lengths of 1.36 and 1.44Å, respectively; the double bond in cis-polyacetylene is found to be 1.38Å. Interestingly, at 77°K we do not observe a rapid interchange of the single and double bonds in trans-polyacetylene in the manner predicted for chains containing a soliton defect, suggesting that the majority of the carbons in the trans isomer are on conjugated segments which do not contain such mobile species.

INTRODUCTION

The nature of the bonding in polyacetylene has long been a matter of both theoretical and practical interest, particularly as regards the extent of bond alternation in the *trans* isomer.[1,2] The highly disordered nature of as-grown polyacetylene films prevents the direct determination of the bonding parameters in this material by normal structural characterization techniques. Recently, however, in X-ray studies of oriented *trans*-$(CH)_x$ Fincher *et al*. were able to demonstrate the existence of bond alternation in the *trans* material.[3] They were also able to obtain indirectly an estimate of the bond alternation parameter, the displacement of the carbon atoms along the chain axis from their positions in a hypothetical bond-equalized structure, on the order of ± 0.03Å.

Using nutation NMR spectroscopy, we have now been able to determine directly the bond lengths in polyacetylene. In addition our results allow new insights in the mechanisms of polymerization and *cis-trans* isomerization in $(CH)_x$, as well as the role of solitons in the *trans* isomer.

EXPERIMENTAL

Polyacetylene was prepared by the procedure of Ito *et al.*[4] The special isotopic labelling required for these experiments was obtained by mixing 4% of doubly ^{13}C enriched acetylene (>99 atom % ^{13}C – MSD Isotopes) with natural abundance acetylene before polymerization. *Cis-trans* isomerization was carried out in sealed tubes under vacuum at 160°C for one hour. The details of the nutation experiment have been described previously.[5,6]

RESULTS AND DISCUSSION

Use of the nutation technique for bond length determination relies on the dipole-dipole splitting of two bonded magnetic nuclei.[5,6] To avoid interference from long range dipole splitting, however, these two nuclei must be relatively isolated from other magnetic nuclei. To achieve this situation in polyacetylene, we polymerized a mixture of 4% doubly ^{13}C enriched acetylene (99% ^{13}C) and 96% natural abundance acetylene. This procedure produces a dilute distribution of bonded ^{13}C pairs in the resulting *cis*-$(CH)_x$. (Removal of the splitting by adjacent hydrogen nuclei is accomplished by decoupling.)

The nutation spectrum of this *cis*-polyacetylene sample at 77°K is shown in Figure 1. The sharp peak in the center results from the isolated carbon-13 nuclei from the natural abundance acetylene used as the diluent. The rest of the spectrum is the Pake doublet expected from the splitting of two ^{13}C dipoles.[7] This pattern can be fit to obtain directly the distance between the two dipoles, the desired carbon-carbon bond length.[5,6] In this case the value obtained is 1.38±0.02Å. It is important to note that only one bond length is observed in the *cis* isomer. Although *a priori* this result could be interpreted in terms of complete bond equalization in *cis* $(CH)_x$, this explanation is quite unlikely for this isomer both on theoretical grounds and in light of the failure to observe bond equalization in the more favorable case of *trans*-polyacetylene *(vide infra)*. Rather the observation of only one bond distance indicates that in the Ziegler-Natta polymerization the carbons of a given monomer unit end up either singly or doubly bonded to one another, but not both. The observed bond distance of 1.38Å strongly suggests that the mechanism of the Ziegler-Natta reaction leaves the original carbon pair doubly bonded in the resulting polymer.

The situation becomes more complex after isomerization of this sample to *trans*-polyacetylene. The resulting nutation spectrum at 77°K is shown in Figure 2. In addition to the central peak, a superposition of two Pake doublets is clearly observed, indicating two different characteristic bond distances in the *trans* isomer. Fitting of this spectrum gives bond lengths of 1.36±0.02Å and 1.44±0.02Å, which can be assigned, respectively, to the double and single bond lengths in *trans*-polyacetylene.

The observation of both bond lengths clearly confirms the results of Fincher *et al.*[3] indicating the presence of bond alternation in the *trans* isomer. Moreover, the bond alternation parameter calculated from our bond lengths is also on the order of 0.03Å. Given the experimental error in each of the methods, this precise agreement may be fortuitous, but the results are clearly comparable.

The generation of approximately equal populations of singly and doubly bonded labelled carbon pairs in *trans* starting with only doubly bonded pairs in *cis* is intriguing. Motion of neutral solitons along a polymer chain would lead to the interchange of single and double bonds,[8] but the observation of two discrete Pake doublets requires that if the single and double bonds are dynamically equilibrating, the rate of interconversion at 77°K must be slow compared to the splitting between the features of the two doublets. Since this splitting is much less than one kHz, any dynamic interchange would have to be occurring at *less than* 10^3 sec^{-1}, a rate far too slow to be attributable to soliton motion.[9,10] In fact, these data require that if the neutral defects in *trans*-polyacetylene are indeed neutral solitons, most of the carbons in this material must be on conjugated segments which do not see these mobile species. Otherwise, the nutation experiment would have revealed only a single separation characteristic of the averaged bond length. This restriction of the solitons to a small fraction of the sample has many implications, and in particular must be considered in any model of nuclear relaxation mechanisms in *trans*-$(CH)_x$[11]

The scrambling of the bonding on *cis-trans* isomerization must then be attributed to sources other than soliton-like defects, and indeed suggests the generation of a substantial number of other types of defects in the conversion process. For example, crosslinks would disrupt the bonding sequence, but NMR results place an upper limit of ~1% on the crosslink concentration in *trans*-$(CH)_x$.[12,13] Other types of defect are also possible, and experiments designed to identify these defects may well provide new insights into the polyacetylene system.

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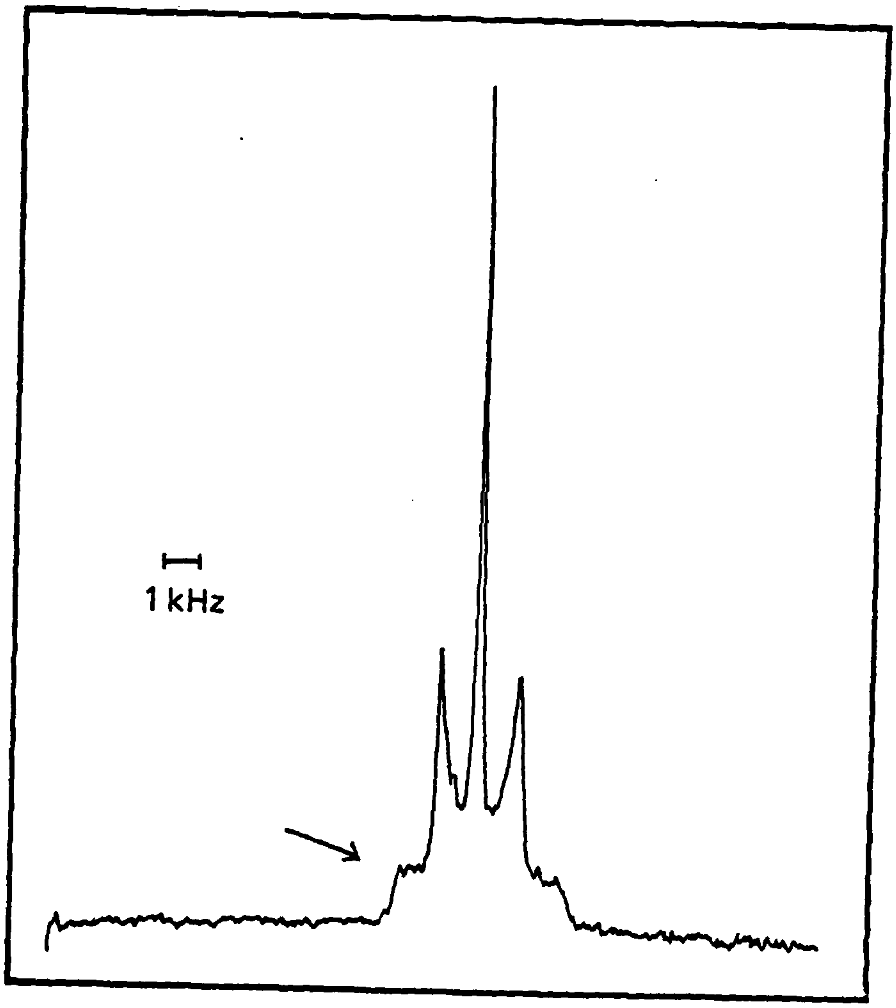

Figure 1. ^{13}C *nutation* spectrum of *cis*-$(CH)_x$ prepared from a mixture of 4% doubly ^{13}C enriched acetylene in natural abundance acetylene.

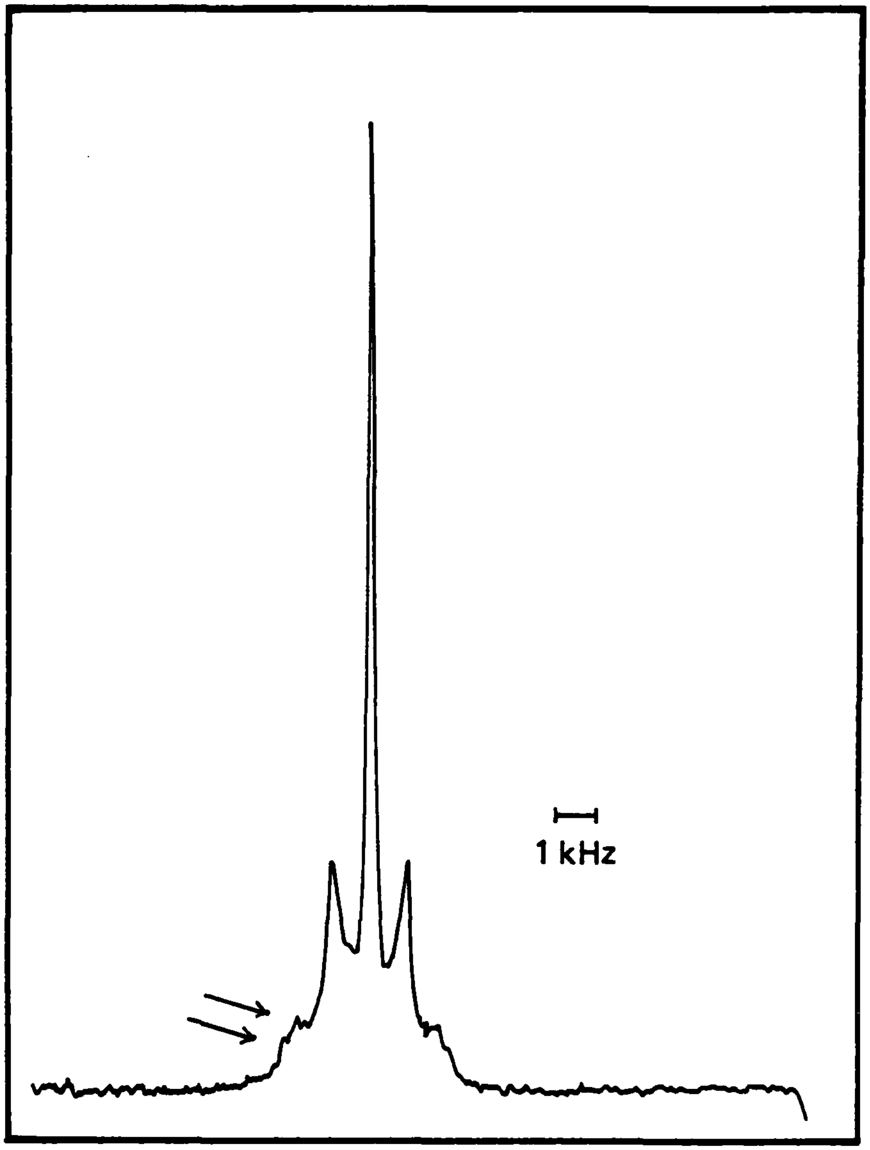

Figure 2. ^{13}C nutation spectrum of *trans*-$(CH)_x$ prepared from a mixture of 4% doubly ^{13}C enriched acetylene in natural abundance acetylene.

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