Molecular Geometry of *cis*- and *trans*-Polyacetylene by Nutation NMR Spectroscopy

C. S. Yannoni and T. C. Clarke
IBM Research Laboratory, San Jose, California 95193

(Received 20 June 1983)

The carbon-carbon bond lengths in polyacetylene have been directly measured with use of nutation NMR spectroscopy. 1.36 and 1.44 Å were found for the double and single bonds, respectively, in *trans*-$(\mathrm{CH})_x$, and 1.37 Å was found for the double bond in the *cis* isomer. Over the temperature range 4.2–300 K, the dynamical single-double bond interchange predicted for chains in *trans*-$(\mathrm{CH})_x$ containing a mobile soliton defect was not observed.

PACS numbers: 72.15.Nj. 61.16.Hn, 61.65.+d, 76.60.-k

The bonding in linear polyenes has long been a matter of fundamental interest.[1] The recent synthesis of polyacetylene,[2] the simplest long-chain polyene, and the subsequent investigations of its transport properties[3] have stimulated a number of structural studies.[4] Although the highly disordered nature of as-grown polyacetylene films has prevented the direct determination of the bonding parameters in this material by the usual structural characterization techniques, the existence and magnitude of the bond alternation in the *trans* material have recently been inferred from x-ray scattering data obtained with use of stretch-aligned films.[5] We wish to report here a direct determination of the bond lengths in both *cis*- and *trans*-$(\mathrm{CH})_x$.[6] These measurements, made on nonoriented samples, were carried out with use of nutation NMR spectroscopy, a method specifically designed to measure interatomic distances in amorphous solids or in materials which are difficult to produce in single-crystal form.[7]

The main results of our study may be summarized as follows: (1) The double-bond length in *cis*-$(\mathrm{CH})_x$ is 1.37 Å; (2) spectra for the *trans* isomer exhibit *two* bond lengths, 1.36 and 1.44 Å for the double and single bonds, respectively, unequivocally establishing bond alternation; (3) over the temperature range 4.2–300 K, the *trans* spectra show no direct evidence of the dynamical interchange of double and single bonds predicted to occur as a result of rapid motion of neutral soliton defects in this material (see Pople and Walmsley[1] and Su, Schrieffer, and Heeger[8]).

In principle, the splitting due to the magnetic dipole-dipole coupling in a $^{13}\mathrm{C}$ NMR spectrum contains the information necessary for the determination of carbon-carbon bond lengths.[7] This splitting varies inversely as the third power of the internuclear distance, and is manifested in a nonoriented sample as a Pake doublet with outer shoulders.[9,10] Nutation NMR spectroscopy can be used to eliminate the effects of chemical-shift anisotropy in the $^{13}\mathrm{C}$ spectrum, which completely mask the Pake doublet.[7] A description of the nutation experiment has been published previously,[10] demonstrating that the method is capable of measuring bond lengths to 1% accuracy. Since the major isotope of carbon ($^{12}\mathrm{C}$) is nonmagnetic, it is necessary to enrich with $^{13}\mathrm{C}$ the two sites whose internuclear distance is to be measured. To avoid broadening of the Pake doublet by long-range dipolar splittings, the $^{13}\mathrm{C}$ spin pairs must be relatively isolated from other magnetic nuclei. We achieved this situation in polyacetylene by polymerizing a mixture of 4% doubly-$^{13}\mathrm{C}$-enriched acetylene in acetylene which has been doubly depleted in $^{13}\mathrm{C}$ to provide a relatively spin-free host material. This produces a dilute, homogeneous distribution of bonded $^{13}\mathrm{C}$ pairs in the resulting $(\mathrm{CH})_x$. Proton decoupling is used to remove dipolar broadening by the adjacent hydrogen nuclei.

Polyacetylene was prepared by the method of Ito, Shirakawa, and Ikeda.[2] The isotopic labeling required for these experiments was obtained by mixing 4% of doubly-$^{13}\mathrm{C}$-enriched acetylene (≥ 99 at.% $^{13}\mathrm{C}$—MSD Isotopes) with doubly depleted acetylene (99.9% $^{12}\mathrm{C}$) before polymerization at 195 K. The resulting *cis* films were packed into sample tubes under dry box conditions and then sealed under vacuum. *cis* samples were stored at 77 K until use to avoid isomerization to the *trans* isomer. The *trans* material was obtained by heating in an evacuated sealed tube at 160 °C for 1 h.

The proton-decoupled $^{13}\mathrm{C}$ nutation spectrum of a *cis* sample prepared in this manner is shown as the solid curve in Fig. 1. The sharp peak in the center arises from isolated $^{13}\mathrm{C}$ nuclei in the sample. The symmetrically disposed satellites and shoulders are the features of a Pake doublet arising from the $^{13}\mathrm{C}$-$^{13}\mathrm{C}$ dipolar coupling of adjacent $^{13}\mathrm{C}$ nuclei in the polyacetylene. With use of a

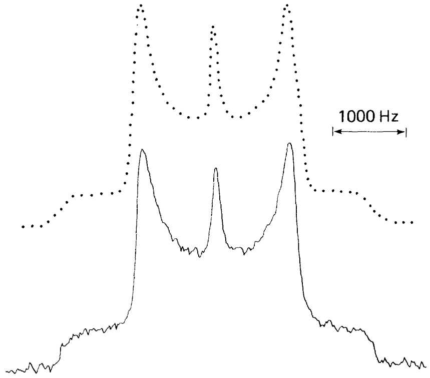

FIG. 1. Solid line: proton-decoupled ^{13}C nutation NMR spectrum at 77 K of doubly labeled *cis*-$(\mathrm{CH})_x$. Dotted curve: simulation of nutation spectrum of *cis*-$(\mathrm{CH})_x$ using a 1.37-Å C-C bond length. The peak in the middle is due to isolated ^{13}C nuclei.

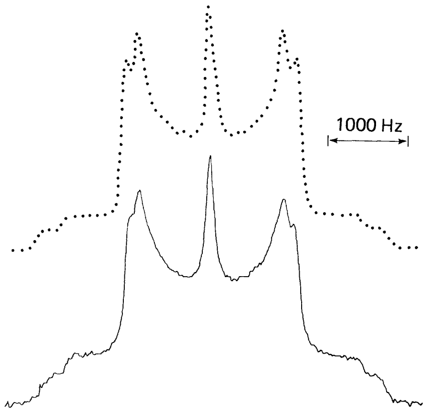

FIG. 2. Solid line: proton-decoupled ^{13}C nutation NMR spectrum at 77 K of doubly labeled *trans*-$(\mathrm{CH})_x$. Dotted curve: simulation resulting from superposition of ^{13}C nutation spectra using bond lengths of 1.36 and 1.44 Å. Again, the central peak is due to isolated ^{13}C nuclei.

comprehensive simulation program,[10] this pattern can be fitted with the desired carbon-carbon bond length as the only adjustable parameter. The best fit to the observed spectrum corresponds to a distribution of bond lengths with a mean value of 1.37 Å (see below); the simulation is shown as a dotted curve in Fig. 1. It is important to note that a nutation spectrum attributable essentially to one carbon-carbon bond distance is obtained for the *cis* isomer. Although *a priori* this result could be interpreted in terms of complete bond equalization in the *cis*-$(\mathrm{CH})_x$, this explanation is unlikely for the *cis* isomer both on theoretical grounds[1,8] and in light of the failure to observe bond equalization in the more favorable *trans* case (see below). 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 length of 1.37 Å strongly suggests that the mechanism of the Ziegler-Natta reaction leaves the original carbon pair doubly bonded in the resulting polymer.[11]

The situation becomes more complex on isomerization of this sample to *trans*-$(\mathrm{CH})_x$. The nutation spectrum of *trans*-$(\mathrm{CH})_x$ at 77 K is significantly different from that of its *cis* counterpart, as shown in Fig. 2. The doublet maxima peaks are now split and a step is observed in the wings of the Pake doublet. Both of these new features indicate two overlapping Pake doublets, and provide unequivocal evidence for a system comprised of not one but two carbon-carbon bonds of different lengths.[12] The simulation (dotted curve) shown in Fig. 2 is a composite of two Pake patterns of comparable intensity corresponding to bond lengths of 1.44 and 1.36 Å, which may be assigned to the single and double bonds, respectively, in *trans*-$(\mathrm{CH})_x$. These bond lengths are in very close agreement with those predicted by Grant and Batra using the tight-binding approximation to calculate the band structure of *trans*-polyacetylene.[13]

The observation of both bond lengths clearly confirms the interpretation of previous x-ray studies in terms of a bond-alternated structure,[5] and the bond-alternation parameter calculated from our results is on the order of 0.03 Å, in agreement with that derived by Fincher *et al.* However, it must be noted that if, as has been suggested on the basis of Raman studies,[14] there is a distribution of conjugation lengths in this material, then one might also expect a distribution of bond lengths to be observed. Indeed, we find the features of the polyacetylene spectra to be broadened considerably when compared to previous nutation studies of acetic acid[10] and to the narrow linewidths obtained in polyacetylene by magic-angle spinning techniques.[15] Thus, the bond lengths derived in the current experiments do correspond to the average values in a narrow distribution of bond lengths.

The generation of approximately equal populations of singly and doubly bonded labeled carbon pairs in *trans*-$(\mathrm{CH})_x$ starting with only doubly bonded pairs in the *cis* material is intriguing. Moreover, spectra of the *trans* isomer are substantially the same over the temperature range from 4.2 to 300 K. Motion of neutral solitons along a polymer chain would lead to the interchange of single and double bonds, but the observation of two discrete Pake doublets requires that if the single and double bonds are dynamically equilibrating, their rate of interconversion over this entire temperature range must be slow compared to the *difference* in splitting of the two Pake doublets. Otherwise the nutation spectrum would have shown a single Pake doublet characteristic of the average bond length. Since the smallest observable difference in splitting is on the order of 150 Hz, any dynamic interchange would have to be occurring at a rate less than 1.5×10^2 sec^{-1}. Given knowledge of the average conjugation length in *trans*-$(\mathrm{CH})_x$, the lack of coalescence in the nutation spectrum could be used to place an upper limit on the diffusion rate of soliton defects in this material. Unfortunately, reliable estimates of the conjugation length are not yet available. Moreover, this analysis would be complicated by the likelihood that many or most of the conjugated segments in the *trans* isomer do not contain a mobile spin.[16]

We thank the U. S. Office of Naval Research for partial support of this work. We are also grateful to R. D. Kendrick for his assistance in both instrumentation and implementation of the simulation program, and to H.-M. Vieth (Free University, Berlin) for stimulating discussions and help with the nutation experiment.

---

[1] J. E. Lennard-Jones, Proc. Roy. Soc. London, Ser. A 158, 280 (1937); C. A. Coulson, Proc. Roy. Soc. London, Ser. A 169, 413 (1939); H. C. Longuet-Higgins and L. Salem, Proc. Roy. Soc. London, Ser. A 251, 172 (1959); J. A. Pople and S. H. Walmsley, Mol. Phys. 5, 15 (1962).

[2] T. Ito, H. Shirakawa, and S. Ikeda, J. Polym. Sci., Polym. Chem. Ed. 12, 11 (1974); H. Shirakawa and S. Ikeda, Polymer J. 2, 231 (1971).

[3] For reviews, see W. D. Gill, T. C. Clarke, and G. B. Street, in "Electrical Properties of Polymers," edited by A. M. Herman (Dekker, New York, to be published); S. Etemad, A. J. Heeger, and A. G. MacDiarmid, Annu. Rev. Phys. Chem. 33, 443 (1982).

[4] R. H. Baughman, S. L. Hsu, L. R. Anderson, G. P. Pez, and A. J. Signorelli, *Molecular Metals*, edited by W. E. Hatfield (Plenum, New York, 1979), p. 187; R. H. Baughman, S. L. Hsu, G. P. Pez, and A. J. Signorelli, J. Chem. Phys. 68, 5405 (1978).

[5] C. R. Fincher, Jr., C.-E. Chen, A. J. Heeger, A. G. MacDiarmid, and J. B. Hastings, Phys. Rev. Lett. 48, 100 (1982).

[6] Preliminary accounts of these results have been presented in Proceedings of the Sixth International Conference on Chemistry of the Organic Solid State, Freiburg, 4–8 October 1982 (to be published), and in Proceedings of the International Conference on the Chemistry and Physics of Conducting Polymers, Les Arcs 11–15 December 1982 (to be published).

[7] C. S. Yannoni and R. D. Kendrick, J. Chem. Phys. 74, 747 (1981).

[8] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. 42, 1698 (1979), and Phys. Rev. B 22, 2099 (1980).

[9] G. E. Pake, J. Chem. Phys. 16, 327 (1948).

[10] D. E. Horne, R. D. Kendrick, and C. S. Yannoni, J. Magn. Reson. 52, 299 (1983).

[11] The implications of these results for the mechanism of Ziegler-Natta polymerization will be presented separately; T. C. Clarke, C. S. Yannoni, and T. J. Katz, to be published.

[12] We have also considered the possibility that the two Pake doublets arise from the anisotropy of the electron-mediated exchange coupling between the bonded carbons (J_{CC}). We have shown, however, that the anisotropy in J_{CC} is negligible in our previous nutation studies on acetic acid (Ref. 10). Moreover, simulations using reasonable estimates for J_{CC} [K. Zilm and D. Grant, J. Am. Chem. Soc. 103, 2913 (1981)] do not result in any splitting. Finally, the fact that the *cis* spectrum is not split also suggests that the J anisotropy is not responsible for the splitting observed in the *trans* material.

[13] P. M. Grant and I. P. Batra, Solid State Commun. 29, 225 (1979), and Synth. Met. 1, 193 (1980).

[14] H. Kuzmany, Phys. Status Solidi (b) 97, 521 (1980); D. B. Fitchen, Mol. Cryst. Liq. Cryst. 83, 95 (1982).

[15] M. M. Maricq, J. S. Waugh, A. G. MacDiarmid, H. Shirakawa, and A. J. Heeger, J. Am. Chem. Soc. 100, 7729 (1978); T. C. Clarke, J. C. Scott, and G. B. Street, to be published; P. Bernier, F. Schue, J. Sledz, M. Rolland, and L. Giral, Chem. Scripta 17, 151 (1981).

[16] J. C. Scott and T. C. Clarke, to be published; M. Mehring, in Proceedings of the International Conference on the Chemistry and Physics of Conducting Polymers, Les Arcs, 11–15 December 1982 (to be published).