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A monthly collection of informal private letters from Laboratories of NMR. Information contained herein is solely for the use of the reader. Quotation is not permitted, except by direct arrangement with the author of the letter, and the material quoted must be referred to as a "Private Communication". Reference to the TAMU NMR Newsletter by name in the open literature is strictly forbidden.

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**NO. 353, FEBRUARY 1988**

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**FORTHCOMING NMR MEETINGS**

- Symposium on Quantitative NMR Spectroscopy, March 29, 1988, in Las Vegas, Nevada, at the 9th Rocky Mountain Regional A.C.S. Meeting (March 27-30, 1988); contact Donald M. Wilson (415-620-2415) or Daniel A. Netzel (307-721-2370); For details, see Newsletter 352, p. 76.

**DEADLINE DATES**

- No. 353 (April) - - - 18 March 1988
- No. 356 (May) - - - 24 April 1988
- No. 357 (June) - - - 20 May 1988
- No. 358 (July) - - - 17 June 1988

*New listing.*

Additional listings of meetings, etc., are invited.
Dr. Bernard L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303.

Dear Dr. Shapiro,

Re: "Dynamic Multiple Quantum Spectra"

In recent years there has been a growing interest in the use of multiple quantum NMR, taking advantage of the relatively simple structure of high-quantum spectra compared with those of conventional single-quantum experiments. These methods have however so far almost exclusively been applied to static systems which are not affected by exchange processes. To fill up this gap we have developed a methodology for computing multiple quantum spectra, in the dynamic regime, and are in the process of comparing the results with experiments. In the theory particular emphasis is placed on symmetry factorization and using approximate equations in the slow and fast dynamic limits.

As an example we consider the evolution of the dynamic lineshape due to the ring inversion process in s-trioxane dissolved in a liquid crystalline solvent. Calculated results for the five quantum order are shown in the figure. They show the evolution of the spectrum from the slow exchange regime where it consists of two doublets due to the four possible \( M = \pm 3 \) to \( M = \pm 2 \) transitions, up to the fast exchange limit where only two such transitions are allowed. These lineshapes are considerably simpler than those for the corresponding single quantum spectrum and emphasize the advantage that this method may have over conventional NMR.

Please credit this contribution to Dr. R. Poupko.

D. Gamliel Z. Luz S. Vega

Cable Address: Weininst (Israel) Phone: (054) 82111-83111 Tel Aviv, Israel 31900
Position Description for an NMR Chemist

The Amoco Corporation has an opening for an NMR specialist at the Ph.D. level in the Analytical Division of the Amoco Research Center located in Naperville, Illinois. The candidate must have an outstanding knowledge of the theory of NMR, and the ability to apply this knowledge to the solution of problems involving a wide range of organic molecular structures including petroleum fractions, macromolecules and monomers. The candidate will be required to have a good knowledge of common 1D and 2D techniques in the solution state, and extensive experience with the operation of NMR spectrometers. This position involves close interaction with a diverse professional staff across the research center, and, consequently, a premium is placed on oral and written communication skills. Computer programming and interfacing skills, and a background in other analytical techniques would be desirable. The candidate will also be encouraged to pursue research in the application of multipulse techniques to solids. Contact G. J. Ray, B-5, Amoco Corporation, Amoco Research Center, P. O. Box 400, Naperville, IL 60566; telephone (312) 420-5217.

\[
\begin{align*}
\text{Computed dynamic proton five-quantum spectra of a-triose dissolved in a liquid crystalline solvent for different ratios, } k, \text{ of ring inversion as indicated in the figure.}
\end{align*}
\]
December 1, 1987  
(received 12/24/87)

Professor B. L. Shapiro  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA  94303

Proton NMR Images of Polymer Retanned Leathers

Dear Barry,

We are interested in seeing what NMR Imaging of materials can do for us at Rohm and Haas. Recently Dr. Ralph Hurd from GE ran several images of polymer retanned leathers and obtained some interesting results. The proton NMR images were obtained on a CSI 2T using high strength, shielded gradients with an image resolution of about 25 micron. The leather pieces were rolled with the grain or smooth side on the outside and the flesh or coarse side on the inside. We are probably imaging the water in the sample as the leathers are approximately 15-20 % by weight water.

The leather sample shown in figure 1A is blue stock (leather tanned with paramagnetic Cr III) retanned with polyacrylic acid. The resulting image is very interesting as we see only a light region along the flesh side of the piece of leather while the rest of the sample appears dark, corresponding to a short $T_2$. We didn't necessarily expect to see an image at all of this sample as the leather is impregnated with paramagnetic chromium. This interesting image is possibly due to a non-uniform distribution of chromium throughout the leather.

The leather sample shown in figure 1B is pickled stock (leather stored in brine solution at low pH) tanned with polymethacrylic acid. The image is much clearer and shows essentially two different microdomains for the water with the shorter $T_2$ on the flesh side and the longer $T_2$ on the grain side of the leather. This could be due to a non-uniform distribution of polymethacrylic acid through the sample. Further work is in progress to more fully understand these proton NMR images.

Sincerely,

Rebecca L. Smith  
Anton el A'mma

Please credit this contribution to the Rohm and Haas subscription of C. T. Hunt.
Figure 1

$^1$H NMR Images of Leather Samples. The grain side of the leather is on the outside and the flesh side is on the inside. (A) Blue Stock Leather Retanned with Polyacrylic Acid. (B) Pickled Leather Tanned with Polymethacrylic Acid.

Position Available

The Basic Food Chemistry Laboratory at the Kraft Technology Center has an opening for a Senior Technologist to work in the area of NMR spectroscopy. Duties will include operation and maintenance of a Bruker MSL 400 NMR spectrometer. The successful candidate will have the opportunity to design experiments and interpret results in collaboration with senior technical personnel, train new instrument users, and update and improve NMR hardware and software.

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Structural Elucidation of a Snow Mold Metabolite

13C COSY of the Biosynthetically-enriched Material

Here is my belated response to your barrage of colored notes.

Some years ago, colleagues of mine in the Agriculture Canada Research Institute on our campus were interested in hydrogen cyanide production by a low temperature basidiomycete, Coprinus psychromorbidus. During this investigation a new fungal metabolite was isolated from the W2 isolate by Et2O or EtOAc extraction of the culture filtrates and the mycelia. Chromatography and crystallization furnished a white solid, m.p. 105-7°C having the molecular formula C15H22O3. Alvin Starratt, the original investigator, asked me several months ago if you might be helpful to confirm or refute his proposed structure for this metabolite, which he named coprinolone. The 13C spectrum contained the expected 15 signals including peaks for carbonyl carbon, quaternary, tertiary and secondary carbinyl carbons, three methyl, three methylene, three methine and two quaternary carbons, none of which are sp2. Thus, coprinolone is tetracyclic.

Directly bonded carbons and hydrogens were identified by heteronuclear correlation and I expected to wrap up the structure with INADEQUATE experiments but such was not to be for reasons that are unclear to me. These spectra led to Skeleton A plus a -CH2CH2- and a CH3- group. However with the results from a long range heteronuclear correlation (XCORRE), the part-structure could be extended to B

An incorporation experiment with [1,2-13C2]acetate furnished labelled material, 4% incorporation, whose 13C spectrum revealed the presence of 6 intact acetate units compatible with structure C. The labelling pattern was similar to that found for other metabolites formed through a protoilludyl intermediate. To establish the entire carbon skeleton a 13C COSY spectrum was obtained and showed all but two linkages (a and b in C) which, however, had been demonstrated by our earlier experiments. Thus structure C was confirmed and coprinolone represents the first example of an oxygen-bridged protoilludane. The stereochemistry has been defined by noe difference spectra.

Sincerely,

J.B. Stothers
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GE NMR Instruments
Dr. Bernard L. Shapiro
966 Elsinore Ct.
Palo Alto, CA 94303

Dear Barry:

Title: Pseudo N-Dimensional NMR

For some years now carbohydrate chemists have used high-field \( ^1H \)-n.m.r. to determine oligosaccharide structures. Resonances arising from "reporter groups" in the molecule (including anomeric protons and H2 of mannose residues) have shifts and coupling constants sensitive to ring configuration and linkages to and from neighboring residues. Structures can be determined by comparing these resonances to those arising from model compounds of known structure. On the other hand, \( ^13C \)-n.m.r., while circumventing many of the problems associated with proton spectra (such as overlapping resonances), suffers from the disadvantage of low sensitivity, making the acquisition of spectra of mg quantities of material difficult or impossible. We initially sought to develop a method which shares many of the advantages of both \( ^1H \)-n.m.r. and \( ^13C \)-n.m.r. Our solution has been to study the carbonyl carbon resonances of peracetylated derivatives. These carbons are easily \( ^13C \)-enriched during the peracetylation reaction and are surprisingly sensitive to structures in the pyranosyl ring. For the purposes of relating changes in structure to changes in shifts, we have used COSY and \( ^13C \)-H shift-correlation spectra to assign these carbonyl resonances to specific acetyl substituents. Fig. 1 shows the sensitivity of the carbonyl resonances in peracetylated galactose residues to changes in the structure of the parent molecule. After having made similar assignments in over 30 parent structures, we came to the initial disappointing conclusion that given the spectrum of an unknown, it was often impossible to identify substructures by looking only at the carbonyl carbon resonances. However, when one includes the shifts of pyranosyl ring and acetyl methyl protons to which these carbonyl carbons are coupled, then unique patterns emerge. Fig. 2 illustrates this for 4 different residue types. Shifts along the edges of the cube correspond to shifts of carbonyl carbons, pyranosyl ring protons and acetyl methyl protons. Different types of data points represent the different assignments (i.e. open circles, ClAc, filled circles, C2Ac, etc.). Hence, rather than trying to identify residues on the basis of these one dimensional shifts, one instead uses a pattern in three dimensional shift space. Residue and linkage types can be identified in a pattern recognition fashion.
An obvious extension is to include other discriminating NMR variables into the scheme. For example the proton NOE's or carbon T1's may be of help in distinguishing a 2-1-4 linked glucose from a similarly linked galactose residue. Unfortunately, with the addition of more variables, one can no longer generate the type of plots shown in Fig. 2 (which usually turn out to be great eye-catchers in seminars) and one must then speak of pattern recognition in "n-dimensional NMR parameter space".

Sincerely yours,

Warren J. Goux
Associate Professor
of Chemistry

Fig. 1
Fig. 2
Dear Professor Shapiro,

We recently performed some $^{11}$B NMR measurements in aqueous solution on mixtures of boric acid and simple diols, which serve as model systems for borate esters of sugar acids and aminosugar acids. While investigating the pH dependence of 2,2-dimethyl-1,3-propanediol borate ester formation (Fig. 1), an interesting phenomenon was observed. At pH 6.6 a signal appeared which shifted from -2.5 ppm to -18.4 ppm ($\text{H}_3\text{B}O_3$: 0.0 ppm) upon going from pH 6.6 to pH 11 (Fig. 2). The linewidth decreased from 260 to 10 Hz, which suggests that the boron atom is more symmetrically surrounded at high pH. Since a chemical shift of -18.4 ppm is characteristic of a 1,3-bidentate monoborate ester, the pH dependable chemical shift has to be ascribed to the equilibrium between the $\text{B}^6\text{L}$ and $\text{B}^-\text{L}$ ester of 2,2-dimethyl-1,3-propanediol (see Fig. 1). This is, to our knowledge, the first time that the existence of a $\text{B}^6\text{L}$ borate ester and the equilibrium between a $\text{B}^6\text{L}$ and $\text{B}^-\text{L}$ ester is clearly demonstrated with $^{11}$B NMR.

Yours sincerely,

J. van Haveren

J.A. Peters
Fig. 1. Equilibria between 2,2-dimethyl-1,3-propanediol (L), boric acid ($B^0$) and borate ($B^-$) in aqueous solution.

Fig. 2. $^{11}$B chemical shifts ($B(OH)_3$: 0 ppm) as a function of pH for the equilibria $B^0L + OH^- \rightleftharpoons B^-L$ (L is 2,2-dimethyl-1,3-propanediol) and $B^0 + OH^- \rightleftharpoons B^-$ as observed in a sample containing boric acid (0.1 mol/l) and L (1 mol/l).
December 17, 1987
(received 1/7/88)

Dr. Bernard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter
Palo Alto, CA 94303

31P NMR Studies of Muscle Metabolism in Humans

Dear Barry:

We have been investigating forearm muscle metabolism in human volunteers using 31P NMR on a 1.9 T Bruker Biospec system. One of the protocols that we use consists of gripping a hand-dynamometer (which we demagnetized so that it can be used inside the magnet) at 30% of maximum capacity while spectra are collected every 30 seconds using a 4-cm surface coil placed over the flexor muscle. The dynamometer is interfaced to a PC which monitors the contraction and a digital display unit which helps the subjects to sustain accurate contractions. After 3 minutes of exercise, the subjects rest for 3 minutes and the process is repeated a second time. The time course of the phosphocreatine (PCr) to inorganic phosphate (Pi) ratio and the intracellular pH during exercise and recovery is shown in Figure 1. Our data to date indicate greater individual differences in intracellular pH than PCr/Pi ratio in the volunteers that we have studied. We are initiating a longitudinal study of our volunteers to delineate the influence of age on muscle metabolism.

Please credit this contribution to Dr. Gunther Eichhorn’s account.

Sincerely,

Raj

Rajasekharan P. Pillai
Isometric Exercise

$^{3}$P NMR

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Dear Prof. Shapiro:

The relationship of a polymer's sidechain to its backbone underlies a variety of physico-chemical attributes of macromolecules. One frequently speaks of the sidechain being (dynamically) "decoupled" from the backbone. The extent of motional decoupling is directly related to the nature of the intramolecular constraints. To a large extent these constraints are dominated by the dihedral angle energetics associated with the bonds in the sidechain. And, at short distances steric or excluded volume considerations come into play.

For the most part, NMR investigations of this aspect of polymer structure involves an analysis of the molecular dynamics of the different fragments of the polymer; i.e., detailed interpretations of NMR relaxation times. Here we illustrate that incompletely averaged quadrupolar interactions in a nematic solution of a homo polypeptide may be used to quantitatively examine the behavior of specifically labelled sites on the sidechain.

The figure shows the quadrupolar splittings from $-\text{CD}_3$ groups terminating the sidechains for a homologous series of ethylene glycol esters of the polypeptide poly(-L-glutamic acid). The polymer (~20% by wt. in chloroform) spontaneously forms a liquid crystalline solution (the helical backbones align parallel to the magnetic field). The residual anisotropy of the motion of the terminal methyls in the sidechains ($-\text{CH}_2\text{CH}_2\text{COO}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{CD}_3$, where $n = 0$ to 4) may be read directly from the magnitudes of the quadrupolar splittings in the $^2\text{H}$ NMR spectra. One may model the splittings via a configurational average over all of the sidechain conformations and from the comparison of calculated and experimental splittings, surmise the extent of "decoupling" between the sidechain and the backbone of these polymers.

Very truly yours,

Edward T. Samulski

P.S. After 1 January 1988, my permanent address is:
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27599-3290
January 12, 1988 (received 1/15/88)

Bernard Shapiro
Editor, NMR Newsletter
966 Elsinore Court
Palo Alto CA 94303

Title: NMR Studies of Proliferating Cancer Cells

Dear Barry:

Your pink "reminder" tells me that you are having a nice time "in retirement" in sunny California, congratulations!

I would like to report the latest improvement to our "gel thread" perfusion method for studying metabolism of intact cells by NMR. Originally we used agarose gel (0.06%) to embed cells grown in culture (1). Although the method is now widely used (2), it has been criticised because it is not good for anchorage-dependent cells, since they do not anchor to agarose gel, (3), and because it does not allow the observation of proliferating cells, only of cells already grown and trapped but not dividing (4).

In our original paper we pointed out that other gels could be used in the same manner. We have now shown that cells can be trapped in natural basement membrane gel (or Matrigel™) thread, at low densities, and that they continue to divide indefinitely under these conditions (5). This was shown by microscopy as well as by direct $^{31}$P NMR observation of the metabolic signals. Most cells have receptors that bind components of the natural protein gel, and allow many experiments to be carried out that were not possible with the agarose gel, particularly for observing effects on cancer cells that occur over periods of days, such as effects of hormones. In a sense the growing conglomeration of cells in basement membrane gel is a "model tumor" for noninvasive studies of metabolism by NMR.

Yours sincerely,

Jack S. Cohen
Biophysical Pharmacology Section

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INTELLIGENT SOLUTIONS FOR YOU
Dear Barry,

The stimulated echo sequence has undergone a revival in the last three years and is now being used for both imaging and localised spectroscopy experiments [1,2]. A timing diagram is shown in Figure A for the version used in localised spectroscopy. It provides an attractive alternative to the ISIS method for proton spectroscopy, because it does not suffer from the dynamic range subtraction problem and naturally provides T2 filtered spin echo spectra. Recently, I coded this sequence for our instrument, and was a little dismayed to find that it did not perform quite as well as advertised. The problem was the presence of small spurious peaks from regions outside the anticipated localised volume (ROI). A second symptom was the presence of spurious hash around the base of the (true?) peaks. Hash is normal and is often blamed (correctly) on eddy currents but in this case the effect was worse than with the corresponding ISIS technique. These symptoms became markedly more pronounced as I extended the acquisition time and varied with the settings of the delays D2 and D3 for a constant acquisition time.
Some investigation has led me to an analysis of the problem and a cure, but to explain it I have to introduce some terminology to describe the sample and the different pulse experiments that different regions of the sample experience. The first concept is "topological equivalence". The relevant equation is shown below and indicates that any sample can be divided into 27 volumes that experience different things when one carries out a plane selective localised spectroscopy experiment.

For the stimulated echo experiment one region (the desired ROI) experiences three plane selective 90° pulses and all other regions experience none, one or two of these pulses and give rise to zero signal, an FID or a spin echo. These unwanted signals from the FIDs and two pulse spin echoes are largely dephased by the gradient pulses used for slice selection. Another insidious problem that occurs is that multiple signals are also generated from the ROI, because the 90° pulses divide the total NMR signal from this region into components that "echo" at different times. The tricky thing is that the timing of the unwanted echoes generated from the ROI corresponds to that for the two pulse spin echoes formed from regions outside the ROI. My tentative assignment of the signals to the symptoms is as follows: Spurious signal from outside the ROI comes from magnetisation that is not completely dephased by the gradient pulses and the hash around the true spectrum from the unwanted secondary echoes generated within the ROI. This would explain why the lengthening of the acquisition time had a bad effect, I was simply extending it sufficiently to collect the unwanted echoes.
The delay times $D_2$ and $D_3$ change the timing for the unwanted echoes and some combinations cause the problems to move into the acquisition window. The cure is a phase cycle suggested to me by Gareth Barker and Tom Mareci (University of Florida, Gainesville). The cycle was originally devised by Richard Ernst (ETH Zurich) I believe. It is as follows: P1: $x$, $-x$, $x$, $-x$, $x$, $-x$, $x$, $-x$; P2: $x$, $-x$, $x$, $x$, $-x$, $-x$, $x$, $-x$; P3: $x$, $x$, $x$, $x$, $-x$, $-x$, $-x$, $-x$; RCVR: $x$, $-x$, $x$, $x$, $-x$, $x$, $-x$, $x$. This cancels contributions from two pulse echoes and FIDs formed from the total NMR signal and preserves the desired stimulated echo. Figure C shows an image and localised spectra from a phantom containing "Australian Hair Salad" obtained at 4.7T. The recipe is: equal parts by volume water, benzene and acetone, spiced with 5 mM CuSO$_4$ and a pinch of chromium acetylacetonate. The mixture has not exploded so far and we believe it to be safe, though one should not drink it because benzene is a carcinogen. The funny lines along the meniscus between the two phases in the image are a three way chemical shift artifact, due to the partition of acetone between the two phases. The idea for using a two phase liquid system was also stolen from the Gainesville group.


Yours sincerely,

J. L. Foxall
Carbon-Carbon Coupling Constants in Indole.

Dear Professor Shapiro,

For our bio-organic studies we needed L-tryptophan, which is selectively isotopically enriched in the indole nucleus. Starting from simple enriched compounds we have prepared indoles 99% isotopically enriched with $^{15}$N at position 1 and with $^{13}$C at the positions 2, 3 and 4. These indoles have been converted biosynthetically in 100% yield into L-tryptophan.$^{1,2}$

The 49.9 MHz $^1$H-noise-decoupled $^{13}$C-NMR spectra (Jeol FX 200) of the $^{13}$C-enriched indoles showed one strong peak at the expected chemical shift value. In the spectrum of (3-$^{13}$C)indole five of the seven non-enriched carbon atoms appear as a doublet (Fig. 1). The signal of C4 is expected not to show much splitting, because it is bonded to C3 via two carbon-carbon bonds and $^{2}$$J$($^{13}$C-C) couplings generally are very small.$^{3}$ The other singlet should correspond with C5 according to the assignment previously reported.$^{4}$ The fact that $^{3}$$J$(C3-C5) < 1 Hz seemed very strange to us because $^{3}$$J$(C-C) coupling constants of transoid carbon atoms in aromatic compounds generally are about 5 Hz.$^{3}$ In order to check the assignment, we have performed a two-dimensional $^{13}$C-INADEQUATE experiment with natural abundance indole in CDCl$_3$ (Fig. 2). We have added a trace of Fe(acac)$_3$ to the solution in order to increase the relaxation rates of the carbon atoms. From this experiment it is evident that the original assignment proposed for C5 and C6 has to be changed. Our re-assignment is in complete agreement with the results recently published by Morales-Rios et al.$^{5}$ $^{1}$$J$(C-N) and $^{1}$$J$(C-C) coupling constants that we have obtained from both one- and two-dimensional $^{13}$C-NMR spectra are listed in the Table.

![Fig. 1: 49.9 MHz $^{13}$C-NMR spectrum of (3-$^{13}$C)indole.](image)

Sincerely yours,

E.M.M. van den Berg J. Raap C. Erkelens F. Lefeber J. Lugtenburg
Table: \(^1J(C-C)\) and \(^1J(C-N)\) coupling constant values (Hz) of indole (resolution 1.5 Hz).

<table>
<thead>
<tr>
<th></th>
<th>(^{1a})</th>
<th>(^{1b})</th>
<th></th>
<th>(^{1a})</th>
<th>(^{1b})</th>
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<tr>
<td>C2 - C3</td>
<td>68</td>
<td>69</td>
<td>C6 - C7</td>
<td>60</td>
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</tr>
<tr>
<td>C3 - C3a</td>
<td>53</td>
<td>54</td>
<td>C7 - C7a</td>
<td>64</td>
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<tr>
<td>C3a - C4</td>
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<td>62</td>
<td>C7a - C3a</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>C4 - C5</td>
<td>c</td>
<td>57</td>
<td>C2 - N1</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>C5 - C6</td>
<td>56</td>
<td></td>
<td>C7a - N1</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

- \(^a\): Obtained from the two-dimensional \(^{13}C\)-INADEQUATE experiment in CDCl\(_3\) with natural abundance indole.
- \(^b\): Obtained from the \(^1H\)-noise-decoupled \(^{13}C\)-NMR spectra of (1-\(^{15}N\))- (2-\(^{13}C\))- (3-\(^{13}C\))- and (4-\(^{13}C\))-indole.
- \(^c\): Because of the small chemical shift difference between C4 and C5, \(^1J(C4-C5)\) could not be determined from the INADEQUATE spectrum.

Fig. 2: \(^{13}C\)-INADEQUATE spectrum of indole in CDCl\(_3\).
(Bruker-WM-300)

References:
2. To be published.
Dr. B. L. Shapiro, Editor  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

Subject: "Tautomeric Forms of D-Arabinose Oxime"

Dear Barry:

The mutarotation of Z-D-arabinose oxime (1) to E-D-arabinose oxime (2) is subject to general acid and specific base catalysis and these reactions are postulated to proceed via one of a number of cyclic N-arabinosylhydroxylamine intermediates (3 - 6)1. The solution structure of 1 has been studied by $^1$H NMR$^2$ and $^{13}$C NMR$^3$ spectroscopy, but the presence of cyclic structures have not been detected.

With the aid of D-[1-13C]arabinose oxime, the postulated intermediates have now been observed. Spectrum A is the $^1$H decoupled 100 MHz $^{13}$C NMR spectrum of D-[1-13C]arabinose oxime (at 30°C) from 60 to 158 ppm. The enriched C-1 carbon of the Z (1) and E (2) acyclic forms, which comprise 22.7 and 74.1% of the equilibrium percentage respectively, resonate at 154.4 and 153.5 ppm (Figure 1). Spectrum B is the 91 to 97 ppm region of Spectrum A clearly showing the four cyclic forms. The tentative assignments based on $^{13}$C,$^1$H coupling constants of these forms follow:

3: α-furanose (96.7 ppm); 4: β-furanose (94.7); 5: β-pyranose (92.6 ppm); and 6: α-pyranose (92.0 ppm). The equilibrium percentage at 30°C of these forms are: 3, 0.7%; 4, 0.3%; 5, 0.4%; 6, 1.8%. The solution conformation and tautomeric equilibria of the four aldopentose oximes will be the subject of a future report.

Sincerely,

Joseph R. Snyder

Figure 1: (A) 100 MHz $^1$H-decoupled $^{13}$C NMR spectrum of D-[1-$^{13}$C]arabinose oxime in $^2$H$_2$O. The two signals at 154.4 (1) and 153.5 ppm (2) represent the Z and E isomers respectively. (B) The 91-97 ppm region of the $^{13}$C NMR spectrum of D-[1-$^{13}$C]arabinose oxime, showing the presence of the $\alpha$-furanose (3), $\beta$-furanose (4), $\beta$-pyranose (5) and $\alpha$-pyranose (6) forms.
Dr. B. L. Shapiro
TAMU NMR Newsletter
966 Elsinore Court
Palo Alto, CA 94303

"Herzfeld-Berger Analysis of Polymers and Blue Hen Flies Coop."

Dear Barry:

The installation of our Bruker MSL-300 spectrometer is virtually complete. One of the first successful experiments carried out with this instrument is a $^{13}$C CP/MAS analysis of a commercial material, Hytrel 4056, made by E. I. du Pont de Nemours and Company. We used a "slow" spinning rate to determine the principal chemical shift tensor elements from the sideband intensities (1). We analyzed the three resonances whose isotropic shifts are at 129 ppm (protonated aromatic carbons), 133 ppm (nonprotonated aromatic carbons) and 164 ppm (carbonyl carbons). A typical spectrum and calculated results for the principal elements are listed in the attached table. The difference in chemical shift elements are comparable to those published by Jelinski et al. (2) for a similar poly(butyleneterephthalate)-poly(ethylenebutyleneterephthalate) copolymer. As one can easily see, it is quite simple to use a system such as the MSL-300 to separate the resonances for sideband analysis in a complex system.

On another note, one of the "Blue Hens" has flown the coop. Dr. Lila Giersch has moved to the Department of Pharmacology, University of Texas, Southwestern Medical Center at Dallas, 5323 Harry Hines Blvd., Dallas, TX 75235-9041. The 9th Annual Blue Hen NMR Conference (in which Lila played a major role) will be continued by the remaining "Blue Hens". It is scheduled for early June.

Best wishes,

Cecil R. Dybowski
Roger W. Crecely
Jon Kauffman

RESULTS OF SIDEBAND ANALYSIS ON HYTREL 4056

\[
\begin{array}{|c|c|c|c|}
\hline
\sigma_{\text{iso}} & 129 \text{ ppm} & 133 \text{ ppm} & 164 \text{ ppm} \\
\hline
\sigma_{\text{ax}} & 33.0 \pm 8 & 40.7 \pm 10 & 85.0 \pm 11 \\
\sigma_{\text{ay}} & 144 \pm 8 & 147 \pm 18 & 202 \pm 7 \\
\sigma_{\text{az}} & 211 \pm 8 & 239 \pm 9 & 205 \pm 7 \\
\sigma_{\beta} - \sigma_{\text{ax}} & 178 \pm 16 & 198 \pm 19 & 120 \pm 18 \\
\sigma_{\text{xx}} - \sigma_{\text{ax}} (\%) & 187 & 203 & 132 \\
\hline
\end{array}
\]
Dear Barry:

Recently we needed a reliable calibration of $\gamma B_2$ for low decoupler powers, as a prelude to doing the Freeman/Bax long range coupling experiment (1). Clearly the usual double quantum experiment (Bruker calls it DEC90) would not work, since the decoupler power in the long range coupling experiment is necessarily set so that $\gamma B_2 < \frac{1}{2} J$. Our solution was simply to do an SPT experiment (2), thereby exploiting the selectivity inherent in weak $B_2$ fields.

A possible complication could arise from signals not due to polarization transfer, i.e., those signals arising directly from equilibrium (or steady state) $^{13}$C magnetization. Such signals are readily removed by alternately adding and subtracting signals, while holding the transmitter phase constant, analogous to EXORCYCLE. The required phase alternation of the SPT signals is then obtained by switching the decoupler frequency between the two $^{13}$C satellite frequencies in the proton spectrum, on alternate scans. Unlike the double quantum experiment, where one looks for a null to determine the $90^\circ$ pulse, in this experiment it is a maximum that one is seeking, which occurs for a $180^\circ$ decoupler pulse. The method can be used with any sample, although one which gives reasonable S/N in a relatively few scans is clearly more convenient. The multiplicity of the carbon signal is unimportant, unlike for the double quantum experiment. The experiment is shown schematically in the sketch below.

Please credit this to the account of Tom Farrar.

Bruce Adams

(1) Ad Bax and Ray Freeman, JACS, 1982, 104, 1099.
Now, Bruker makes research routine.

The Bruker AC-E and AC-P NMR spectrometers are high performance, easy-to-use systems. At the touch of a button, automation takes control of everything from lowering the sample and shimming to plotting, integrating and picking the peaks.

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Manning Park, Billerica, MA 01821

In Europe: Bruker Analytische Messtechnik GmbH, Silberstreifen, D-7512 Rheinstetten 4, W. Germany
### Spectrometer Performance – AC Series

**Summary of Specifications for Basic System Configurations AC Series 100, 200, 250, 300 MHz**

<table>
<thead>
<tr>
<th>Probehead (5 mm)</th>
<th>Nucleus (Test)</th>
<th>90°pulse (µs)</th>
<th>S/N (100)</th>
<th>200</th>
<th>250</th>
<th>300</th>
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<tr>
<td>1^H</td>
<td>1^H</td>
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<td>85</td>
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<tr>
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<td>&lt;15</td>
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<td>70</td>
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<tr>
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<td>31P</td>
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<td>10</td>
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<td>EB</td>
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<td>70</td>
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<tr>
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<tr>
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<td>&lt;15</td>
<td>15</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>All Probes (5 mm)</td>
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<td>0.2</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13C</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Magnet:
- **Standard**: 120 120 120 120
- **Long hold time**: 200 200 190 150
- **Ultra-long hold time**: 365 365 359 340

#### Helium refill interval (days):
- **Standard**:
  - **120**
  - **200**
  - **365**

#### Nitrogen refill interval (days):
- **Minimal room height (cm)**:
  - **9**
  - **10**
  - **14**

#### Console:
- **Height with display**: 123 cm
- **Weight approx. (kg)**:
  - **220**
  - **250**

#### Power consumption:
- **220 V/150 Hz/3 kW**

### Transmitter
- **Freq. range**: 1H/13C ± 100 kHz
- **Full multinuc.**
- **Offset steps**: 100 Hz
- **Phase shift steps**: 0.0 Hz
- **Power**: 5 W
- **Max. power**: 50 dB
- **Attenuator range**: 0 dB
- **O.D.1**: 150 kHz

### Computer
- **Memory**: 256 K/24-bit
- **Max. FT size**: 128 K words
- **Multi-gate timing resol.**: 0.1 sec
- **Pixel matrix**: 256 x 512
- **Frequency range**: 150 kHz
- **Array processor**: 8 K/15 sec
- **Graphical display**: 8 colors
- **Plotter**: A3 flat bed
- **Printer**: HP with auto-feed
- **Storage**: 250 MByte disk, floppy tape
- **Communication**: RS 232

### Dimensions and weights are approximate; voltage 10% /-5% max.

---

**Australia**: BRUKER (Australia) Pty. Ltd., Ewbank, New South Wales, Tel. 02-5589747

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**Switzerland**: SPECTROSPIN AG, Frieden, Tel. 031-59 1111

**W.-Germany**: BRUKER ANALYTISCHE MECHTECHNIK GMBH, Rheinstetten, Tel. 0711-5970-70

**USA**: BRUKER INSTRUMENTS, Inc., Billerica, MA 01821, Tel. 978-281-1111

**Regional offices in ChicagoIL, Wilmington/DE, Houston/TX, San Jose/CA**
Dear Barry:

During the past 10 months we have been going through the process of ordering receiving and installing the first persistent 600 MHz system in the USA. Two of our main worries were (a) whether the 600 would be ready on time as it is needed for a rush project (curing AIDS!) and (b) whether it would be a workable instrument. Would sensitivity be higher than on the 500's, would line shapes be as good and what about reproducibility? Other worries concerned remodeling our entire basement to accommodate the "beast". Bruker claimed the room was too small, too much metal nearby, etc.; nevertheless we went ahead and crammed it in there and it seems to be meeting all specs, which brings me to the point: what specs?

What are the most critical requirements for a 600, and how can one test them quickly? The ASTM sensitivity test is pretty useless for anything biological and forces the manufacturers to design and construct probes with very high Q and bad E/M ratio. Great for getting 800:1 on ethylbenzene, but the shifts and assignments should be known by now. Since the 600 is to be used for biological samples it is more relevant to know its sensitivity for a "real sample" or something close to it, at least with some salt in it. When we first tested the system in Karlsruhe, the sensitivity on anything in a non-organic solvent was quite low, despite 800:1 on ethylbenzene. As a test we use a sample of 250 µg (give or take a few, I made the samples myself) sucrose in 0.5 ml 99% D2O in a Wilmad 528 tube, with and without the presence of 250 mM NaCl. Presaturation of the residual HOO is used, so this setup reflects somewhat the normal measuring environment. All tests are done in the non-spinning mode at 25°C and a sweep width of 7 ppm, using 1 Hz exponential line broadening, measuring intensity on the anomeric glucose proton. In the accompanying figure you see that the salt has only about a 25% effect and sensitivity is more than double of what we get on our aging but well-maintained NT-500.

Some of our protein samples have a large total number of protons, even at low molar concentrations, and so dynamic range might affect the beautiful S/N figures obtained for the dilute sucrose. We decided to combine the test for this with a short-term reproducibility test. Long term reproducibility might not have approached its final limits within few weeks after bringing up the field, although it appears to be very good already on our system. As a test we look at the S/N on the satellites of a concentrated sucrose solution (75 mg/0.5 ml D2O,
no salt, no lyophylization to remove residual hydroxyl protons, 25°C), using 2 scans (preceded by two dummy scans) using the Mareci-Freeman spin echo difference scheme:

\[ 90^\circ_x \text{H-}3.1 \text{ ms-}180^\circ \text{H/90^\circ_x 13C-}3.1 \text{ ms-Acq.} \pm \]

For this test we needed an extra \(^{13}\text{C}\) (151 MHz) bandpass filter, not standard with the inverse detection accessory (!), but quickly designed and constructed by Rolf Tschudin. In any case, the result was very interesting. At the 300 times greater concentration (and increased line width because of viscosity) the "satellite" concentration is about 1.6 times higher than that for the central peak in the dilute sample, and naively one might expect an increase by 60% over the "no salt spectrum". The increase in line width, combined with the low receiver gain (necessary because of the intense signal per single scan), actually decreased the S/N by about 30%, a very good number indeed. This spectrum is the bottom trace in the figure, representing the median out of five attempts (not the irreproducible best ever).

Suppression of the center peak (for two scans!) is spectacular, at least a factor of five better than on our 500. Some 60 Hz modulation sidebands can be seen, however. They appear to originate from pickup at the audio level and disappear at higher receiver gain settings. They also nicely average and are invisible after 8 scans but they may nevertheless result in some artifacts in our 2D spectra. Just wait and see if necessary. Line shape and resolution (non-spinning) meet the spinning specs and altogether, we're very happy so far. Rolf will be too, as soon as he receives the schematics that correspond to the electronics actually present in our console.

One last little thing that disturbs me: the boost in S/N seen in the past year or two appears to be based largely on everybody starting to use the ultrathin sample tubes for sensitivity testing (14% gain in active volume). Why do engineers have to risk their health to satisfy our (customers) desire for high numbers? Some of that stuff, benzene, CHCl₃, ethylbenzene etc., is not exactly innocuous. At least they deserve full strength sample tubes if used routinely. I know that sucrose too may be hazardous to your health*, but at 250 µg per regular thickness tube, you'd have to break quite a few before it starts getting serious.

Best regards,

\[ \sim \]

Ad Bax
Laboratory of Chemical Physics

* Some members of our section are currently testing the LD₅₀ of sucrose when ingested in conjunction with cocoa butter and milk solids. Results will be presented elsewhere.
Top: Anomeric glucose proton in a sample of 250 µg sucrose in 0.5 ml 99% D₂O with 250 mM NaCl with presaturation of the HDO, non-spinning. Middle: Same as top but without salt. Bottom: spin-echo difference spectrum from 2 scans, 75 mg per 0.5 ml. All spectra were recorded using the "inverse" probe.

VACANCY for a Postdoctoral Research Assistant to study membrane transport of alkali metal ions using multinuclear magnetic resonance techniques. Anyone interested please contact Dr F G Riddell, Department of Chemistry, The University, Stirling, FK9 4LA, Scotland, sending a curriculum vitae and the names and addresses of two referees.
Dr. Bernard L. Shapiro  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, California 94303  
U.S.A.

APPLE TO ASPECT COMMUNICATION PROGRAMME

Dear Dr. Shapiro:

APPSPECT is a communication program for APPLE to ASPECT computers. In our lab it is used mainly to permit the APPLE, connected to channel B of an ASPECT computer, to run the BRUKER programs LIGHTNET and TAPE which perform file transfers between two BRUKER instruments via fiber optics and file transfers from disk to tape drive. Hence, all file handling functions can be handled from a remote terminal without interfering with the normal operation of the spectrometers from the main consoles which run the DISNMR programs.

All incoming data to the APPLE terminal can be stored in a file on an APPLE disk (Ctrl-D) or sent to a printer (Ctrl-P) connected to the APPLE. In this way, directories of disks and tapes or any ASCII file can be saved on the remote terminal.

Files can also be sent from the APPLE to the ASPECT using the Transmit File command (Ctrl-T). The user is then asked for the APPLE filename and an ASPECT filename. The directory on the ASPECT disk is checked for the presence of the file, and a REPLACE Y or N confirming question is asked to prevent accidental erasing of an existing file. APPSPECT then automatically starts TECO on the ASPECT, sends the file, and closes it. At every formfeed encountered in the file being transmitted, the TECO buffer is emptied, thus permitting transmission of files of any size. Separate PASCAL utility programmes are to insert and remove formfeeds in a file. Thus, micro-programs or PASCAL programs can be developed much more effectively on a computer which uses a more versatile word processor (i.e. WORDSTAR) than TECO on the ASPECT.

APPSPECT is running under the CP/M operating system and is written in 8080 assembler code. The APPLE Ile is equipped with a Grappler Plus printer board, a 280 card and a AIO-II parallel and serial interface board. Baud rates from 300 to 9600 can be selected with the Ctrl-B option of the program. The AIO-II board was modified slightly to allow hardware handshaking on the serial RS232 line.

Copies of the programs and hardware modifications are available if you send us a formatted floppy diskette.

Sincerely,

Andre Simard  
Jean-Robert Brisson
Mr. Bernard Shapiro  
Editor/Publisher  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

Dear Barry:

Recently we have become very interested in obtaining NMR spectra at moderately high temperatures in the range of 200-300°C. In order to attain these temperatures we purchased a high temperature/high resolution nmr probe from Doty Scientific. Incorporating this probe into our JEOL-GX-270 system has been fairly easy, but not without a number of hurdles.

1. The JEOL VT air sensor (CN4) was disconnected since the air pressure of the VT exhaust from the Doty probe was insufficient to activate the sensor.

2. A separate controller system was built to control both the JEOL VT heating system and the cartridge heater in the Doty probe. The JEOL VT heater is used to preheat the VT air before it enters the probe and the cartridge heater is used to control the final temperature. For feedback, the controller system uses a thermocouple in the probe.

3. Finally, we synthesized a deuterated tetraglyme from deuterated methyl iodide and tetaethylene glycol. This d6-tetraglyme has a boiling point near 275°C, a nice sharp deuterium resonance suitable for lock/shimming, and three C-13 resonances at 72.4, 71.1, and 70.9 ppm. We have selected the major resonance at 71.1 ppm as a secondary reference.

The results of the temperature calibration on this probe are shown in Figure 1. Following normal temperature calibration procedures we first monitored the temperature using ethylene glycol in the temperature regime of 40 to 140°C. We next measured the melting points of anthracene and carbazole. A spectrum of carbazole is shown in Figure 2.
Figure 1. Temperature calibration

Figure 2. Spectrum of carbazole at 270 C

Figure 3. Spectrum of polypropylene at 220 C
Using a 5/10 mm coaxial tube system, with d6-tetraglyme in the center, we were able to obtain a high resolution NMR spectrum of polypropylene in the melt at 220°C (Figure 3). We are in the process of extending this method to other polymers and higher temperatures.

Sincerely,

Stephen Wharry
144 PL, Research Center

Bruce Wade
121 CPL, Research Center

Dan O'Donnell
148 PL, Research Center

_____________

Dear Barry:

Management of an NMR Spectrum Database

The NMR facility at Philip Morris is charged with running NMR spectra for resident R&D scientists in addition to research activities. Since the days of the A-60, long ago departed, we have accumulated more than 16,000 NMR spectra. While this number is not likely to be large compared to the number of spectra obtained in a chemical or pharmaceutical company, it nonetheless presents sizable problems in storing the NMR charts and locating individual spectra. The best solution for archiving spectra would be to transfer the raw data (FID’s) over our local area network to a computer with capacious disk or other type memory so that each spectrum can be recalled at any time in the future for reprocessing and plotting. While we work towards this goal, we have developed an NMR database that permits us to readily track and locate an NMR spectrum whether it is a hard copy chart or a digital image saved in a remote computer. The database was created using BASIS, a product of Battelle Development Corporation which is being utilized by our R&D library and other groups. The information saved in the database is simply the same records that were formerly recorded in a laboratory ledger including the name of the sample submitter, sample number, and run date. In addition we have added data fields for the chemical name, molecular formula, and other information such as the nucleus observed, location of the spectrum (a notebook or computer file) and any other information that is deemed valuable (solvent, 2D, CP/MAS, etc.). The database is updated by a laboratory technician at the time the spectrum is run and can be searched by any scientist from computer terminals throughout R&D.

The following BASIS session indicates how the database can be searched. In the great tradition of computer obfuscation, the field names are thoroughly cryptic.

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Union Carbide Corporation
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* 9 1/ mf=c4 h6 o5
* 329 2/ sub=woo*
* 2826 3/ rund gt 840801
* 2 4/ mf=c4 h6 o5 and sub=woo* and rund gt 840801

5/ display all for 2

ITEM 2

NMR #: 15676
SUBMITTER: wooten, j.
DATE RUN: 840817
SAMPLE #: 8032-25b
NAME OF COMPOUND: (-)-malic acid
MOLECULAR FORMULA: c4 h6 o5
NMR DATA: lab nb# 8032 solid state carbon

5/ quit

Sincerely,

J. B. Wooten, Ph.D.
Research Scientist

P.S. The name "Elsinore" figures prominently in the movie "Strange Brew." Are you now affiliated with the MacKenzie brothers?

I rarely go to the movies, have not seen "Strange Brew," and am not knowingly affiliated with the MacK. Bros. Am willing to, however, if they are Speyside distillers or they'd like to advertise in the Newsletter. Or both. Else-wise I'll 'nore them . . .

BLS
January 7, 1988
(received 1/13/88)

Dear Barry:

Here is a useful circuit which as far as he and I know was invented first by John Sorge of the University of Pennsylvania. He has kindly allowed me to describe it here, with a few embellishments that I found helpful.

This circuit is derived from the well-known quarter-wavelength line Transmit/Receive switch. That switch is only useful over the restricted range of frequencies where the line is the right electrical length. With the present circuit one can work with an arbitrary number of frequencies $f_a, f_b, f_c...$ e.g. for $^1H, ^3P, ^2C...$ and, by means of a set of series LC's tuned to these frequencies select the appropriate length of transmission line during the Transmit pulse. The 1N4148 diodes short circuit, so that the top of the selected length of line is open circuit, and the transmitter power goes to the probe, as in the classic circuit.

The circuit has been tested with 1kw pulses. The fuse senses the average power (even though it is frequency-sensitive) and protects the sample and the PIN diodes against CW etc.

We used RG223/U cable which withstands high voltages and has low loss. At 10 MHz a quarter wavelength of cable is 16.2 ft. Higher frequencies call for proportionately shorter cable. The increase in Noise Figure compared with a plain preamplifier is around 0.3 dB at 35 MHz.

The PIN diodes are able to withstand high current pulses, yet have such a low stray capacitance that the left-hand side of the circuit is well isolated during the Receive time (in which mode the preamplifier sees a 50 ohm source.)

The 10 microhenry (non-ferrite) choke provides for quicker discharge of possible forward bias of the 1N4148 diodes after the Transmit pulse, so that noise will disappear quickly.
This circuit should mount near the probe and preamplifier on the magnet, and so should have no ferrites.

For the series LC's a rule of thumb at the chosen frequency is to have $X_L = X_C = 200$ ohms approximately. Use high voltage (500 WVDC) capacitors. The coils may be tuned by spreading turns.

Please credit this to Mr. Eugene Poppel's subscription.

Sincerely,

James L. Engle
Assigning quaternary carbons by \(^1\)H-detected \(^1\)H-\(^{13}\)C correlation

Brian Hunter and I, together with my graduate student Chris Hunter, have recently been looking at porphyrin crystals by CPMAS NMR (1). In order to interpret the results fully we needed a complete assignment of the solution state \(^{13}\)C spectrum of Zn mesoporphyrin-II-dimethyl ester. The protonated carbons were trivially assigned by conventional \(^1\)H-\(^{13}\)C two-dimensional correlation, but the eight quaternaries around the ring looked more difficult.

Fortunately, James Keeler and John Cavanagh came to our rescue. They have just developed an improved phase-cycling scheme which gives much better suppression of protons which are not bonded to \(^{13}\)C; it is based on an apparently redundant 'double difference' method that eliminates those unattributable but ruinous systematic errors which are not supposed to be there in the first place (2). The result is that 'reverse', \(^1\)H-detected, long-range \(^1\)H-\(^{13}\)C correlation is now a practical technique. The accompanying structures and part spectrum show that virtually every possible 2- and 3-bond correlation is present, allowing an instant and unambiguous assignment of all the quaternaries.

We have also used the same technique on samples as diverse as diterpenes and polysaccharides with similar success. Our subjective judgement is that the reverse approach is much more powerful than the conventional, partly on sensitivity grounds and partly because it puts all the digital resolution in the proton dimension where it is really needed.


with best wishes

Jeremy
Contour levels set higher
Two bond reverse $^{13}\text{C} - ^1\text{H}$ correlations

Three bond reverse $^{13}\text{C} - ^1\text{H}$ correlations
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New Methods Research, Inc., 719 E. Genesee Street, Syracuse, NY 13210
(315) 424-0329 FAX (315) 424-0356
Dear Barry:

We have used aluminum-27 MAS NMR to characterize many 2:1 clay minerals. These materials are comprised of stacked ten angstrom-thick layers. The layer consists of an octahedral sheet sandwiched between two tetrahedral sheets. The octahedral sheet is a planar array of connected octahedrons with oxygen atoms at the vertices. The center of the octahedron may contain a metal ion such as aluminum (VI). The tetrahedral sheet is a planar array of connected tetrahedrons with oxygen atoms the vertices and an atom such as silicon in the center. The octahedral and tetrahedral sheets are connected by shared oxygen atoms. The crystal unit cell contains three octahedrons.

The dioctahedral mineral pyrophyllite has aluminum in two of the octahedral sites (the third octahedron being vacant) and only silicon in the tetrahedral sites. The 6.35 Tesla aluminum-27 single-pulse MAS NMR spectrum in Figure 1 shows a symmetric peak, as expected from a second-order quadrupole broadened 1/2 to -1/2 transition. Measurements of the first moment of the peak made at 2.35 and 6.35 Tesla indicate a quadrupole coupling constant (QCC) of 1.4 MHz.

The dioctahedral mineral beidellite, like pyrophyllite, has aluminum in two octahedral sites and a vacancy in the third site. However, one-eighth of the tetrahedral sites contain aluminum instead of silicon. The octahedral peak shown in Figure 2a is very asymmetric and it cannot be simulated with only one QCC value. Apparently, the tetrahedral aluminum substitution results in a multiplicity of octahedral QCC values, one of which being considerably greater than that for pyrophyllite. This interpretation is supported by the spectrum in Figure 2b. The single-pulse sequence for this spectrum is preceded by a saturating blast of ninety-six 90° pulses and a one-millisecond relaxation delay. The shape of this spectrum indicates that the narrow peak (small QCC) is relatively suppressed compared to the broad peak (large QCC). The peak with the smaller QCC value should have the longer $T_1$ value and a greater amplitude suppression.
Figure 1. Al-27 MAS NMR of pyrophyllite

Figure 2. Al-27 MAS NMR of Blackjack beidellite
The QCC of $\text{VI}_{\text{Al}}$ is sensitive to atomic substitution in both the octahedral and tetrahedral sheets and we have detected multiple QCC values for $\text{VI}_{\text{Al}}$ in many 2:1 clay minerals. A report of this work has been submitted for publication.

Sincerely,

D. E. Woessner
Senior Research Associate

cc: E. L. Jones
T. H. Bushaw
B. C. Arnwine
Records Center 602-857

--

Job Available: NMR SPECTROSCOPIST/APPLICATIONS SCIENTIST

A full-time position is available as an NMR Applications Scientist to study customer samples to determine the proton NMR parameters that provide reliable material analyses, e.g., free/bound water ratios, oil content, percent esterification, etc. The position offers significant scientific challenges in supporting Auburn's NMR process control business. Equipment available includes a 200 MHz Bruker CXP Spectrometer and low-frequency NMR instruments in a well equipped laboratory. Publication of results, collaboration with university research programs, and professional development are encouraged.

The successful candidate will have an M.S. or Ph.D. in Chemistry or Chemical Physics and at least two years experience actively using commercial NMR spectrometers. Familiarity with Bruker NMR instruments and an interest in developing practical industrial applications of proton NMR, working with a wide variety of samples, are pluses. Excellent written and oral communication skills for presenting results of research are essential.

Please contact Ellory Schempp at the address above.
Dear Barry,

Ligand exchange reactions involving transition metal complexes are fundamental processes in coordination chemistry. Whereas line shape analysis and magnetization transfer studies are important tools, we have found that $^{31}\text{P}$ 2-D exchange NMR provides a useful complement. The trimetallic triazine complex 2, when dissolved in CuCl$_2$, is in equilibrium with 1 and 3. Although it is possible to show the exchange using $^1\text{H}$-NMR, it is much easier with $^{31}\text{P}$ 2-D (see figure). Clearly, all three species are exchanging.

Please credit this to the account of Prof. L.M. Venanzi.

Suggested Title - $^{31}\text{P}$ Exchange Spectroscopy in Platinum Chemistry.

Best wishes

Prof. P.S. Pregosin

Christian Aumann
POSITION AVAILABLE. Postdoctoral appointment available June 1, 1988 to study molecular biophysics of model bile and glyceride digestion systems. Current areas of investigation include (a) molecular organization in bile salt-phosphatidylcholine aggregates, studied by 2D $^1H$ NMR relaxation and $^1H$ magic-angle spinning; (b) aggregate size and surface composition in model digestive substrates, studied by quasielastic light scattering, $^{13}C$ NMR, and enzyme kinetics; (c) conformation of pancreatic colipase and its bile-salt complexes, studied by 2D $^1H$ NMR.

NMR equipment available for these projects includes an IBM 200 MHz spectrometer with solids accessory and a JEOL 400 MHz spectrometer for solution-state work. The position requires a Ph.D. in chemistry or biochemistry, with experience desirable in advanced NMR techniques, quasielastic light scattering, enzyme kinetics, and lipid biochemistry.

Send a resume and two letters of recommendation to Dr. Ruth E. Stark, Department of Chemistry, City University of New York - College of Staten Island, 50 Bay Street, Staten Island, New York 10301. EO/AA Employer.
Imaging of a Rotating Object

Dear Dr. Shapiro:

I have recently completed a new type of imaging experiment in which the object is rotating and a static image of the rotating object is obtained. The experiment was done on a two-dimensional phantom (x,z), two water-filled tubes, rotating at 180 Hz about the axis, Y, parallel to the tube axes (y). The field gradients are not rotated synchronously with the object rotation, but instead they are applied such that the NMR signal from the rotating object observed under the applied gradients results in appropriate scanning in the spatial frequency domain, or the k space. The scanning pattern must cover the k space (plane in the experiment) uniformly. A static image of the rotating object can be obtained from such a scanning pattern.

Generally, the scanning pattern or the NMR signal can be written in the moving object frame as

\[ S(k_t) = \int \rho(r) \exp \left(i \cdot r \cdot k_{r}(t) \right) \, dr \]

where \( \rho(r) \) represents the spin density and

\[ k_{r}(t) = Y \int_{t_0}^{t} G_{r}(t') dt' \]

\( G_{r} \) and \( G_{l} \) represent field gradients in the object and laboratory frame, respectively. The transformation \( D_{h} \) is characteristic of the object motion.

For rotation about the Y axis in the laboratory frame at an angular frequency \( \omega_{y} \),

\[
D_{h} = \begin{pmatrix}
\cos \omega_{y} t & 0 & \sin \omega_{y} t \\
0 & 1 & 0 \\
-\sin \omega_{y} t & 0 & \cos \omega_{y} t
\end{pmatrix}
\]

Since the object is rotating, a circular or quasi-circular trajectory in the
In the preliminary experiment, the latter pattern, a spiral trajectory, was chosen. Application of the gradient sequence, $G(t) = (G_0 \sin \omega t, 0, q)$, in the laboratory frame results in a spiral trajectory pattern, $r(t) = (G_0 \sin \omega t, 0, r_0 \cos \omega t)$, in the object frame. An image can be obtained from the trajectory data by Fourier transformations along the radii and back projections of the transformed data. Some experimental conditions were such that $G_0 = 0.329$ mT/m, (number of rotations per measurement) = 8, and (view width) = 12.8 mm. The phantom image is shown below. The considerable deviation from a circle may result from field inhomogeneity which was not sufficiently small.

I believe this experiment can be a basis for solid-state imaging under magic-angle sample spinning.

Sincerely yours,

Shigeru Matsui, Dr. Sc.

* Currently on leave at Department of Chemistry, University of California, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
Dr. Bernard L. Shapiro  
TAMU NMR Newsletter  
966 Elsinore Court  
Palo Alto, CA 94303

Re: Missing Resonances Found on Surfaces

Dear Barry:

We have recently been attempting to study dynamics of polymers adsorbed to surfaces by deuterium NMR. As a preliminary step, we are determining the adsorption isotherms for several polymers. The first isotherm to be completed was that of poly(isopropyl acrylate).

We obtained CP-MAS spectra of this polymer in bulk and adsorbed to the surface (Cab-O-Sil grade M-5 amorphous fumed silica) at various coverages. The spectra were taken on a VXR-200 spectrometer from Varian at 50Mhz for C-13. The spectra for the bulk polymer, for the polymer adsorbed to the surface at one monolayer coverage, and in deuterochloroform solution are shown below.

As may be seen, the spectrum of the bulk polymer shows only two relatively narrow resonances. The adsorbed polymer, however, gives rise to a spectrum showing 4 distinct peaks. One other resonance is visible as a shoulder on one of the peaks (spectra taken at other coverages show this as a separate peak). For comparison, the solution spectra is included, showing resonances at the frequencies of the "missing" peaks in the bulk polymer.

Sincerely,

Funchess  
Chancellors Fellow

Frank D. Blum  
Associate Professor of Chemistry
I have an immediate opening for a postdoctoral fellow in my laboratory. The project involves the study of liquid crystals and liquid crystal mixtures using nuclear magnetic resonance techniques. The project will include deuteron nmr studies of deuteriated liquid crystals as well as high-resolution nmr studies of partially oriented solutes. Our goal is the understanding of the intermolecular forces responsible for orientational ordering in such systems.

Interested candidates should send me a resume along with letters from three referees.

Yours sincerely,

Elliott Burnell
(received 1/25/88)

Dr. B.L. Shapiro,  
Editor/Publisher,  
TAMU NMR Newsletter,  
966 Elsinore Court,  
Palo Alto, CA, 94303.

19F MAS Studies of Strongly Hydrogen Bonded Fluorides

Dear Dr. Shapiro,

Encouraged by your pink prompt, we are reporting on some MAS 19F n.m.r. studies of strongly hydrogen bonded fluorides. We originally described the use of MAS n.m.r. for the study of ionic fluorides (Clark et al: Chem. Commun. (1986) 657) using the decoupling coil of a CXP 200 spectrometer as our fluorine observe coil. In an attempt to overcome the 19F background of this probe we have constructed our own fluorine free probe for use on our AC200 spectrometer, based on the design of Fyfe et al. (J. Magn. Reson. 47, (1982) 168), but with more modern sliding rather than rotary capacitor tuning. This is an improvement on the CXP probe, but we still get some 19F background, presumably from Teflon insulation used in the shim coils etc.

Although the hydrogen bonded complexes are generally solids, in the absence of magic angle spinning they show one or occasionally two peaks which are sharper than those observed for ionic fluoride salts. For example, the complex KF-(4-cyanophenol) shows a peak at -121 ppm, with a half width of ~1300 Hz. This narrows to ~200 Hz with the application of MAS.

There are two regions in which sharp peaks are generally found; at about -123 ppm. and at about -142 ppm. This shift in position probably reflects different coordination about the fluoride anion. Broad peaks appear at higher field in a few spectra, at about -165 ppm., possibly caused by the formation of bifluoride. The background signals are usually clearly distinguishable by their breadth and position.

Dr. Catherine Duke is doing further studies on the nature of the 19F spectra of these complexes, including possible reasons for the sharpness of the peaks.

Yours Sincerely,

Jack M. Miller,  
Professor of Chemistry.
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Equipment Wanted: Used Magnets from Electron Spin Resonance Spectrometers

We are building a homemade ESR spectrometer for materials and medical imaging applications. However, we urgently need a large magnet with power supply and Hall field controller of the Varian E-9, E-12 or preferably E-15 type.

We are aware that several Departments are currently replacing old Varian ESR spectrometers. If anyone in your Department has an old magnet system which you are wanting to "unload", please call (collect) or write to:

Professor Lawrence J. Berliner
Department of Chemistry
The Ohio State University
120 W. 18th Avenue
Columbus, OH 43210
614-292-0134
Bitnet: TS0288 at OHSTVMA
Telex 332911 OSU CHEM UD

Positions Available - The Ohio State University

We have been recently funded by NIH for a Research Resource Development Project on "Topical In-Vivo ESR" for a three-year period beginning September, 1987. Our research program will focus primarily on spin probing, spin labeling, spin trapping, and detection of natural free radicals in mice, rats and plant systems. The project involves development of an L-band in-vivo ESR spectrometer and feasibility studies of the technology involved in studying several pathophysiological states in animals (eg. tumors, ischemia, brain physiology).

I appeal to you for references to appropriate scientists interested in postdoctoral, technician or research associate positions in:

1. Engineering (microwave electronics, field gradient technology, software development, controllers).
2. Medical/biology - animal physiology and biochemistry.
3. Physical biochemistry/magnetic resonance - spin labeling, biochemistry, good overall grasp and knowledge of all three areas.

We seek talented, versatile scientists regardless of formalized training and degree. The person selected should be able and interested in becoming familiar enough with other aspects of this project to be both critical, helpful and at times, undertake those other responsibilities.

I would be pleased if you could both recommend people to me and to request that they provide names of 3-4 references besides a complete c.v. A short paragraph from the candidate encompassing what he/she has done, would like to do and where they feel they complement our program would be most helpful. Send to: Lawrence J. Berliner (address above).
Our reference  Your reference  Telephone  Date
S/SYB/016/88   

Dear Professor Shapiro,

"2D OR NOT 2D?"

I have recently been utilising Bruker 2D-software to record, process and display 1D-NMR experiments on our AM250 spectrometer. A number of experiments can be recorded in this manner including relaxation-time measurements (both \(T_1\)-inversion-recovery or \(T_2\)-CPMG), and simply following a reaction of process versus time and/or temperature.

A significant advantage is that data handling and presentation is greatly improved. Use of the 2D \textit{XF2} command significantly speeds-up Fourier transformation. The array processor function (AP2D) can then be used to view the entire data set (or selected regions) as either a contour or stacked display, and individual rows or columns can be readily extracted. Finally, a wide variety of 2D contour/stack plot outputs can be easily be performed. A further advantage in using such methods is that, with ever increasing size of disk storage and hence mile-long directories, a whole data set can be hidden in a single filename.

The inversion-recovery automation sequence can be easily modified to include an incrementable delay, rather than a delay list, and \textit{.SER} file storage. \(^1\)H-NMR \(T_1\)-inversion-recovery data was recorded for an ethylenzene test sample with tau delays from 0.12 msec to 15.48 sec. The data set obtained was then transformed as a phase-sensitive matrix (MC2=n) using the \textit{XP2} command (by using phase parameters from the final \textit{.SER} sub-file). Further phase-correction can be performed using \textit{XP2P} if necessary. Figure 1 shows stack plots of (a): the full spectrum and (b): the methylene quartet. Columns of the 2D-data (real points only!), extracted using the \textit{VWC} command, give individual \(T_1\)-recovery curves. These could then be input to curve-fitting routines, without needing to go through the laborious TIPMTS procedure. A problem at present is that the FL-domain scaling is in meaningless, frequency units rather than time.

Using another simple automation microprogramme, \(^1\)H-NMR spectra of a methylmethacrylate solution undergoing polymerisation (with AIBN initiator at 65°C) were recorded at regular intervals and stored in a

cont...
.SER file. This data was processed as above, using the first .SER sub-file for the correct phase parameters. Figure 2 shows (a): a contour plot of the whole spectrum, and (b): a stack plot of the polymer methyl resonances (isotactic, atactic, and syndiotactic from left to right). These increase and shift to lower frequency initially, then severely broaden and disappear into the baseline as the polymerisation rate 'takes-off' and the sample starts to solidify.

Please credit this contribution to the BP account.

Yours sincerely,

J R BALES (Dr)
Spectroscopy Branch

FIGURE 1 (a): Stack plot of the $^1$H NMR spectrum of ethylbenzene, and (b): An expansion showing the methylene quartet.

FIGURE 2 (a): Contour plot of the $^1$H NMR spectrum of methyl methacrylate/poly(methylmethacrylate), and (b): An expansion showing the polymer methyl resonances.
Greetings, Barry,

TITLE: LOW COST OFF-LINE PC-NMR© DATA STATION.

I am responding to your ultimatum letter with some information about an off-line NMR data station which we have developed here in collaboration with the now extinct IBM Instruments Company. The PCNMR Data Station © is alive and well. It is producing about 150 spectra per day here in Madison and is also being used at the University of Iowa, Carleton College, IBM Research (Almaden Labs), UCLA, Bristol Meyers Research Labs and so on.

This package includes code for PC-NMR©/UWNMR© which can be run on an IBM PC-AT or equivalent computer (e.g. an AST Premium 286). The computer should be equipped with 512K memory or more, have an EGA color monitor, an HP-7475A plotter and a dot matrix printer (an IBM Proprinter or equivalent). We also provide a complete set of manuals for the installation and operation of the data station. The hardware consists of two interface boards and several cables.

It takes four or five seconds to get a 16K data set (32 bit data) from an Aspect 2000 or an Aspect 3000 to the PC-AT. On the IBM token ring network it takes about four seconds to send 16K of data. We have two WP-200 instruments and a WP-270 all interfaced to a single PC-AT file server. There are then four data stations on a token ring network. We will be adding two more data stations since four are not sufficient to serve three spectrometers. We typically run more than 150 proton spectra per day here.

Anyone interested in obtaining the hardware and software for this data station should contact me at the above address or they may call me (do not call collect) at (608)-262-6168.

With best regards,

Tom.

Thomas C. Farrar
Professor of Chemistry
Dr. Barry Shapiro
TAMU NMR Newsletter
966 Elsinore Ct.
Palo Alto, CA 94303

Dear Barry,

EXTENDED DATA STATION NETWORKS

Bob Johnson and I recently moved into the Polymer Science and Technology group here. We have combined forces with one of the NMR groups previously resident (Bill Fleming) and upgraded the capabilities with new instrumentation. Instrumentation in our department now includes: AM500, AF300, AF 250 (all hi-res) and SY 200 (CP/MAS). The 250 is equipped with a sample changer and is dedicated to automated, menu-driven, hands on proton/carbon operation for synthetic chemists.

Since the 250 has time constraints common to all routine usage NMRs we are beginning to use networked data stations for offline processing. The basis of our data stations is a 1D NMR processing and plotting program, PCNMR, which runs on IBM PC-AT and PS/2 computers. This program, developed by IBM Instruments, is menu driven and allows plots on Hewlett-Packard plotters. It was originally released for the AT, and Jim Cooper (IBM ACIS, Milford, CT) graciously provided a version for the PS/2. In use, data is sent in background from the ASPECT 3000 computer in the spectrometer to the disk on the AT. Then the data can either be processed directly or sent via a network to other datastations. We have two network choices: PCNET, a local area network which links users in this facility or IBM VM, a network which connects all IBM sites and employees. Since many of the labs and offices have PC ATs or PS/2s in use as terminals, we can send FIDs directly to the users for processing. Because the VM system circles the globe, we can send data to the ends of the earth, even as far as Texas, if necessary! (While we haven't found it necessary to go to that extreme, we have exchanged data with IBM labs in New York.)

Unfortunately, PCNMR is no longer available from IBM. However, the rights to it have been obtained by the University of Wisconsin at Madison, and people interested in obtaining the program should contact Prof. Tom Farrar in the Chemistry Department there. Please credit this to my account.

Chas. G. Wade  
R.D. Johnson  
W.W. Fleming
Dear Prof. Shapiro,

Many of us have experienced the mixed fortune of having a journal article rejected or delayed by reviewers. "Mixed" because although we have confidence in our work and consider the material to be worthwhile, a reviewer’s comments can be very useful and the paper may be much better because of it.

In my case, one criticism concerned a 2D COLOC (Correlation by Long-range Coupling) spectrum of vinylidene chloride-isobutylene copolymer in which "the connectivities are as strong (or weak?) as noise that is ignored." The COLOC experiment is, however, inherently insensitive, more sample could not be easily obtained (already 20% w/v), and the experiment time was over 12 hours. So instead, I chose to apply a 2D MEM (maximum entropy method) calculation to improve signal contrast in the spectrum. Figure 1 depicts the marked improvement in a 128x128 segment of the 2D spectrum, showing clearly the non-protonated vinylidene chloride carbons correlated to the protons on the neighboring methylene carbon. The calculation required about 15 minutes of cpu time on a VAX 8800. Assignments can subsequently be deduced from the connectivity pattern that results from triad (the non-protonated carbons) and tetrad (the methylene protons) sequence overlap along the polymer chain.

Another justifiable criticism from the reviewers was that the "connectivity scheme (does not) necessarily establish assignments" and that an independent method to confirm the assignments is desirable. Figure 2 shows the results from a simulation of the region in the carbon spectrum that is projected in Figure 1 following a second-order Markov propagation model.3 Triads were determined by the 2D experiment and pentads are simulated in Figure 2. The simulation looks very much like the experimental spectrum securing the identity of the assignments and the use of the MEM enhancement.

I believe this to be a good example of the utility of computer applied chemistry and, perhaps, a lesson in premature submission of a paper!

Sincerely,

Molly W. Cawthor, Ph.D
NMR Applications and Quality Control

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Thanks !!
The MEM processing routine was written by Fang Ni. An extended version of the program is available in NMR2\textsuperscript{TM}.

Re-submitted to the Journal of Polymer Science.

The Polymer Analysis program in NMR\textsuperscript{TM}.

---

Figure 1. Conventional FT and MEM processing applied to the non-protonated vinylidene chloride carbon region of the vinylidene chloride-isobutylene copolymer spectrum. Contours are drawn at equivalent levels.

Figure 2. The experimental and simulated spectrum of the region in the carbon spectrum that is projected in Figure 1. The simulated spectrum uses a second-order Markov propagation model.
Dear Dr. Shapiro,

MAGNETIC SUSCEPTIBILITY REVISITED

Following the receipt of your pink missive and in the traditional desperation which it induced we thought that your readers, many of whom probably think that CW spectroscopy has something to do with cold water, might be interested in our resurrection of an experiment published in 1959. We wanted to investigate the hypothesis that one of our test substances might complex to ferrous iron and alter its spin state from high spin (S=2) to diamagnetic low spin (S=0) or even affect its oxidation state. In the absence of low temperature ESR or even a Guoy balance we used the Evans (J.Chem.Soc., 2003 (1959) co-axial NMR tube method to look at the effect of the compound on the iron induced contact shift relative to a control in the annulus. We used both aqueous and H_2O/MeOH 1:1 solvents and the diagram shows the results in the mixed solvent, run of course unlocked. We checked the method using Ni(II), Cu(II) and Fe(II) and found that it still worked! Despite a number of assumptions implicit in the calculation which result in an over-estimation of S, we found no ambiguity in interpreting the results, viz.

<table>
<thead>
<tr>
<th>Concn(M)</th>
<th>S calc</th>
<th>S actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCl_2·6H_2O</td>
<td>0.133</td>
<td>1.15</td>
</tr>
<tr>
<td>CuCl_2·2H_2O</td>
<td>0.034</td>
<td>0.55</td>
</tr>
<tr>
<td>FeSO_4·7H_2O</td>
<td>0.010</td>
<td>2.1</td>
</tr>
</tbody>
</table>

The shift Δν can be related to the molar susceptibility χ_m taking into account magnet geometry which in turn leads to the magnetic moment μ in Bohr magnetons. Ignoring orbital angular momentum contributions the
number of unpaired electrons can be deduced. The diagram shows (a) the co-axial tube with MeOH/H₂O in both compartments (b) the addition of Fe(II) to the outer tube giving a high frequency shift (c) adding our test compound unfortunately showing no change and (d) adding 2,2'-bipyridyl which abolishes the shift by converting the Fe(II) to its diamagnetic form.

Yours sincerely,

JOHN LINDON THEA BAKER JANET WILLIAMS
Department of Physical Sciences

Enc.

JCL/ag
Cyclic Oligomers in Butyl Rubber Polymerization

January 19, 1988

Dear Barry:

The cationic copolymerization of isobutylene with small amounts of isoprene produces an item of some commercial importance, butyl rubber. Because of the economic value of this copolymer, considerable effort has been invested over the years by many groups to establish the details of the copolymerization process including the mode of enchainment of the diolefin isoprene, the sequence distribution in the copolymer, and the unsaturation levels typical of different copolymer grades.

Recently, my colleague, Irv Kuntz in Exxon's Polymers Group, produced in the lab a low molecular weight copolymer (Mv of about 30,000) and discovered in the product some small amounts of much lower molecular weight by-products. These by-products were also detected in commercial high molecular weight copolymers using thermal desorption/pyrolysis GC-MS but were present at much lower concentration than observed in the laboratory synthesis. By a combination of liquid-liquid extraction and vacuum distillation, several different by-products were isolated from the laboratory preparation in sufficient quantity to identify their possible origin and structure using MS and NMR techniques.

In an NMR laboratory used to dealing with synfuels and petroleum materials, the problem of identifying the structural characteristics of these by-products presented a refreshing challenge. The $^{13}$C spectrum of the first and major purified fraction consisted of just thirteen resonances and was consistent with mass spectrometry information (C.S. Hsu in our Corporate Research Lab) obtained on the same fraction that reported a C$_{13}$H$_{24}$ empirical formula. The heteronuclear $^1$H-$^{13}$C chemical shift correlation shown in the figure, along with the DEPT-type descriptions of all the $^{13}$C resonances, helped to identify that the C$_{13}$H$_{24}$ by-product must have arisen from the oligomerization and subsequent cyclization of one isoprene and two isobutylene molecules.

Although we surmised most of the subtleties of this by-product by this point, the C$_{13}$H$_{24}$ fraction provided us a very "real world" proving ground for some of the NMR techniques that rarely find application in our more complicated samples. The two-dimensional INADEQUATE result, for example - partially shown in the figure - mapped out for us the cyclohexyl structure in this molecule as well as the attachment positions for the four methyl groups. Fortunately, good agreement was obtained between all of the available MS and NMR evidence on this fraction, ascribed in the end to the molecule 1-isopropenyl-2,2,4,4-tetramethyl-cyclohexane.
Higher molecular weight fractions isolated from the same reaction mixture were also examined using the characterization techniques described above. Although the structure of the C13H24 material was reasonably well established before our most recent experiments, the structures of the higher oligomers were not known previously. Heteronuclear chemical shift correlation and 2D-INADEQUATE data have proved instrumental in developing a better understanding of the structure of these higher oligomers.

These fractions were found to consist of a family of molecules formed from one isoprene and increasing numbers of isobutylene monomers. The concentration of each family member, however, appeared to depend in a non-regular way on the number of isobutylene monomers included in the molecule.

The work that we've completed to date using all of our best NMR and MS tricks suggests that the higher boiling products exhibit most of the same structural fragments as the C13H24 parent including the tetramethyl-cyclohexyl ring and the terminating isopropenyl group. There have been some surprises too, however. Unlike the rather straightforward spectrum observed for the C13H24 molecule, a highly purified fraction of the C21H40 family member exhibited forty-two 13C resonances and has been assigned to roughly equal concentrations of two structural isomers. Needless to say, we continue to be interested in the origin and significance of these cyclic oligomers in the copolymerization process.

Yours sincerely,

Kenneth D. Rose

Heteronuclear Chemical Shift Correlation for the C13H24 Oligomer.

2D - INADEQUATE for the C13H24 Oligomer.
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Tutorial and posters sessions are also planned : Those wishing to contribute a poster should enclose a preliminary abstract.

Organizing Committee

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Students and postdoctoral fellows should ask research supervisor to write a letter of recommendation directly to the school Director.

CLOSING DATE FOR APPLICATION : MAY 15th, 1988

For more information, please write to: Prof. P. GRANGER

A.S.I. School Director on NMR
UNIVERSITE LOUIS PASTEUR
Institut de Chimie
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Barry,
I hope you'll be there,
2000 MHz is coming!!

Christian
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Effective this date, *new and renewal* subscription orders from commercial subscription services (EBSCO, Faxon, Read-More, etc.) for the TAMU NMR Newsletter will be respectfully declined.

While there are several reasons which make this step necessary, the major factor is the difficulty of making potential new subscribers properly aware of the Newsletter requirement of a periodic technical contribution in addition to paying an appropriate subscription fee.

It should be emphasized strongly and understood clearly that a) there is no intent or desire to limit the Newsletter availability, commensurate with our needs for adequate funding and an adequate flow of technical contributions, and b) all active, paid subscriptions will be honored for the current Newsletter year, which ends September 30, 1988.

The details of the Newsletter policies are otherwise unchanged; copies of our statement of *Policies and Practical Considerations* are available on request. New subscriber/participants are always welcome; new Sponsors and Advertisers are doubly welcome - details on request.

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Bernard L. Shapiro
Editor/Publisher
TAMU NMR Newsletter.

*This notice has been sent to the three commercial subscription services named above. Those current subscribers who have used one of these, or any similar, services, please take note. If this new policy raises problems, feel free to contact me. I tend to be more interested in problems of scientific colleagues than in allowing librarians and bureaucrats to keep their hallowed positions atop their strange versions of Newton's second law . . .*

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1. Please provide short titles for all topics of your contributions. Failure to provide titles suitably succinct ones - may result in my doing so, with possible attendant loss of signal. Ask Alan Marchand...

2. "Positions Available", "Equipment Available", and similar notices should be formatted so as to use the minimum vertical space. Please do not double space such notices, or leave wide margins at the sides. I believe that such notices should rarely if ever need to exceed one-half of a page, and henceforth, such notices which exceed 4.5" (11.4 cm) in the vertical dimension, including letterhead, address, etc., will be respectfully declined, and returned for condensing (This will usually result in the notice being delayed until the next Newsletter issue.). A notice which really needs to be more than 4.5" tall must be agreed to in advance.

3. Technical contributions may not exceed three pages without prior approval.

4. All contributions must be formatted so as to leave 1" (25.4 mm) margins on all four sides. This is especially important for foreign subscribers, whose paper is usually larger than that used in the U.S.A. and Canada.

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