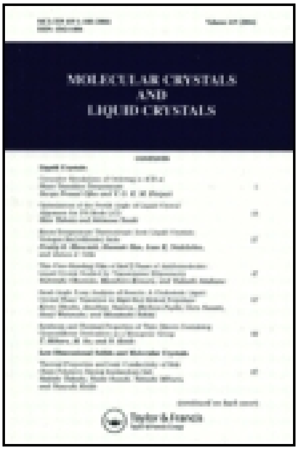

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Molecular Structure and Dynamics in Organic Solids: High Resolution Low Temperature ^{13}C NMR Studies

Costantino S. Yannoni [a], Thomas C. Clarke [a], Raymond D. Kendrick [a], Volker Macho [a], Robert D. Miller [a] & Philip C. Myhre [b]

[a] IBM Research Laboratory, San Jose, California, 95193

[b] Chemistry Department, Harvey Mudd College, Claremont, California, 91711

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MOLECULAR STRUCTURE AND DYNAMICS IN ORGANIC SOLIDS: HIGH RESOLUTION LOW TEMPERATURE ^{13}C NMR STUDIES.

COSTANTINO S. YANNONI, THOMAS C. CLARKE,
RAYMOND D. KENDRICK, VOLKER MACHO,[1]
ROBERT D. MILLER
IBM Research Laboratory, San Jose, California 95193

PHILIP C. MYHRE
Chemistry Department, Harvey Mudd College, Claremont,
California 91711

Abstract: The development of cross polarization-magic angle spinning (CPMAS) has resulted in the achievement of near-liquid resolution in solid state ^{13}C NMR spectra. Therefore, the structure and dynamics of organic solids can now be studied on a carbon-by-carbon basis. Low temperature CPMAS capability permits the investigation of molecular dynamics in solids, and in particular in a temperature range heretofore inaccessible to high resolution NMR (15-200 K). We have developed and used low temperature CPMAS to study solid state effects on chemical exchange processes in organic and organometallic compounds and in carbonium ions. We have also developed a technique for measuring carbon-carbon bond lengths in amorphous solids using NMR. The geometry of cis- and trans-polyacetylene has been determined using this method.

CROSS POLARIZATION-MAGIC ANGLE SPINNING

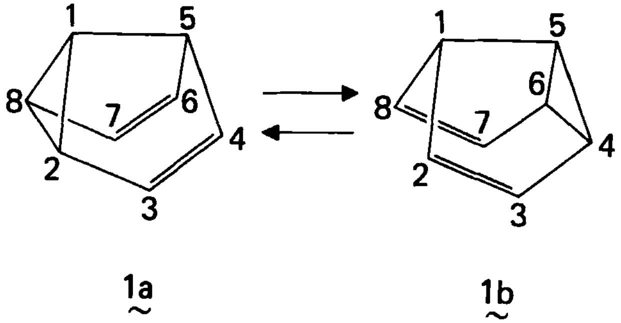
Solid state ^{13}C NMR spectra obtained using conventional methods have linewidths of several kilohertz, thereby masking the observation of individual carbon resonances. Highly resolved ^{13}C spectra of solids can be obtained by a combination of rf pulse and sample spinning techniques.[2] The dominant source of line broadening, coupling to nearby protons, is removed by decoupling as in solution ^{13}C NMR spectroscopy. The residual width, due to the anisotropy of the chemical shift, is reduced by spinning the sample about an axis which makes an angle of 54.7° with the external magnetic field. This results in liquid-like ^{13}C NMR spectra with a resonance for each chemically distinct carbon. Since the ^{13}C nucleus is only 1.1% in natural abundance, sensitivity is low, but can be enhanced by cross polarization, a method for transferring polarization to the carbons from the more abundant protons.

^{13}C NMR spectroscopy has been a powerful method for studying dynamic molecular processes (motion, chemical exchange) in solution. The temperature dependence of the width and shape of the resonances can be analyzed to yield rates and activation energies for such processes.[3] With the advent of high-resolution NMR in solids, it should be possible to carry out similar studies in solids. Toward this end, we have developed the capability for doing the CPMAS experiment at temperatures from 15 to 300 K.

APPLICATIONS OF LOW TEMPERATURE CPMAS NMR SPECTROSCOPY

Removal of Degeneracy in a Mirror-Image Rearrangement by Solid State Effects: Semibullvalene[4]

The degenerate Cope rearrangement of semibullvalene, shown below,



has been studied by solution NMR, and found to have a low activation energy (5.1 kcal/mol).[5] Since the molecule possesses a plane of symmetry bisecting the 2-8 and 4-6 bonds and containing carbons 1 and 5, the low temperature solution ^{13}C spectrum shows five carbon resonances. This is also found in the CPMAS spectrum we have observed in solid semibullvalene at -185°C, shown in Fig. 1.

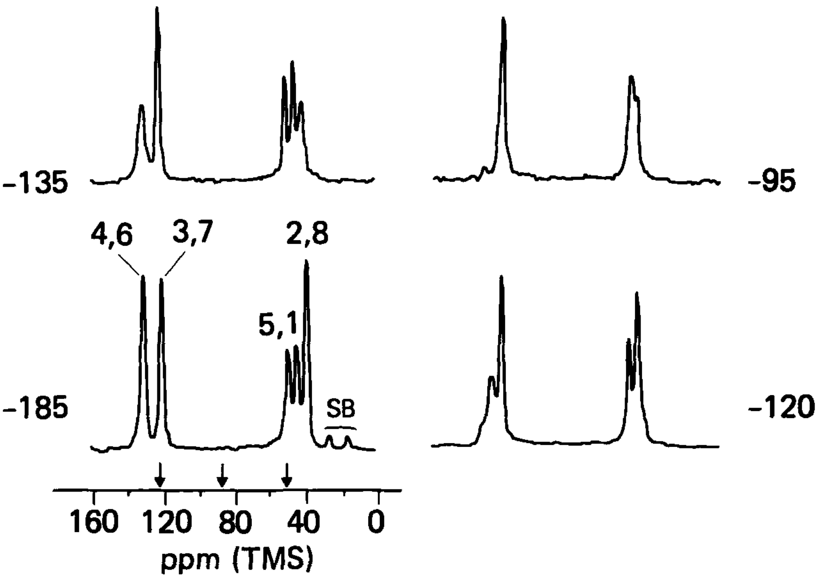


FIGURE 1. ^{13}C CPMAS spectra of solid semibullvalene. The peaks marked SB are the spinning sidebands of the vinylic resonances. Numbering refers to structure 1a.

In solution at higher temperatures, a three-line spectrum is obtained due to acceleration of the rearrangement and concomitant averaging of the resonances of carbons 1 and 5, and of the pairs 2,8 and 4,6. Since the interconverting structures 1a and 1b are iso-energetic in solution, the solution-averaged shifts are the average of the shift in each isomer, and are shown by the arrows in Fig. 1. It is clear from the spectra in Fig. 1 that the solution-averaged spectrum was never observed over the accessible temperature range in the solid state (semibullvalene melts at ~-85°C). *In fact, a complete lineshape analysis shows that the spectra are consistent with a rapid Cope rearrangement which is no longer degenerate. The removal of degeneracy is due to perturbations by the lattice.* The analysis results in the energy profile for the rearrangement shown on the following page. Without a crystal structure, it is difficult to speculate on the exact nature of the perturbation, but it is possible that packing effects favor one isomer (*e.g.*, 1a). When the rearrangement does occur, the other

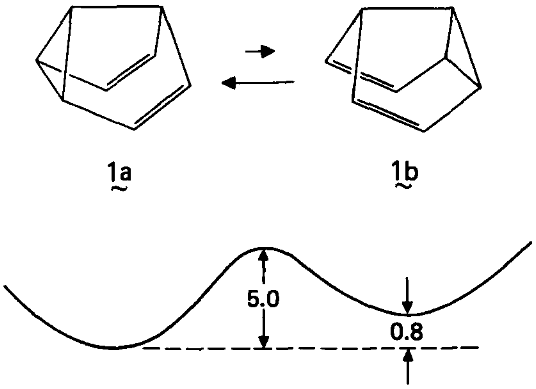


FIGURE 2. Activation energy and free energy difference (in kcal/mol) between isomers for the nondegenerate Cope rearrangement of solid semibullvalene in the solid state.

isomer is formed, and less favorable packing raises the energy. The analysis also shows that even though the activation energy for the conversion of 1a to 1b is the same as that found in solution, the rates in the solid are ten to twenty times slower.

We have also observed that semibullvalene samples prepared by rapid cooling could be thermally annealed to produce another solid phase.

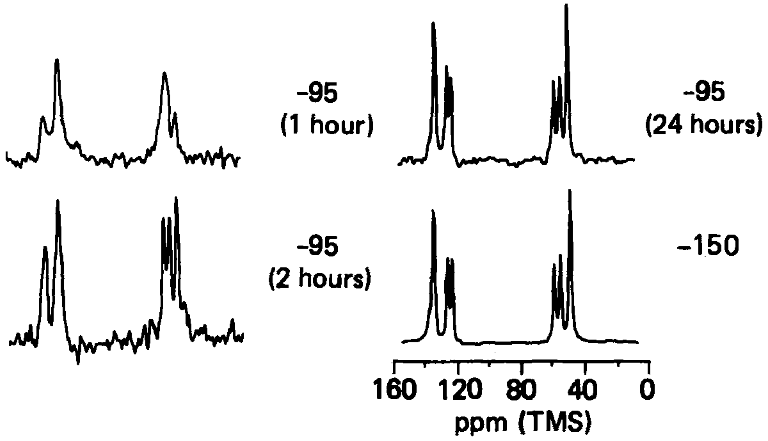


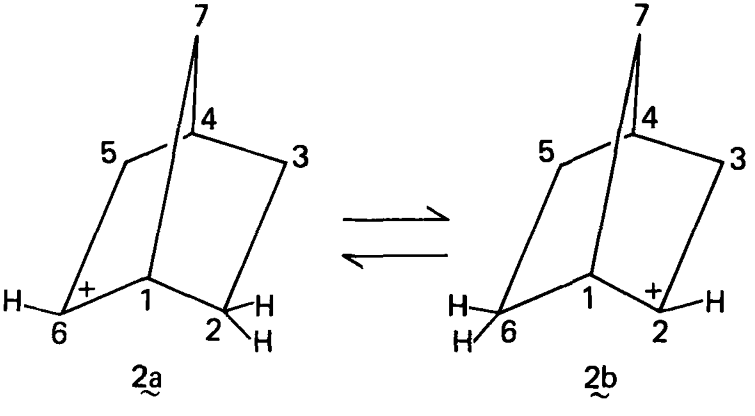
FIGURE 3. ^{13}C spectra of solid semibullvalene taken during and after annealing. After several hours at -95°C, the spectra no longer change with temperature.

As shown in Fig. 3, significant changes occur in the sample if it is kept at -95°C for several hours. After this, no further changes could be induced by thermal cycling, as shown by the spectra at -95°C (24 hours) and -150°C. Thus, it appears that the sample has been annealed into a stable phase. Furthermore, the lack of dynamical spectral behavior suggests that either the Cope rearrangement is suppressed, or that the free energy difference between isomers in the annealed phase is increased significantly compared with the dynamic phase. The splitting of the olefinic carbon peaks (C_3 and C_7) indicates that the molecular symmetry is broken in the annealed phase, and furthermore suggests that the same forces which alter the potential surface for the Cope rearrangement are also responsible for this subtle perturbation of molecular electron distribution.

On the basis of these results, we expect that crystal morphology will affect the potential surface of most molecular rearrangements, and that it may be possible to alter this surface by manipulation of the sample.

Carbonium Ion Structure and Dynamics: The 2-Norbornyl Cation at 5 K[6]

Degenerate rearrangements are very much a characteristic of carbonium ion structure. For example, the 2-norbornyl cation undergoes the rearrangement shown below (the "6,2-hydride shift") which has been studied in the solid state using CPMAS techniques[7] as well as in solution.[8] The activation energy for this process in the solid state was found to be the same as in solution, but as in semibullvalene, the rate was slower (but only by a factor of three or four). Owing to a



fortuitous combination of large chemical shift (due to the charge-bearing carbons) and small chemical shift anisotropy, resolved ^{13}C spectra of the norbornyl cation could be obtained at temperatures as low as 5 K without the benefit of magic angle spinning. Proton- and fluorine-decoupled ^{13}C spectra of the norbornyl cation between 5 K and 200 K are shown in Fig. 4.

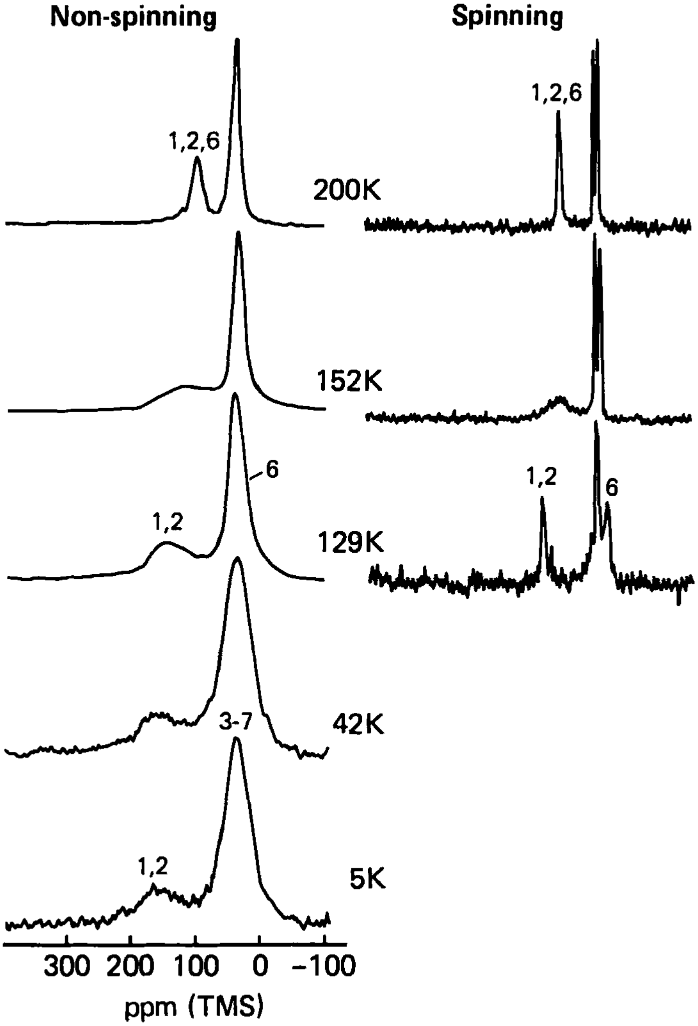
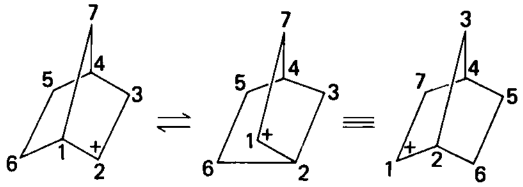


FIGURE 4. ^{13}C spectra of the 2-norbornyl cation with and without magic angle spinning.

For comparison, corresponding MAS spectra recorded previously[7] are also shown. A notable change in the spectrum occurs at about 150 K where the downfield band broadens and the center of gravity shifts downfield. At lower temperature, this band narrows and the center of gravity stabilizes at about 125 ppm. This change reflects the known slowing in rate of the 6,2-hydride shift (2a,2b), a process which is seen more clearly in the MAS spectra in Fig. 4.

At temperatures below 129 K the spectrum remains unchanged all the way down to 5 K. The temperature-invariant downfield band is the nonspinning equivalent of the low field resonance observed in liquid-state and MAS solid-state spectra. This resonance can be interpreted in terms of the time average of rapidly equilibrating localized (classical) ions (3), or as the positively charged carbons of the σ-bridged (nonclassical) structure (4).[9] If the former view is adopted,



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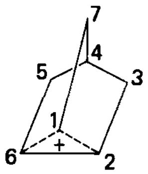

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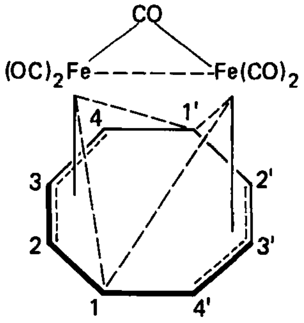
the spectrum at 5 K, which does not show even the onset of dynamic behavior, requires that the activation energy for interconversion of localized (or partly localized) ions be no greater than 0.2 kcal/mol.

The results reported here could also be taken as the most direct evidence yet obtained for the σ-bridged ion in super acid media.

CPMAS at Cryogenic Temperatures[10]

We have developed an apparatus which can be used for CPMAS experiments at temperatures as low as 15 K. The possibility of obtaining high resolution ^{13}C spectra at such low temperatures permits the study of dynamical processes with very low activation energies ($\leq$2 kcal/mol). To demonstrate the utility of this apparatus, ^{13}C CPMAS spectra of the fluxional organometallic compound (5)[11] have



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been obtained at cryogenic temperatures. X-ray studies show that the iron atoms are bonded locally to the cyclooctatetraene ring; therefore, there should be three inequivalent ring carbons yielding a three-line NMR spectrum.[12] The spectra, shown in Fig. 5, show only a single

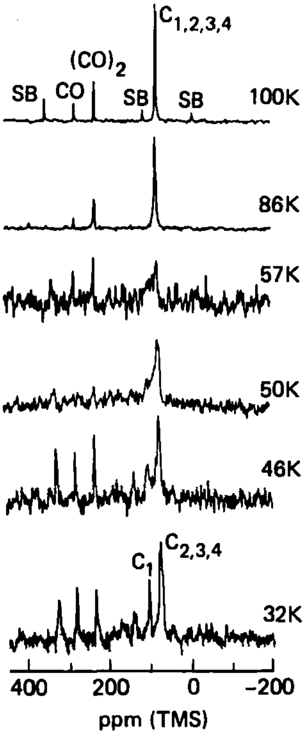


FIGURE 5. ^{13}C CPMAS spectra of cyclooctatetraene diironpentacarbonyl (5), showing slowing of ring rotation at very low temperatures. The peaks marked SB are spinning sidebands.

peak in the olefinic region at 100 K, suggesting the possibility of a valence tautomerism consisting of a rotation of the eight-membered ring with respect to the $Fe_2(Co)_5$ moiety.[12] This was further inferred from proton NMR relaxation measurements, from which an activation energy of 2.0 kcal/mol was obtained.[13] Direct proof that such a chemical exchange occurs has never been possible, because the process is so rapid at temperatures previously accessible to high resolution NMR measurements.

We have been able to obtain spectra of $\underset{\sim}{5}$ at very low temperatures, as shown in Fig. 5. As the temperature is lowered, the single line in the olefinic region (~90 ppm) first broadens, then develops a downfield shoulder, which develops further into a resolved peak at temperatures below 50 K. The downfield peak, which is one-third the intensity of the upfield resonance, moves three times as far downfield from the position of the average line (at 100 K) as the upfield resonance. These spectral changes constitute the first direct evidence for the slowing of a chemical exchange process in this material. Further work is planned to obtain the activation energy directly using a complete lineshape analysis.

A DETERMINATION OF GEOMETRY BY NMR SPECTROSCOPY: POLYACETYLENE

Nutation NMR Spectroscopy: A Method for Measuring Bond Lengths in Amorphous Solids

We have developed a method for measuring carbon-carbon bond lengths in amorphous solids with about 1% accuracy.[14] The distance is obtained from a splitting in the ^{13}C NMR spectrum resulting from the dipolar interaction between two ^{13}C nuclei.[15] Since ^{13}C is only 1.1% abundant, double enrichment is required to observe such a splitting. The nutation pulse sequence permits observation of the dipolar splitting, which is masked in conventional spectra by chemical shift effects.

The Bond Lengths in cis- and trans-Polyacetylene[16]

The geometry of $(CH)_x$ is of considerable interest, especially the degree of bond alternation in the trans isomer.[17] It has not been possible to produce single crystals of $(CH)_x$ so that diffraction methods are difficult to use. An alternation parameter of ±0.03Å has, however, been inferred from an analysis of x-ray scattering data on stretch-oriented films of trans-$(CH)_x$.[18] Since nutation NMR spectroscopy can be used to measure internuclear distances in amorphous solids in a very direct manner, we have applied it to determine the C-C distance in both cis- and trans-$(CH)_x$. Acetylene doubly enriched in ^{13}C (99 atom-%) was diluted (4%) in acetylene and polymerized following known procedures.[19] The material (cis-$(CH)_x$) was handled and loaded into the NMR tube with precautions to avoid contamination by oxygen, and kept at 77 K until use to avoid conversion to the trans isomer. The ^{13}C nutation spectrum, shown in Fig. 6, was also obtained at 77 K.

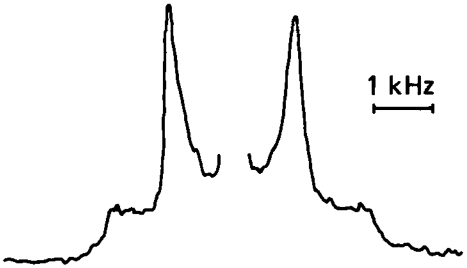
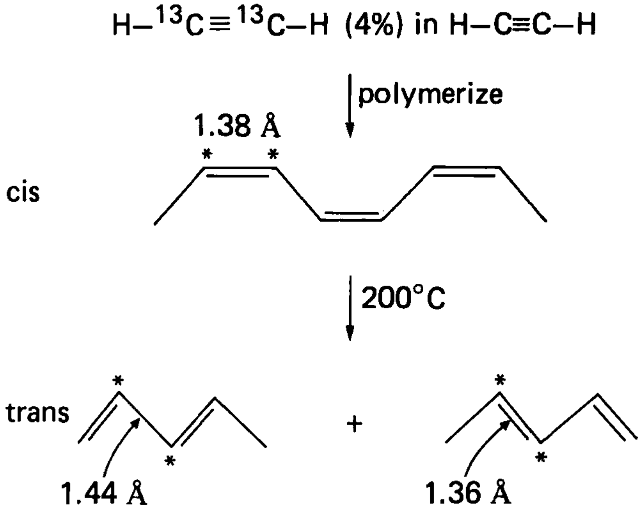


FIGURE 6. ^{13}C nutation spectrum of cis-$(CH)_x$ prepared from a sample of $(^{13}CH)_2$ diluted 4% in natural-abundance $(CH)_x$.

The strong single center line (clipped to save space) is from isolated ^{13}C nuclei (from the host material).[14] The symmetrically disposed satellites and shoulders are the features of a Pake doublet resulting from ^{13}C-^{13}C dipolar coupling.[15] Using a comprehensive simulation program,[14] we find that the bond length in the cis isomer is 1.38Å.[20] The sample was then converted to the trans isomer by heating to 200°C for one hour. The nutation spectrum of the trans material, taken at 77 K, is shown in Fig. 7.

FIGURE 7. ^{13}C nutation spectrum of trans-$(CH)_x$ prepared from the sample used for the spectrum shown in Fig. 6.

This spectrum differs importantly from that of the cis material: (1) the width of both of the doublet maxima peaks is larger, and (2) there is a step about halfway up the leading and trailing edges (shoulders) of the spectrum. ***Both of these new features provide unequivocal evidence for a system comprised of not one, but two carbon-carbon bonds of different lengths.*** In fact, simulations based on such a model show precisely the same broadening and steps, and the best fit corresponds to bond lengths of 1.36 and 1.44Å.[20] The results are summarized in the reaction scheme shown below.



The observation in trans-$(CH)_x$ of a spectrum consisting of a superposition of two Pake patterns of roughly equal intensity, but with differing bond lengths, is significant. We can unequivocally state that the trans isomer, obtained according to the reaction scheme shown, consists of chains with alternating bond lengths. From the reaction scheme, this must mean that the chemistry of isomerization involves transfer of the labeled ^{13}C pairs from location across a bond of one length in cis-$(CH)_x$ (represented as a double bond in the scheme) to location across bonds of two different lengths in trans-$(CH)_x$ (represented as single and double bonds). This result suggests that the defect moieties which are invoked in discussions of $(CH)_x$ structure may play a role in the chemistry of the isomerization process.

Furthermore, since the dipolar splitting is directly observable in the nutation NMR experiment, the existence of two bonds of different lengths is unequivocally demonstrated by the spectrum of trans-$(CH)_x$ (Fig. 7) without recourse to interpretation. The lengths obtained (1.36 and 1.44Å) lead to an alternation parameter (±0.04Å) in agreement with theoretical predictions.[17]

ACKNOWLEDGMENTS

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20. These numbers should be considered preliminary, since the center line (clipped in Figs. 6 and 7) due to isolated ^{13}C spins in the host $(CH)_x$ may distort the Pake splitting. We plan to repeat this experiment using acetylene doubly enriched in ^{12}C as a host to reduce this distortion.