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<th>7mm</th>
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<tr>
<td>2.5mm</td>
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<td>38mm</td>
</tr>
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Programming Phase Permutations

Dear Dr. Shapiro:

All TAMU Newsletter readers will be familiar with the importance of phase permutations in pulse sequences, for cancellation of systematic instrumental errors, for polarization transfer, for enhancement or cancellation of multiple quantum transitions, for composite pulses, etc. Recent versions of the NMR operating programs from Nicolet (1) use an elegant algebraic representation for the relation between the phase quadrant in a pulse interval and the number of completed acquisitions. I wanted to use a similar scheme in programs for numerical simulation of spectra resulting from multiple acquisitions with complex excitation schemes. Since the Nicolet formulae are described (ref.1. p. 117) in a grammar notation, it seemed worthwhile programming the formula translation using a compiler directly compatible with this notation, Yacc (2) a UNIX* compiler. After rather more than the half-hour’s effort I had projected, I obtained a general subroutine which takes in the formula directly and then produces the values of the various settings for any acquisition number (5 in the formulae).

These formulae yield values of the phase letters (on the left, fig) with the operators having the usual algebraic meaning except that assignment ("=") and parentheses ("(expression)") yield the result modulo 4. Figure 1 illustrates a pulse sequence. I shall be happy to supply listings of the routines to anyone interested, but unless you have a UNIX operating system with Yacc, these are really only usable for wallpaper.

The grammar for phase permutation prepared by Nicolet is a powerful, general (3), and complete definition, and should be suitable for reporting permutations in phase sequences.

Sincerely,

David Cowburn

DC:mmn

(1) NMC-1280 manual, June 1982, Nicolet Magnetics, Fremont CA.

(2) Yacc, Yet-another-compiler-compiler. S. C. Johnson in "UNIX manual", Bell Laboratories, Inc. 1978. Yacc is rather similar in class of application to the more familiar LISP, but they differ considerable in style and operating detail. * UNIX is a trademark of Bell Laboratories.

(3) For example, it would be easy to extend it to phase shifting with n positions in the 2π radian range, with n > 4.
Figure 1. Programming Phase Permutations - Example

Phase permutation expressions for 13C-13C satellite detection via double quantum coherence

\[
\begin{align*}
  a &= s/8 \\
  &\begin{array}{c}
  1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
  2 & 2 & 2 & 2 & 2 & 2 & 3 & 3 & 3 & 3 & 3 & 3
  \end{array} \\
  b &= s/(8+(2*(s/4)+1)) \\
  &\begin{array}{c}
  1 & 1 & 1 & 3 & 3 & 3 & 2 & 2 & 2 & 2 & 2 & 2 \\
  3 & 3 & 3 & 1 & 1 & 1 & 1 & 1 & 1 & 1
  \end{array} \\
  c &= s/s+s \\
  &\begin{array}{c}
  1 & 2 & 3 & 1 & 2 & 3 & 1 & 2 & 3 & 1 & 2 & 3 \\
  2 & 3 & 1 & 2 & 3 & 1 & 3 & 1 & 2 & 3 & 1 & 2
  \end{array} \\
  d &= s/s-s \\
  &\begin{array}{c}
  1 & 2 & 3 & 1 & 2 & 3 & 1 & 2 & 3 & 1 & 2 & 3 \\
  2 & 3 & 1 & 2 & 3 & 1 & 3 & 1 & 2 & 3 & 1 & 2
  \end{array}
\]

Sequence:
1. 90° deg pulse at phase a
2. delay
3. 180° deg pulse at phase b
4. delay
5. 90° deg pulse at phase a
6. 90° deg pulse at phase c
7. acquire at relative phase d
8. delay for equilibration

Sequence diagram:
- 90 pulse at phase a
- 180 pulse at phase b
- 90 pulse at phase c
- acquire at phase d
- inter-cycle delay

Diagram shows the timing and sequence of pulses with delays and acquisitions.
December 20, 1982

Professor B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Dear Barry:

EDITING OF THE $^{15}$N NMR SPECTRA OF AMINOGLYCOSIDES BY THE DEPT TECHNIQUE

We have recently applied spectrum editing by the DEPT technique (Distortionless Enhancement by Polarization Transfer; Doddrell et al., J. Magn. Resonance 48, 323, 1982; Bruker literature, 1982) to the structural analysis of aminoglycosides by $^{15}$N NMR. In Figure 1 are shown the natural abundance, 40.6 MHz $^{15}$N NMR spectra of solutions of isofortimicin in 9:1v/v CF$_3$CO$_2$H:CD$_3$CO$_2$H, a solvent mixture that protonates all nitrogen atoms except that of the amide group, and thereby suppresses the rapid NH proton exchange which occurs at higher pH. For the purpose of a deuterium lock signal for our WM-400 spectrometer, the less expensive CD$_3$CO$_2$D solvent was not used, in order to avoid the complication of partially deuterated amino-groups.

The $^{15}$N assignments indicated by the proton decoupled NH, NH$_2$, and NH$_3$ sub-spectra shown in Figures 1a, 1b, and 1c, respectively, neatly confirm those which we had made earlier by analysis of the multiplicities of the proton coupled, $^{15}$N spin multiplets of isofortimicin (see Figure 1e) combined with $^{15}$N chemical shift correlations with structural analogues. The work is being done in collaboration with Dr. Jim McAlpine of Abbott Laboratories, and thanks are due Dr. W. E. Hull for his advice.

Yours sincerely,

Bruce Coxon
Organic Analytical Research Division
Center for Analytical Chemistry
15N NMR SPECTRUM EDITING BY THE DEPT TECHNIQUE — LINEAR COMBINATIONS

**ISOFORTIMICIN**

(a) \( \text{NH}_3 \)

(b) \( \text{NH}_2 \)

(c) \( \text{NH}_3 \)

(d) \( \text{NH}_n \) \( (\ell, = n/4) \)

Chemical shift reference:— saturated aqueous \( \text{NH}_4^15\text{NO}_3 \)

Figure 1.
Relaxation Mechanisms of the t-Butyl Cation

Dear Barry,

Despite the existence of a large body of chemical shift and coupling constant data, there are virtually no $T_1$ data for carbocations in the literature. This fact, together with our observation that cationic carbons often give relatively intense absorptions compared to other non-protonated carbons in the same molecule, prompted us to investigate the relaxation mechanisms of carbocations generated in superacids at sub-ambient temperatures.

The results for the t-butyl cation, generated from the alcohol in excess SbF$_5$/SO$_2$ClF (ROH:SbF$_5$ 1:7.3) with a solution viscosity of 23.6 cp at 213 K are summarized in the Table. The spin rotation mechanism makes no contribution to the relaxation of either carbon nucleus, since plots of $\ln R_{1OB}$ against $10^3/T$ give excellent straight lines. Whilst the dipole-dipole mechanisms is the major contributor to relaxation at 14 kG, it contributes only 50% and 20% to the relaxation of the methyl and cationic carbons respectively at 59 kG.

For the cationic carbon, relaxation is by the chemical shift anisotropy mechanism to the extent of 20% at 14 kG and a massive 80% at 59 kG.

Analysis of the relaxation data by the Woessner equations provides a value of the ratio of the rotational diffusion coefficients $D_{1}/D_{2} = 6$ but not a value for the internal rotational coefficient $D_i$ of the methyl group.

Thus the t-butyl cation in this medium reorients anisotropically, with rotation about the C$_{3v}$ axis being favoured over that of the perpendicular axes by a factor of six.

Full details will be published in the Journal of Magnetic Resonance.

Merry Christmas!

Yours sincerely,

D. R. Leslie

D. P. Kelly.
TABLE I

$^{13}\text{C}$ NUCLEAR RELAXATION PARAMETERS FOR THE t-BUTYL CATION 0.75 M IN SbF$_5$/SO$_2$ClF AT 213 K

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0$</td>
<td>14.1</td>
<td>58.8</td>
<td>14.1</td>
<td>58.8</td>
</tr>
<tr>
<td>$T_1$</td>
<td>3.3 ± 0.1</td>
<td>3.3 ± 0.1</td>
<td>5.0 ± 0.3</td>
<td>1.2 ± 0.04</td>
</tr>
<tr>
<td>$n$</td>
<td>1.6 ± 0.1$^b$</td>
<td>1.6 ± 0.1</td>
<td>1.0 ± 0.1</td>
<td>0.19 ± 0.06</td>
</tr>
<tr>
<td>$R_1$</td>
<td>0.30 ± 0.01</td>
<td>0.30 ± 0.01</td>
<td>0.198 ± 0.005</td>
<td>0.83 ± 0.03</td>
</tr>
<tr>
<td>$R_{1DD}$</td>
<td>0.24 ± 0.02</td>
<td>0.24 ± 0.02</td>
<td>0.10 ± 0.01</td>
<td>0.08 ± 0.03</td>
</tr>
<tr>
<td>$R_{1CSA}$</td>
<td>-</td>
<td>-</td>
<td>0.038 ± 0.002</td>
<td>0.67 ± 0.04</td>
</tr>
<tr>
<td>$R_{1OTH}$</td>
<td>0.06 ± 0.03</td>
<td>0.06 ± 0.03</td>
<td>0.06 ± 0.02</td>
<td>0.08 ± 0.10</td>
</tr>
</tbody>
</table>

$^a$ Uncertainties are the standard deviations of the least squares values of $T_1$.
$^b$ Estimated maximum uncertainties.
$^c$ Uncertainties calculated by propagation of those for $T_1$ and $n$.
$^d$ $R_{1OTH} = R_{1OBS} - R_{1DD} - R_{1CSA}$
Dear Barry

Although the NMR-spectroscopy of oriented molecules provides an elegant method for the measurement of shift anisotropies, there are various problems stemming predominantly from the reference signal which may depend upon temperature in the gradient method, upon the phase in the phase-transition method or upon the change of local effects in the 90° rotation method. These problems are particularly important for measurements of small anisotropies as e.g. of the nucleus ¹H. On the contrary, for ¹³C, the results seem quite reliable as we have demonstrated some time ago for CH₃CN ¹) and now for 2-butyne. The results are summarized in the table.

Tab: ¹³C Chemical Shift Anisotropies of 2-Butyne (Δν in ppm)

<table>
<thead>
<tr>
<th>Method</th>
<th>Solvent</th>
<th>Methyl Carbon</th>
<th>Acetylenic Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>gradient</td>
<td>ZLI 1167</td>
<td>15.5 ± 0.3</td>
<td>223.7 ± 0.8</td>
</tr>
<tr>
<td>&quot;</td>
<td>EBBA</td>
<td>18.6 ± 0.5</td>
<td>227.6 ± 0.5</td>
</tr>
<tr>
<td>NEMIX ¹)</td>
<td>ZLI 1132</td>
<td>17.4 ± 1.1</td>
<td>227 ± 1</td>
</tr>
<tr>
<td>solid state-NMR ²)</td>
<td>ZLI 1167 + ZLI 1132</td>
<td>201 ± 10</td>
<td>237.6</td>
</tr>
<tr>
<td>theory ³)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹) CH₃CN
²) ZLI 1132 + ZLI 1167
³) Theory
Our results for the acetylenic carbon disagree with a recent publication \(^4\) which gave the value 160±7 but was based on spectra of lower quality and on an assumed molecular structure. The agreement with theoretical predictions \(^3\) is very satisfactory.

With best regards, yours sincerely

P. Diehl
F. Moia

References:

Dear Professor Shapiro,

Although there are reports in the literature (1) of the $^{121}$Sb and $^{123}$Sb nmr spectra of SbX$_6^-$ (X = F or Cl) in non-solvolysing media, these reports do not give reliable linewidth data. One source (2) has observed broader resonances from $^{123}$Sb in SbF$_6^-$ than $^{121}$Sb. This is not to be expected and indeed it can be shown that for a given species the $^{121}$Sb linewidths should be broader than those of $^{123}$Sb by a factor of 1.2.

The relevant equation (3) is:

$$w_q = \frac{3\pi}{10I^2} \frac{(2I+3)}{(2I-1)} \chi^2 (1 + \frac{1}{3\eta^2}) \tau_1$$

where $I$ is the spin of the nucleus in question ($^{121}$Sb $I = \frac{5}{2}$, $^{123}$Sb $I = \frac{7}{2}$), $\chi$ is the nuclear quadrupole coupling constant and is defined: $

\chi = \frac{eQ}{h}.$

In our calculations the electric quadrupole moment $Q$ was substituted for $\chi$ as the $q_{22}$ factor should be constant for each pair of symmetrical octahedral species that we have studied. Similarly the asymmetry factor $\eta$ should be constant in octahedral species. $\tau_1$ is the isotropic tumbling correlation time which is constant in our samples, since we have studied the $^{121}$Sb and $^{123}$Sb nmr spectra of 1 molar solutions of both (C$_2$H$_5$)$_4$N$^+$SbX$_6^-\text{and}$ (C$_2$H$_5$)$_4$N$^+$SbF$_6^-\text{in }d^3\text{-methyl cyanide.}$

Our experimental results are collected in the table and the $^{123}$Sb spectrum of SbF$_6^-$ is also shown.
The linewidth of the SbCl⁻ signal in its $^{121}\text{Sb}$ spectrum has been previously reported (4) as 300 Hz, whereas we have observed a value of 175 Hz in our work.

The linewidths for $^{123}\text{Sb}$ are indeed narrower than those for $^{121}\text{Sb}$ and it is the larger spin of $^{123}\text{Sb}$ which produces this substantial effect. The ratio $\frac{1J(123\text{Sb-F})}{1J(121\text{Sb-F})} = 1.84$ is in good agreement with the ratio $\frac{\gamma_{123}\text{Sb}}{\gamma_{121}\text{Sb}} = 1.8456$.

Although $^{123}\text{Sb}$ nmr spectra do give narrower linewidths, the coupling constant to a given nucleus is smaller by a factor of approximately 2, which could make resolution of overlapping signals more difficult.

Yours sincerely

[Signature]

Dr MFA Dove  
JCP Sanders

(3) Ref. (1), p.17.
Nucleus | Observing freq./MHz | Compound | Chem. * Shift | $^1J$(Sb-F) /Hz | Linewidth /Hz |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{121}$Sb</td>
<td>59.859</td>
<td>$\text{Et}_4\text{N}^+\text{SbCl}_6^-$</td>
<td>0</td>
<td>-</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Et}_4\text{N}^+\text{SbF}_6^-$</td>
<td>86.7</td>
<td>1938</td>
<td>Septet 85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Et}_4\text{N}^+\text{SbF}_6^-$</td>
<td>88.1</td>
<td>1053</td>
<td>Septet 51</td>
</tr>
<tr>
<td>$^{123}$Sb</td>
<td>32.415</td>
<td>$\text{Et}_4\text{N}^+\text{SbCl}_6^-$</td>
<td>0</td>
<td>-</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Et}_4\text{N}^+\text{SbF}_6^-$</td>
<td>88.1</td>
<td>1053</td>
<td>Septet 51</td>
</tr>
</tbody>
</table>

* Relative to $\text{SbCl}_6^-$

$^{123}$Sb n.m.r. spectrum of $\text{Et}_4\text{N}^+\text{SbF}_6^-$ in CD$_2$CN (recorded on a WM 250 Bruker n.m.r. spectrometer).

[Graph showing n.m.r. spectrum with labeled peaks]
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Dear Professor Shapiro,

Some time ago we reported $^1J(^{195}\text{Pt},^{119}\text{Sn})$ coupling constants in excess of 28,000 Hz and have recently extended this range to > 35,000 Hz. These values are rather large, but to our surprise $^2J(^{119}\text{Sn},^{117}\text{Sn})$ is even larger, e.g. 37,164 Hz, for trans-[Pt(SnCl$_3$)$_2$(AsEt$_3$)$_2$]. Moreover, in the past few months Heinz Rüegger has synthesized complexes in which this two-bond spin-spin coupling exceeds 46,000 Hz, e.g. 46,582 Hz for the [PtCl(SnCl$_3$)$_2$(PEt$_3$)]$^-$ anion. It seems likely that we will shortly need a new computer with a digitization rate suitable for $^2J$ values of 50 KHz or more.

We are not quite certain why these $^2J$ values are so large, although we have a few ideas, and would certainly welcome further suggestions.

Please credit this contribution to the account of Professor L. M. Venanzi.

Sincerely,

[Signature]


Suggested Title Large $^2J^{119}\text{Sn},^{117}\text{Sn}$ values.
Professor B.L. Shapiro,
Department of Chemistry,
Texas A & M University,
COLLEGE STATION,
Texas 77843,
USA

5th January 1983.

Dear Dr. Shapiro,

SPINNING SPEED MODULATOR

Having completed the construction of an automatic sampling device on our Bruker WM-360, we have also incorporated a spinning speed modulator to minimise the appearance of sidebands. The equipment consists simply of a supplementary gas regulator, a solenoid valve and some associated electronics.

Using the existing regulator inside the spectrometer console, a minimum flow rate is set which, with the needle valve on the front, is adjusted to say a 5 Hz spin rate. The new regulator is set to give a maximum flow rate to enable say a 50 Hz spin rate. The electronics then accomplishes two things. It causes the solenoid valve to close at variable time intervals so as to avoid any coherence with the data collection. It also detects when the spin speed falls below 20 Hz and causes the valve to open. The natural inertia of the system does the rest.

The apparatus was built by Kevin Brooks following Alan Strutt's design, who can provide more details if anyone is interested. The diagram shows an example of the suppression achieved.

Yours sincerely,

J.C. LINDON
A.C.R. STRUTT
Department of Physical Chemistry

Enc.

JCL/ag
Optimised field

Spin rate: 27Hz

SSB = 0.20%

64 scans (3.5min)

Optimised field

Modulated spin rate: 20-50Hz
Cycle time ≈ 25sec

64 scans (3.5min)

SSB < 0.03%

13C

impurity

13C

SSB

SSB

x20

x20
Dear Barry:

We have been using high-field $^{19}$F MAS-NMR to study the fluoridation of hydroxyapatite surfaces, with the goal of better understanding the mechanism of dental enamel fluoridation. One long-standing problem has been the need to quantitatively distinguish between the formation of calcium fluoride and fluoroapatite ($\text{Ca}_5\text{F}$(PO$_4$)$_3$). Although both compounds have similar $^{19}$F chemical shifts, at moderate (4kHz) spinning speeds only the inhomogeneously-broadened resonance from fluoroapatite is significantly narrowed and exhibits spinning sidebands. Figure 1a shows the spectrum of a hydroxyapatite sample exposed to aqueous fluoride; both the broad peak of calcium fluoride and the sharper peak with sidebands characteristic of fluoroapatite can be observed. Since calcium fluoride has a $T_2$ orders of magnitude shorter than that of fluoroapatite, a Hahn spin echo can be used to eliminate the calcium fluoride signal and clearly reveal the fluoroapatite component (Figure 1b).

We have used $^{19}$F MAS-NMR to study the effects of fluoride solution concentration and solid-state transformations upon the form of fluoride at the surface. One example of the intriguing information available from the technique concerns the ultrastructural relationship between calcium fluoride and fluoroapatite at the surface.

The results of an inversion-recovery measurement of $T_1$ in a surface-treated sample containing both calcium fluoride and fluoroapatite are shown in Figure 2 for three delay values. The existence of a null for both components at the same delay value (1.6s) demonstrates that the $T_1$ values are identical. Unless this equality is fortuitous (which is not supported by measurements on the bulk compounds), spin-diffusion between the calcium fluoride and fluoroapatite spin systems appears to be responsible. Thus, we can conclude that the fluoroapatite and calcium fluoride at the surface are in intimate contact at the molecular level.

A note describing preliminary results has been submitted for publication (J. P. Yesinowski and M. J. Mobley, "$^{19}$F MAS-NMR of Fluoridated Hydroxyapatite Surfaces"). Further data is included in the proceedings of an ACS Symposium on the Adsorption on and Surface Chemistry of Hydroxyapatite, to be published by Plenum Press in 1983 (J. P. Yesinowski, R. A. Wolfgang, and M. J. Mobley, "New NMR Methods for the Study of Hydroxyapatite Surfaces"). A manuscript on the detailed characterization of bulk model compounds is in preparation (J.P.Y.).

Sincerely yours,

THE PROCTER & GAMBLE COMPANY
Research & Development Department

James P. Yesinowski
(513) 977-2551
Figure 1: a) $^{19}$F MAS-NMR spectrum of hydroxyapatite treated with 33 mM fluoride, 0.73% total fluoride uptake, 30° pulses, 3.7 kHz spinning speed.

b) Hahn spin-echo with 273 µs delay time (≈ one rotation period) of same surface sample, showing only fluoroapatite component.

Figure 2: $^{19}$F MAS-NMR spectra obtained with inversion recovery sequence to measure $T_1$ of surface fluoride signals (unequal amplitudes of short and long delay time spectra are probably due to rf inhomogeneity).
Dear Professor Shapiro,

"The $^{29}$Si NMR Spectrum of a Constrained Molecule"

Recent investigations of siloxane polymers resulted in the isolation of a white crystalline solid which sublimed at approximately 60-70°C.

The $^{29}$Si NMR spectrum of the solid was obtained using a Varian XL-200 NMR spectrometer operating in the Fourier transform mode at 39.75 MHz with broad band decoupling to remove all (SiH) scalar couplings (Figure 1). The deuterated chloroform solvent was used for the internal field frequency controlled lock system. The decoupler was gated off during the pulse delay and the sample was doped with 0.1 M tris(acetylacetonato)chromium to allow maximum relaxation of the nuclear spins. The spectrum showed two peaks one at -14.64 ppm and the other at -58.35 ppm relative to tetramethylsilane in a 3:2 intensity ratio. This information in conjunction with the mass spectrum of the solid (m/e: M+ -15 = 341, 94.9%) indicated the following chemical structure:

![Chemical Structure Diagram]

The Me$_2$SiO and MeSiO$_3$ units are shifted downfield from the -20 and -65 ppm chemical shifts normally observed for these units, respectively.
Such downfield chemical shifts have been noted for strained siloxane ring systems (Table 1). This is the first time such downfield shifts have been noted for rotationally-hindered or constrained molecules.

Sincerely yours,

Sunny Lo, Ph.D.
Elastomers and Engineering Industries Research


<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Siloxane Chemical Shifts in ppm Relative to TMS</strong></td>
</tr>
<tr>
<td>D</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>$D_3$</td>
</tr>
<tr>
<td>$D-T$</td>
</tr>
<tr>
<td>$I-D$</td>
</tr>
<tr>
<td>$I-D$</td>
</tr>
</tbody>
</table>

P.S. Please credit this contribution to Tom Carr's account.
Figure 1: $^{29}\text{Si}$ NMR spectrum of $(\text{MeSiO}_3)_2(\text{Me}_2\text{SiO})_3$ in $\text{CDCl}_3$. Chemical shifts are in ppm from TMS.
Some manufacturers claim these experiments are difficult

The above spectra were obtained during a 3-hour run on an XL-300 Superconducting FT NMR Spectrometer System.

Varian owners perform them all before lunch

Here's what one XL Series owner says:

Dr. Peter Rinaldi is a chemist at the Major Analytical Instruments Facility, Cleveland, Ohio. MAIF is a research and testing facility serving Case Western Reserve University and scientists throughout the northeast Ohio region. All quotes are from the MAIF NEWSLETTER, Vol. 1, Issue 3, March 1982, reprinted courtesy of MAIF.

Software written for chemists: “Special experiments are a standard part of the XL-800 NMR software package,” says Dr. Rinaldi. “We have been routinely running experiments such as INEPT, APT, solid state cross polarization, and most of the commonly used 2D-FTNMR experiments. Having run many of these myself, I can personally vouch for the tremendous advantage they offer.”

Multi-tasking capabilities: “We need not be concerned about idling the instrument while time-consuming data processing and plotting is being performed; a long acquisition can be run simultaneously. It is not uncommon for the more experienced users to have the XL-200 occupied doing three or even four tasks simultaneously for extended periods of time.”

More information in less time: “In the rare instance that a new experiment is needed for which the pulse program does not exist, it can easily be written in convenient Pascal language, and no hardware modifications are required. Thus, most of the barrier to utilizing new NMR techniques has been eliminated.”

Here's what Varian software can do for you: To receive your free copy of “Software: New Ways to Solve Difficult Problems,” write NMR Software, Varian Associates, D-070, Palo Alto, CA 94303; or call the sales office nearest you today.

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January 6, 1983

Professor B. L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Subject: "Long Range H-F and C-F Coupling Constants in Fluorinated Cinnamates"

Dear Barry:

We have recently studied the NMR spectra of butyl esters of o-(trifluoromethyl)cinnamic acid(I) and o-fluorocinnamic acid(II). No coupling was observed between the vinyl protons and the fluorine nucleus in II. On the other hand, a 5-bond coupling between the 6-vinyl proton and fluorines was observed in I. The H-F coupling constant is 2.2 Hz. We believe the H-F coupling constant is transmitted "through-space" rather than through bonds. The result implies that the conformation of I is Ia rather than Ib. Apparently,

interaction between the α-vinyl proton and the trifluoromethyl group destabilizes conformer Ib.

The H-F and C-F coupling constants between the vinyl group and the fluorine nucleus are listed in the table.

Long Range H-F and C-F Coupling Constants*

<table>
<thead>
<tr>
<th></th>
<th>J(H,F)</th>
<th>J(C,F)</th>
<th>J(C,F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.2</td>
<td>2.0</td>
<td>-0</td>
</tr>
<tr>
<td>II</td>
<td>~0</td>
<td>3.2</td>
<td>6.5</td>
</tr>
</tbody>
</table>

*Expressed in Hz. Solvent is CDCl₃.

Sincerely,

C. K. Tsen

[Signature]

[Signature]
Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843

Dear Barry:

I've switched from deuterons to protons since our last communication on bile salt-lecithin (BS/L) mixed micelles – am taking advantage of the National Magnet Lab's 500 MHz spectrometer while on leave in Mary Roberts' lab at M.I.T.'s Department of Chemistry. \( ^1H \) chemical shift and linewidth studies for BS, L headgroup, and L backbone resonances are a nice complement to our \( ^2H \) relaxation work on L acyl chains (1); and together they provide important new information on the molecular arrangement and surface features of these aggregates.

The most intriguing observation so far is a peak splitting for the lecithin choline methyl groups (see Figure 1), which appears at a variety of compositions as the total lipid concentration is decreased. Two populations are present in slow chemical exchange; they could be inner and outer monolayers of large phospholipid vesicles, or else both vesicle layers plus the BS/L micelles. Formation of single walled vesicles (along with BS monomers) has been proposed from quasielastic light scattering measurements (2) and is understandable in terms of the model in Figure 2: dilution pulls BS molecules from the disk perimeter and also forces the bile salts below their critical micelle concentration in the bulk solution.

Further experiments are in progress, focusing particularly on peak susceptibility to lanthanide reagents and quantitative characterization of a mixed micelle-vesicle equilibrium. Among the more obvious flies in the ointment: (a) formation of metastable states and (b) probable enhancement of inner-outer vesicle flip-flop rates by the presence of bile salts. More to follow as the picture becomes clearer ...

Sincerely yours,

Ruth
Assistant Professor of Chemistry

P.S. to all NATO Rowdies: Hope to stage reunion at E.N.C. Please bring slides, giggles, thirsty throats and dancin' shoes.
Figure 1. 500 MHz proton NMR spectra (partial traces) of 70:30 mol % taurocholate-egg lecithin solutions as a function of total lipid concentration. Chemical shifts are referenced to DSS; resolution enhancement by the correlation difference technique was applied to the top trace.

Figure 2. Molecular structures of the components and schematic model for one proposed structure of the bile salt-lecithin mixed micelle, shown in longitudinal and cross section.

1-palmitoyl-2-oleoyl-phosphatidylcholine (POPC), the major constituent of egg yolk lecithin.

References:
Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dear Professor Shapiro:

Re: Reflected-Wave Detector/Interlock

In NMR spectrometers used for studies of solids, dielectric breakdown resulting from high humidity in the NMR probe in the presence of the intense radiofrequency excitation pulse, and disintegration of the sample rotor due to forces caused by high rotation rates are two of several conditions that may be expected in normal use which will cause adverse effects in the radiofrequency transmission path and may result in damage to spectrometer parts.

An electronic circuit which detects reflected-waves in a radiofrequency transmission path and a simple interface to the spectrometer computer has been incorporated into our Nicolet NT-200 NMR spectrometer. The circuit protects expensive equipment (transmitter, probe, receiver preamplifier) from prolonged exposure to excessive reflected voltages (and preserves the collected data) by automatically causing an experiment in progress to stop when adverse conditions occur.

A block diagram of the rf reflected-wave detector is shown in Figure 1. The voltage comparator circuit provides a user selectable variable sensitivity from 50 mW to 100 W. The detection circuit has been tested over a frequency range from 10 to 500 MHz making it suitable for a variety of existing spectrometers. A full report is scheduled to appear in the April, 1983 issue of Journal of Magnetic Resonance.

Cordially,

Robert W. Dykstra

RWD/1c

Attachment
FIGURE 1 - Block diagram of the essential ingredients of the reflected-wave detector, and the simple change required to interface the circuit to an NMR spectrometer. (The specific dual directional coupler used should be selected for the frequency range of interest.)
Dear Barry,

Some preliminary work done in collaboration with Dr. Graham Knox and Debbie Willison on the iron carbonyl derivative (1) may be of interest. This is one compound among many formed by the reaction of Fe₃(CO)₉ and Me₂N.NO.  

The molecular formula was found initially by mass spectrometry, but the presence of four non-equivalent methyl groups is confirmed by peaks in the ¹H (δ 2.65, 3.10, 3.90, 4.00) and in the ¹³C n.m.r. spectrum (δ 33.9, 39.2, 51.5 and 53.0). At 383K the carbon spectrum shows seven separate carbonyl peaks (δ 210.2, 213.0, 213.1, 213.5, 213.7, 214.6, and 215.9) and a low field quaternary carbon atom (δ 328.15).

That the compound is fluxional is indicated by the fact that three of the carbonyl peaks coalesce at 313K, while there are indications (despite decomposition occurring) that all the carbonyls are changing at 353K.

We presume that the more ready process involves NMe₂ groups exchanging roles, with movement of the three carbonyl groups attached to the iron atom (A), while the higher temperature process involves movement of a carbonyl group from one iron atom (B) to the other (A) (via a bridging intermediate). We must admit that the proposed structure is rather strained and we are considering others for this compound which is still under investigation.

Yours sincerely,

Peter Bladon
$^{13}\text{C}$ spectrum of Fe$_2$(CO)$_7$C(NMe)$_2$ in toluene $d_8$.

Solvent peaks marked (S)

WM-250 at 62.9 MHz
January 20, 1983

Bernard L. Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, TEXAS
77843

Title: Alterations to VT Apparatus on NT-300WB

Dear Barry:

With the arrival of your yellow notice I must spring into action. We have been checking out our new Nicolet 300WB spectrometer over the last couple of months although this has been made difficult because of pile driving going on just outside our building. Anyone interested in the frequency spectrum of our building in response to periodic pulsed excitation and its analysis as a driven damped harmonic oscillator can contact me.

One of the things we are impressed with on the spectrometer is the computer controller VT. However, we like to time average for days at slightly low temperatures (0–4°C for biological systems) and I have always hated the coil in the ice bath/slush approach so we immediately converted over to using a NESLAB Cyro Cool unit as a cooling source (Model CC-100 lowest temperature range is -100°C probe). For our limited temperature range we find it is sufficient to just pass the dry air over the probe which is placed inside a relatively loosely fitted, insulated copper tube.

We also modified the Nicolet VT stack by having the glassblower put a bend in the tube where the inlet air is attached and bringing this out through the bottom of the probe where the tube is attached using nylon swage lock fittings. This we think is simpler and more reliable than trying to pull the VT air tube off each time.

Speaking of reliability, the results of having a leak in the system just before the VT stack are interesting. We obtained the following aberrant behavior with a leak that resulted in insufficient air passing out the heater coil so that it repeatedly overheated and then took too long to cool.
Bernard L. Shapiro, January 20, 1983

What one really needs as a safety device in these systems is a flow detector on the exit air.

Best regards,

Brian Sykes
Gerard McQuaid
Tom Williams
Dear Professor Shapiro,

Distribution About the NMR-determined Average Structures of Coal-derived Asphaltenes

Asphaltenes comprise some of the higher molecular mass (MM, 200-3000) constituents of coal liquefaction products, and are of interest both as precursors of the more tractable oil fractions and intrinsically as substrates for further processing to fuels and chemical feedstocks.

$^1$H and $^{13}$C NMR methods of determining the statistically averaged structures of coal-derived asphaltenes are well established, but, because of the very localised nature of the chemical-shift parameter on which they are based, there is no direct way of knowing how well such average structures represent the extremely large number of individual constituents actually present. Moreover, since the asphaltene fraction contains molecules with a wide range of masses, and the proposed structures are averages over all of these, information concerning the variation of structure with MM is also lacking.

In cooperation with Terry Martin and Colin Snape of the National Coal Board Coal Research Establishment, we have addressed the first of these problems in two ways. Firstly, the agreement between NMR averages and the results of GC and GC/MS analyses which allow identifications of many hundreds of compounds in low-MM coal-derived mixtures engenders some confidence in extrapolations to the fractions of higher MM. More directly, differential pulse voltammetry of the asphaltenes enables many of the aromatic nuclei linked together in the structures (e.g. naphthalenes, fluorenes, anthracenes, phenanthrenes, pyrenes etc.) to be identified; for high-yield extracts obtained from coals of different rank by a variety of methods, agreement with NMR-determined average structures is good in all cases so far examined.

$^1$H and $^{13}$C NMR of almost monodisperse preparative size-exclusion chromatographic sub-fractions of coal-derived asphaltenes revealed considerable variations about the average structure determined for the whole asphaltene fraction. With increasing MM, the following trends were observed: aromaticity decreased, but the degree of condensation of aromatic nuclei did not vary significantly; the size of aliphatic substituents increased.

Please credit this contribution to the Bradford University subscription.

Yours sincerely,

Keith D. Bartle  
Norman Taylor  
Derry W. Jones
References


Title: NMR investigation of the reaction between diketene and methanol.

Dear Prof. Shapiro,

Diketene reacts with alcohols according to the following scheme\(^1\):

\[
\begin{align*}
\text{CH}_2=\text{C}-\text{CH}_2 \quad 0=\text{C}=0 & \quad + \text{ROH} \quad \rightarrow \quad \text{CH}_3\text{COCH}_2\text{COOR} \\
\text{I} & \quad \text{II}
\end{align*}
\]

The reaction is catalysed by bases and acids. We have studied by pulse \(^1\)H NMR the kinetic of the reaction of diketene with methanol using triethylamine as catalyst (deuteroacetone as solvent). Under our conditions the reaction gives yields of >95% of II indicating that the alcoholysis is essentially complete. The experimental data obtained at several temperatures and concentrations of the reagents, in absence of water, can be interpreted according to the general equation:

\[
\frac{d[A]}{dt} = -K [A][B]
\]

where \([A]\), \([B]\) are the concentrations of diketene and methanol respectively. The data show also the linear dependence of the reaction rate, \(K\), on the catalyst's amount (fig. 1), so that the reaction
is first order in all three components. The Arrhenius plot (fig. 2) let us calculate an energy of activation of 8.5 kcal/mole.

The NMR spectra of the reacting system in presence of water (0.5 mol. 1^{-1}) do not show any significant side reactions such as hydrolysis of diketene to acetoacetic acid which can decarboxylate to acetone^{2}). The kinetic of the reaction is lower than that one in absence of water. The experimental data are not described by the previous equation so that the reaction mechanism could be different in the two cases.

Using deuteromethanol solvents several reaction products can be recognized in the reaction mixture. The products differ in the deuterium position. According to the ^1H and ^13CNMR spectra the following structures have been assigned:

\[
\begin{align*}
\text{CH}_2\text{D-CD-CH}_2\text{-COO-CD}_3 \quad \text{III} \\
\text{CH}_3\text{-CO-CHD-COO-CD}_3 \quad \text{IV} \\
\text{CH}_2\text{D-CO-CHD-COO-CD}_3 \quad \text{V}
\end{align*}
\]

Compound III is initially produced, however, at the end of the reaction, compound IV is the main reaction product. The production of III is explained by the following scheme:

\[
\text{diketene} + \text{CD}_3\text{OD} \rightarrow \left[ \text{CH}_2\text{C=CH}_2\text{-COO-CD}_3 \right] \rightarrow \text{III}
\]

As II (and III, ...) is a \(p\)-ketoester, the \(\text{CH}_3\) protons are strongly acidic and can be easily exchanged with deuterium^3). In fact an \(^1\text{H}NMR\) investigation of the system II + \text{CD}_3\text{OD} with \text{NET}_3 as catalyst (deuteroacetone as solvent) shows that the \(\text{CH}_3\) protons are exchanged with deuterium several orders of magnitude faster than methyl protons, reaching the equilibrium in a short time. The final extent of deuteration is a function of the relative concentrations of mobile protons and deuteriums.

Yours sincerely,

\begin{align*}
\text{(E. Santoro)} & & \text{(P.I. Cantini)} & & \text{(L. Rivolta)}
\end{align*}
REACTION RATE (K) VS. CONCENTRATION OF THE CATALYST [C]

REACTION RATE (K) VS. INVERSE OF THE TEMPERATURE (1/T)

REFERENCES

Maximization of Spectral Data Throughput with the Multi-Terminal GX PLEXUS System...

The JEOL Theory of NMR Productivity: Multi-terminals are better than one...
Over the last decade, the contribution that FT NMR spectroscopy has made for the chemical analysis community is enormous. Some scientists have even claimed that NMR spectral data is the single most important source of structural information available to the organic chemist. NMR spectroscopy provides information on structural analysis, quantitation, the behavior of molecules in various environments and the nature of an environment.

Until recently, NMR spectral throughput was dependent upon the sensitivity limits of the NMR spectrometer hardware. For example, ten years ago a simple carbon spectrum could take hours to collect. Nowadays, that same experiment takes only several minutes (See Figure 1). Hence, the profusion of routine and complex data now being generated by modern, commercially available NMR spectrometers has placed an ever increasing demand for high quality spectral throughput.

The Throughput Dilemma

In many cases, a spectroscopist can collect spectral data at the same rate or faster than the data can be processed and output. Continuing advances in NMR signal detection and high sensitivity probe design have created a "throughput dilemma."

The typical single operator/single terminal data system available in most NMR spectrometer systems cannot efficiently handle such fast rates of data acquisition.

In a typical single access scenario, operators must wait in line in order to collect data from that single terminal. One by one, each operator takes his or her turn at the instrument, places a sample in the probe, collects data and finally works up the results for hardcopy output.

Any operation (such as FFT, integration, printing and plotting of spectra) which takes place after spectral accumulation is data system intensive. However, they all cause unnecessary and costly dead time on the system. The spectrometer cannot be utilized in any manner until the operator currently using it completes his or her work and allows the next operator in line to have physical access to the instrument.

This scenario, of a typical single terminal instrument, effects a tremendous waste of valuable time. The waste is magnified when the cost of commercially available NMR systems is considered.

To solve the throughput dilemma, the most efficient and logical recourse would be to increase operator access to the spectrometer thereby eliminating costly dead time. In other words, the answer is the PLEXUS solution.

The PLEXUS Solution

The GX Series of FT NMR spectrometers with the PLEXUS data system, offers multiple user access to maximize operator interaction and data throughput. JEOL has achieved the unique position of offering multi-terminal spectrometer systems by incorporating the unsurpassed expertise of DEC hardware. The GX multiple-user access systems include a DEC LSI 11/23 microprocessor with the RSX multi-terminal/multi-tasking operating system, and a 32-bit word, high speed "NMR processor." This data system package yields the uncompromising speed and efficiency demanded by today's sophisticated NMR market.

The advantages of a multi-terminal/multi-tasking NMR spectrometer are numerous as well as obvious. When an operator is actively collecting data and maintaining privileged control of the spectrometer, it is possible for other operators to manipulate previously accumulated data (e.g., process two-dimensional spectra, write pulse programs or request FFT operations on two or more different sets of data). A typical three-terminal PLEXUS system is illustrated in Figure 2 below. Here Terminal One is being used to collect and display a Free Induction Decay (FID). This implies temporary spectrometer control by Terminal One. Concurrently, Terminal Two is involved with data manipulation of a previously accumulated data set. The data set could have been accumulated minutes before on Terminal Two or weeks before and read from a disc. Terminal Three is being used for pulse program editing. Consequently, the often time-consuming job of writing novel pulse sequences or experimental menus can be achieved without...
stations. First of all, in a multi-terminal system, there is no time wasted by the transfer of data through a RS-232 interface or by physically moving a disc from the spectrometer to a work station. Secondly, there is no difference in software from one terminal to another; since the entire data system uses a one multi-terminal monitor program.

Thirdly, and most importantly, each JEOL graphics terminal has potential control of spectrometer operation. This fact alone eliminates the bottleneck of single-user interaction as shown in the maximized throughput scheme of Figures 4a and 4b. The throughput of a multi-terminal system is double that of a single terminal spectrometer without a satellite station. When compared to a single terminal system with a satellite station, the throughput of a multi-terminal station is still faster. Under the best of circumstances, transfer time is usually several minutes for each spectrum. When large data sets, such as 2-D data, are relocated, transfer time may approach one-half hour.

A further benefit (and one that shouldn't be overlooked), is a psychological benefit. In a multi-terminal set-up, each operator at the spectrometer remains at one terminal for the full duration of the experiment. This continuity allows for greater concentration on each job without the distraction of moving from the spectrometer to a satellite station for final data processing.

RSX Operating Systems
RSX systems allow realtime activities to execute concurrently with less-time-critical activities. Through priority-based scheduling, the assigned priority and activities of a task determine the level of service it needs. With an RSX system, each terminal can operate independently of others in the system. That way, each terminal can run a different task and each can run more than one task.

In addition, RSX systems are highly reliable. They feature data integrity and increased system availability. For example, in a multi-user/multi-programming environment, the LSI-11 micro-computer processor provides protection as well as multiple access.

Multi-Programming
Multi-programming is the simultaneous execution of two or more tasks that reside in memory. Since task execution usually involves more than the central processor unit (CPU), multi-programming is feasible. For example, a realtime task that initiates a procedure and then waits for the completion of the procedure, may not need access to the CPU while it is waiting. Therefore, with multi-programming taking up valuable instrument time. In short, the activities of Terminal One, Two, and Three can be accomplished simultaneously with only one spectrometer and data system.

Advantages Over Conventional NMR Systems
The operational configuration of a multi-terminal system has distinct logistical benefits over non-instrument interactive satellite...
Carbon-13 spectrum of solid camphor at 67.5 MHz. Total accumulation time was 8.5 minutes.
February 2, 1983

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, TX 77843

Dear Barry:

RE: AWU POSTDOCTORAL APPOINTMENT

The Laramie Energy Technology Center has announced a postdoctoral position in NMR Spectroscopy to be filled immediately. This position is sponsored through the Associated Western Universities, Inc. (AWU) and is for a maximum of two years.

Applicants should have experience in the operation of FT-NMR spectrometers and should have the ability or interest to perform spin-echo, polarization transform, and 2D-NMR spectroscopic techniques and apply these to the analytical characterization of fossil fuels.

The starting stipend is approximately in the $18,000-20,000/year range with some paid transportation and relocation expenses. An orientation visit to the Center could also be arranged for qualified candidates.

Applicants may contact me or may write directly for application forms to:

Program Administrator
Associated Western Universities, Inc.
142 East 200 South--Suite 200
Salt Lake City, UT 84111
(Telephone: 801/364-5659)

Sincerely,

Daniel A. Netzel
Section Supervisor, Spectroscopic Research and Chemical Analyses Section
(Telephone: 307/721-2370)
Professor B. L. Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A & M University
College Station, TX 77843

H - 19 F Chemical Shift Correlations in Macromolecules

Dear Barry:

Two-dimensional heteronuclear chemical shift correlation experiments are now being applied to large molecules including proteins. Given our interests in proteins containing the fluorophenyl group we thought that this type of experiment might provide the chemical shifts of the protons of the fluorophenyl reporter group, results that would not be available by direct observation. Crucial to the success of such a correlation experiment is the ratio of the heteronuclear coupling constant \( J_{AX} \) to the transverse relaxation rates \( R_2 \) for either spin A or spin X; the larger \( J_{AX} \) is relative to \( R_2 \), the better the odds for a successful experiment. In the fluorophenyl system \( J_{AX} \) is relatively small (\( \approx 5 \) or \( \approx 9 \) Hz) and, because of the csa contribution, \( R_2 \) for the fluorine resonances can be quite large at high magnetic fields.

Some initial results with atactic poly(p-fluorostyrene) dissolved in CDCl\(_3\) are shown in the Figure. The proton and fluorine transverse relaxation rates were estimated and used to define optimum delays in the conventional experiment (See A. D. Bax, "Two-dimensional NMR in Liquids", D. Reidel, Boston (1982), p. 60). Although the directly observed fluorine or proton spectra of this polymer are essentially featureless at lower fields and have very little structure at 282/300 MHz., the correlation map and its projections to the \( 1^9F \) and \( 1^H \) axes clearly show that there are many magnetically distinguishable environments for the fluorophenyl ring, presumably due to various local stereochemical situations. How strongly each of these contributes to the spectra depends on transverse relaxation times as well as the intrinsic concentration of each form. Sorting these out will likely keep us occupied for some time.

Concurrently, similar experiments are underway with a chymotrypsin derivative containing the fluorophenyl ring and we have been able to produce a correlation map for this system even though the proton \( R_2 \) values (\( \approx 70 \) sec\(^{-1}\)) and fluorine \( R_2 \) value (\( \approx 200 \) sec\(^{-1}\)) are large.

Sincerely,

J. T. Gerig
Professor of Chemistry
Caption for Figure. $^1$H - $^{19}$F Chemical shift correlation in poly(p-fluorostyrene) obtained at 25°, on a Nicolet NT-300 instrument. The proton chemical shifts are referenced to TMS at 0 ppm.
Dear Barry:

We previously reported that a Faraday shield employed in conjunction with a surface coil permits spectra of subcutaneously implanted tumors to be monitored without interference from normal tissues outside the tumor (1). Surface coils, however, have two disadvantages - low sensitivity, which limits detection to tumors larger than \( \sim 0.6 \text{gm} \), and rf field inhomogeneity, which complicates experiments such as inversion recovery, spin echo and magnetization transfer. Replacing the surface coil with a solenoidal coil while retaining the Faraday shield substantially improves sensitivity and effectively eliminates rf field inhomogeneity while still eliminating spurious signals from normal tissues.

The probe design is schematically depicted in Figure 1. The solenoidal coil, constructed from gauge 16 copper wire insulated with vinyl tubing, consists of a 4-turn coil with a diameter of 15.5mm and a length of 13mm. This coil has a 90° pulse width of 22 \( \mu \text{sec} \) and a Q-value of 87.2 at 80.96 MHz. The other materials employed in constructing the probe have been described elsewhere (1).

This probe design yields about a three-fold improvement in sensitivity over a surface coil of the same diameter. The effect of the Faraday shield on spectra obtained with a solenoidal coil is illustrated in Figure 2. No \(^3\)P signals were detected from a tumor-free C\(_6\)H/He mouse monitored in the shielded solenoidal probe (Figure 2a), but signals were detected when the grounded copper cage was replaced by a polyethylene cage (Figure 2b). The \(^3\)P NMR spectrum of a mammary 16/C adenocarcinoma (\( \sim 0.6 \text{gm} \)) implanted in a C\(_6\)H/He mouse was measured with a polyethylene cage (Figure 2c) and with a grounded copper cage (Figure 2d). The larger phosphocreatine (PCr) peak observed without the Faraday shield probably reflects resonance contributions from normal tissues in the body of the host. All spectra were collected with a 3 sec repetition time, 13 min total accumulation time.

Sincerely yours,

Thian C. Ng

References:

Jerry D. Glickson
FIG. 1

Copper cage
rf coil

FIG. 2
27 January, 1983

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843
U.S.A.

Biaxiality in the discotic, D₁₀₆, mesophase

Dear Professor Shapiro,

During the last three years or so we have been applying (with Z. Luz and H. Zimmermann) deuterium NMR, of deuterated guest as well as host compounds, to study discotic mesophases. Our current topic of interest is biaxiality in the discotic D₁₀₆ and D₁₀ tetragonal mesophases.

In a single domain the deuterium NMR spectrum exhibits a doublet whose spacing \( \Delta v(0,0) \) depends on the orientation \( \theta, \phi \) of the magnetic field, on the average interaction constant \( v^{LC} \) and on the asymmetry parameter \( \eta^{LC} \) of the quadrupole tensor:

\[
\Delta v(\theta, \phi) = \frac{3}{4} v^{LC}_0 \left[ (3 \cos^2 \theta - 1) + \eta^{LC}_0 \sin^2 \theta \cos 2\phi \right]
\]

In multidomain powder samples, the observed spectrum consists of a superposition of such doublets weighted by the domains distribution. The parameters \( v^{LC} \) and \( \eta^{LC} \) can then readily be obtained from the characteristic features in the spectrum lineshape. In particular \( \eta^{LC} \) can be computed from the splittings corresponding to the three canonical orientations \( x, y, z \) of the liquid crystalline phase.

\[
\eta^{LC} = \frac{\Delta v(\pi/2, 0) - \Delta v(\pi/2, \pi/2)}{\Delta v(0, 0)}
\]

This parameter depends in general on a large number (25) of molecular motional constants and on the asymmetry parameter \( \eta^D \) of the deuterium quadrupole tensor in its principal frame. However, for certain molecular and mesophase symmetries, some predictions on \( \eta^{LC} \) can be made without actually knowing the motional constants. Specifically for a biaxial orthorhombic phase the following will apply:
(i) For a uniaxial molecule (i.e. having a $C_n$ axis with $n>3$) the parameter $\eta^{LC}$ depends only on the ratio of two motional constants and it should therefore be the same for all tensorial properties. In particular two or more inequivalent deuterons should exhibit the same $\eta^{LC}$.

(ii) For a molecule with $D_{2h}$ or lower symmetry $\eta^{LC}$ will depend on four or more motional constants as well as on the molecular geometry and the corresponding $\eta^P$. Therefore in such a molecule, inequivalent deuterons will in general exhibit different $\eta^{LC}$ parameters.

These rules are demonstrated in the attached figure showing the isotropic powder spectra of two probes i.e. mesitylene and p-xylene dissolved in the orthorhombic $D_{rd}$ phase of hexadecanoyloxytriphenylene (THA9). In mesitylene which is axial, $\eta^{LC}$ for both the aliphatic and the aromatic deuterons has the value of 0.13, while for p-xylene the two deuterons have different $\eta^{LC}$ values, 0.17 and 0.07 respectively.

Please credit this contribution to the account of Dr. Rafi Poupko.

Sincerely,

Daniella Goldfarb

Deuterium NMR spectra of p-xylene and mesitylene (4.7 wt%) in the $D_{rd}$ phase of THA9. The lower traces are experimental and were recorded at $T_c-T$=4°C and 41°C respectively. The upper traces are theoretical spectra computed with the $\eta^{LC}$ indicated above.
January 31, 1983

Dr. Bernard L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843

19F NMR with 31P Decoupling

Dear Barry,

In attempts to better understand various facets of mixed metal carbonyl-trifluorophosphine complex chemistry, we have performed a variety of NMR experiments. There are a number of reasons for studying these mixed metal carbonyl-trifluorophosphine species by NMR, either individually or as mixtures. However, the extreme similarity of PF₃ and CO as ligands toward lower valent metals is one of the complications present.

The ³¹⁵Mo NMR spectra of Mo(PF₃)ₓ(CO)₆₋ₓ species are first order, but the species are not chemically shifted from each other. Any NMR studies involving mixtures would be virtually impossible.

Simple ¹⁹F or ³¹P NMR spectra are complicated to an extreme degree by higher order couplings. For example, a triphosphine like Fe(PF₃)₃(CO)₂ which is classified as an AA'X₃ system presents an incomprehensibly broad spectrum as illustrated in Figure 1b.

The ¹⁹F decoupled ³¹P NMR spectra (the "normal" decoupling experiment) again demonstrates the extreme similarity of PF₃ and CO by yielding superimposed spectra for all species except the monophosphine for the iron complexes Fe(PF₃)ₓ(CO)₆₋ₓ.
Our most recent experiments have taken advantage of the previous simple $^{19}$F spectra which implied that there was adequate chemical shift between species if the problem of the higher order couplings could be resolved. A new variable temperature probe has been constructed for FSU's Seminole Spectrometer (3.5T) which decouples $^{31}$P (60.7MHz) while observing $^{19}$F (141.1MHz).

Figure 1 is an example of its performance on a preparative-scale, GC-separated Fe(PF$_3$)$_2$(CO)$_2$ sample. Note the small amounts of Fe(PF$_3$)$_2$(CO)$_3$, Fe(PF$_3$)$_4$(CO) and Fe(PF$_3$)$_5$ disproportionation products which are somewhat obscured in the coupled spectrum (Figure 1b).

This experimental approach will greatly aid in on-going studies of these complexes in diverse areas such as photocatalysis, stereochemical non-rigidity, and nuclear hot-atom work.

Sincerely,

Dr. Thomas Gedris
Dr. Ronald J. Clark
Dr. M. F. Menoufy
Richard C. Rosanske

Figure 1. $^{19}$F spectra, at 3.5T, for Fe(PF$_3$)$_3$(CO)$_2$ sample a) $^{31}$P decoupled and b) coupled. Note the Fe(PF$_3$)$_2$(CO)$_3$, Fe(PF$_3$)$_4$(CO) and Fe(PF$_3$)$_5$ disproportionation impurities seen clearly in a.
Prof. Barry Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dear Dr. Shapiro:


I would like to point out that the Federation of Analytical Chemistry and Spectroscopy Societies is having their Tenth Annual Meeting in Philadelphia this Fall. I will be arranging a two day NMR Spectroscopy program. At the present we are planning to have four half day symposia:

- Symposium NMR in Solids Dr. Michael T. Melchior
- Two-dimensional NMR Prof. Ian Armitage
- Multinuclear NMR Prof. George C. Levy
- Instrumentation Dr. William L. Earl

The deadline for submission of titles is April 3, 1983 and the deadline for submission of abstracts is June 15, 1983. Title submission forms can be obtained from any of the symposia chairmen, from myself at the above address or from Dr. John O. Lephardt, Philip Morris Research Center, P.O. Box 26583, Richmond, Virginia 23261 (Program Chairman).

I think that the meeting should be an excellent one and I encourage anyone interested in presenting a talk or simply attending to contact myself or the program chairman for further information.

Sincerely,

William L. Earl.

Title submission form enclosed.
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