Texas A&M University
N - M - R Newsletter

P. K. Burkert
I. and II. Order Quadrupole Effects in Solid State ¹²¹I NMR

¹⁰⁰NMR of Molybdenum Carbonyl Compounds

G. Fraenkel
Hindered Rotation in Tin Compounds; a Useful Non-Polar NMR Solvent

W. L. Earl and D. L. VanderHart
Radio Frequency Field Strengths and Rotor Impurities in Cross Polarization in Solids

M. Hájk and P. Trska
Use of Analysis of Variance for the Determination of Experimental Conditions of NMR Quantitative Measurement

S. Berger
Supercon Installation and Helium Recovery

R. S. Egan
Group Leader Spectroscopy

F. P. Miknis and D. A. Netzel
An NMR Comparison of Shale Oils Produced by the Fischer Assay and the IGT Hytort Process

M. D. Johnston, Jr.
Easily 90°-Pulses

J. J. Barieux and M. Demarcq
NMR Evidence for the Existence of P₄ S₈

G. Wagner and K. Wüthrich
Combined DQY-NOESY Connectivity Diagram for Sequential Resonance Assignments in Extended Polypeptide Chains

T. Wirthlin, R. Richarz and W. Ammann
* C * O S M * * M * C *

W. A. Thomas and J. W. Whitcombe
The Release of Serotonin (5-HT) from its Storage Complex

R. E. Block
Current vs. Field Strength Curve for Varian 15-Inch Magnet

T. Zens
New Level of 10 mm N-15 Sensitivity

K. L. Martin, H. Martineau and M. Trierweiler
Selective Population Inversion of Satellites of Satellites

K. V. Vasweda, J. T. Kaplan and
B. D. Nageswar Rao
Strong Coupling Effects in Rapidly Exchanging Weakly Coupled Spin Systems

A. Ericsson and J. Kowalewska
Internal Rotation of CH₃ and CD₃ Groups

K. Roth
Optimal Parameters in the Convolution Difference Technique

D. J. Raber
LIST of etalons

M. Brauer and B. D. Sykes
Relaxation of Protein Bound Phosphorus Nuclei

E. A. Williams and P. E. Donahue
¹⁳C NMR of Brominated Poly(phenylene oxide) (Br-PPO)

D. D. Traficante
JEOL Institute

D. J. Serdella
Equipment Needed

J. I. A. Thompson, B. Sayer, N. Hao and M. J. McGlinchey
¹⁹F-¹¹B(¹H) Spectrum of Zr(BH₄)₄

A. Briquet
GERM

M. D. Rosenberger
Positions Available - Postdoctoral Fellowship, NMR Spectroscopist/Natural Products Chemist

M. Smith, C. Rodger and A. Bain
An Accustomed Level of 10 mm C-13 Sensitivity

H. V. Riggs
Long-Range Coupling in Esters

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.

These restrictions apply equally to both the actual Newsletter participant-recipients and to all others who are allowed access to the Newsletter issues. Strict adherence to this policy is considered essential to the successful continuation of the Newsletter as an informal medium of exchange of NMR information.
Consummate care in the storage and preparation of spectroscopic samples is just as integral a part of good spectroscopic practice as running the investigation or analyzing the spectra. And consummate care, of course, begins with equipment.

Our new, expanded Wilmad line of vials, storage and septum bottles, and a broad variety of stoppers, caps, and septa help materially to simplify the handling, storage, and preparation of samples ... eliminate expensive sample loss ... and save unnecessary waste of time and money.

Wilmad vials and bottles are manufactured of top-quality borosilicate glass to prevent any pH modification of the contents. The variety of caps available match any sampling or storage need. Snap caps of polyethylene, open-top types with elastomer septa, aluminum seals with Teflon-faced septa ... whatever you need we now carry in stock.

Write or call for our new Catalog 781.

WILMAD GLASS COMPANY, INC.
World Standard In Ultra Precision Glassware
Route 40 & Oak Road • Buena, N.J. 08310 U.S.A.
Phone: (609) 697-3000 • TWX 510-687-8911
**FT NMR was never “hard,” only certain samples were.**

Now with the low cost JEOL FX60QS System

High Resolution Solid State NMR becomes routine

---

**TAMU NMR NEWSLETTER — ADVERTISERS**
- Bruker Instruments, Inc. — see p. 6
- JEOL Analytical Instruments, Inc. — see p. (i) and outside back cover
- Nicolet Magnetics Corp. — see inside back cover
- Varian Instrument Division — see p. 30
- Wilmad Glass Company, Inc. — see inside front cover

**TAMU NMR NEWSLETTER — SPONSORS**
- Abbott Laboratories
- The British Petroleum Co., Ltd. (England)
- Bruker Instruments, Inc.
- JEOL Analytical Instruments, Inc.
- Dr. R. Kosfeld, FB 5 Physikalische Chemie, University of Duisburg, D-4100 Duisburg 1, Germany
- The Lilly Research Laboratories, Eli Lilly & Co.
- The Monsanto Company
- Nicolet Magnetics Corp.
- Shell Development Company
- Unilever Research
- Union Carbide Corporation
- Varian, Analytical Instrument Division

**TAMU NMR NEWSLETTER — CONTRIBUTORS**
- E. I. DuPont DeNemours & Company
- Eastman Kodak Company
- HITACHI, Ltd.
- Intermagnetics General Corporation
- The NMR Discussion Group of the U.K.
- The Procter & Gamble Co., Miami Valley Labs
- Programmed Test Sources, Inc.
- Xerox Corp., Webster Research Center

---

| DEADLINE DATES: |
| No. 272 | 4 May 1981 |
| No. 273 | 1 June 1981 |

All Newsletter Correspondence, Etc., Should be Addressed To:
Dr. Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843 U.S.A.

**AUTHOR INDEX**

<table>
<thead>
<tr>
<th>Author</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amann, W.</td>
<td>23</td>
</tr>
<tr>
<td>Bain, A.</td>
<td>35</td>
</tr>
<tr>
<td>Barlow, A. J.</td>
<td>19</td>
</tr>
<tr>
<td>Berger, S.</td>
<td>13</td>
</tr>
<tr>
<td>Block, A. E.</td>
<td>20</td>
</tr>
<tr>
<td>Brown, M.</td>
<td>42</td>
</tr>
<tr>
<td>Brignole, A.</td>
<td>91</td>
</tr>
<tr>
<td>Brown, R.L.</td>
<td>3</td>
</tr>
<tr>
<td>Burdick, P. K.</td>
<td>1</td>
</tr>
<tr>
<td>DeMar, R. M.</td>
<td>19</td>
</tr>
<tr>
<td>Donahue, P. E.</td>
<td>45</td>
</tr>
<tr>
<td>Earl, W.</td>
<td></td>
</tr>
<tr>
<td>Egan, R. J.</td>
<td>14</td>
</tr>
<tr>
<td>Ericsson, A.</td>
<td>37</td>
</tr>
<tr>
<td>Franke, G.</td>
<td>5</td>
</tr>
<tr>
<td>Hajna, M.</td>
<td>49</td>
</tr>
<tr>
<td>Hsu, M.</td>
<td>49</td>
</tr>
<tr>
<td>Kaplan, J. L.</td>
<td>35</td>
</tr>
<tr>
<td>Kowalski, J.</td>
<td>37</td>
</tr>
<tr>
<td>Martin, M. L.</td>
<td>21</td>
</tr>
<tr>
<td>Martindale, H.</td>
<td>33</td>
</tr>
<tr>
<td>Mester, A. F.</td>
<td>3</td>
</tr>
<tr>
<td>McIlhenny, R. J.</td>
<td>49</td>
</tr>
<tr>
<td>McNeil, F. T.</td>
<td>15</td>
</tr>
<tr>
<td>Nasehra, N. K.</td>
<td>35</td>
</tr>
<tr>
<td>Netzel, D. A.</td>
<td>15</td>
</tr>
<tr>
<td>O'Connell, N. J.</td>
<td>3</td>
</tr>
<tr>
<td>Raber, J. J.</td>
<td>41</td>
</tr>
<tr>
<td>Richard, R.</td>
<td>23</td>
</tr>
<tr>
<td>Riggs, R. Y.</td>
<td>57</td>
</tr>
<tr>
<td>Rodgers, E.</td>
<td>36</td>
</tr>
<tr>
<td>Rosenberger, K. D.</td>
<td>54</td>
</tr>
<tr>
<td>Ruhl, E.</td>
<td>40</td>
</tr>
<tr>
<td>Saffier, D. V.</td>
<td>48</td>
</tr>
<tr>
<td>Sager, B.</td>
<td>49</td>
</tr>
<tr>
<td>Satterthwaite, M.</td>
<td>33</td>
</tr>
<tr>
<td>Smith, B.</td>
<td>45</td>
</tr>
<tr>
<td>Snyder, B. D.</td>
<td>42</td>
</tr>
<tr>
<td>Thomas, W. A.</td>
<td>26</td>
</tr>
<tr>
<td>Thompson, J. I. A.</td>
<td>49</td>
</tr>
<tr>
<td>Traficante, D. D.</td>
<td>47</td>
</tr>
<tr>
<td>Truettner, M.</td>
<td>33</td>
</tr>
<tr>
<td>Tsuchiya, T.</td>
<td>11</td>
</tr>
<tr>
<td>Trzasko, P.</td>
<td>31</td>
</tr>
<tr>
<td>Vagena, K. T.</td>
<td>25</td>
</tr>
<tr>
<td>Wagner, G.</td>
<td>51</td>
</tr>
<tr>
<td>Weld, A. G.</td>
<td>3</td>
</tr>
<tr>
<td>Whitehead, W. D.</td>
<td>25</td>
</tr>
<tr>
<td>Williams, E. A.</td>
<td>45</td>
</tr>
<tr>
<td>Wirth, J. C.</td>
<td>47</td>
</tr>
<tr>
<td>Zemski, T.</td>
<td>31</td>
</tr>
</tbody>
</table>

---

FTNMR was never "hard," only certain samples were.

Now with the low cost JEOL FX60QS System

High Resolution Solid State NMR becomes routine

---

Write for a copy of:
"Your High Resolution Solid State
NMR Problems and their Solutions..."

235 Birchwood Avenue, Cranford, NJ 07016
201-272-8820
Dear Professor Shapiro:

Experimentally it is not easy to measure pure quadrupole resonance frequencies in the region \( \nu < 10 \text{ MHz} \). We had a lot of such problems when we tried to find the \(^{127}\text{I}\) quadrupole coupling constants of some periodates, structured in the scheelite-, pseudoscheelite- or \((\text{cation} > \text{anion})\)-type. In this situation it was very helpful to use the fact that the \(^{127}\text{I}\) NMR frequency of 40.02 MHz at the field \( H_0 = 4.698 \text{Tesla} \) of our Bruker FT-NMR CXP 200 allows to fulfill the condition \( |\epsilon^2 Q / h| \ll |\mu_\text{NMR} H_0| \) for the observation of I. order effects (satellites) or II. order effects (splitting of the \(+1/2 \leftrightarrow -1/2\) transition) in \(^{127}\text{I}\) NMR powder spectra for the above mentioned low NQR coupling constants \( \epsilon^2 Q / h \). Evidently, sufficiently high magnetic fields give a possibility to measure quadrupole coupling constants by NMR spectroscopy to orders of magnitudes, which were accessible until now only by pure NQR spectroscopy.

Fig. 1 and 2 show as an example of measured I. and II. order effects the completely unusual positive temperature dependence of the \(^{127}\text{I}\) quadrupole coupling constants in \(\text{NH}_4\text{IO}_4\). The values in the region \( T > 273 \) K are identical with those measured by pure NQR spectroscopy. Great care has to be taken in this region because \(\text{NH}_4\text{IO}_4\) tends to decompose explosively into \(\text{NH}_3, \text{O}_2, \text{H}_2, \text{I}_2\) and \(\text{H}_2\text{O}\).

This unusual and strong positive temperature dependence resembles that of the \(^{185}\text{Re}\) and \(^{187}\text{Re}\) quadrupole coupling constants of the analogue \(\text{NH}_4\text{ReO}_4\), we measured earlier \(^1\). Both are not well understood until now \(^{1,4}\).

Another example is demonstrated in fig. 3, where in a small region about \( T \approx 296 \) K the large II. order quadrupole splitting...
disappears, indicating a phase transition in the pseudoscheelite structured CsIO₄.

These two and other examples show that measuring quadrupole effects is another area which makes highest magnetic fields desirable.

Please credit this letter to the subscription of Prof. H.P.Fritz.

Sincerely,

P.K. Burkert

1) P.K. Burkert and M.F. Eckel, Z. Naturforsch. 28b, 379 (1973)

Fig.1. ¹²⁷I NMR signals of NH₄IO₄ with I. and II. order quadrupole effects for T>145 K

Fig.2. Anomalous temperature dependence of the ¹²⁷I quadrupole coupling constant in NH₄IO₄

Fig.3. ¹²⁷I NMR signals of CsIO₄ with phase transition
Dear Barry,

We have been using our specifically tuned (6.5 MHz) $^{95}$Mo probe for our JEOL PFT-100 for about a year now and have gained considerable experience searching for these sometimes elusive signals.

Natural abundance $^{95}$Mo (15.8%; $I=5$) NMR gives signals with half widths ranging from a few Hz for MoO$_4^{2-}$ to several hundreds of Hz for the polyoxometallates such as [Mo$_7$O$_{24}$]$^{6-}$. Many systems however have line widths in the 10 Hz range, and hence spectra can be obtained in a reasonable time at useful concentrations. The chemical shift range is large (-22000 to +35000) which helps the identification of $^{95}$Mo signals from similar compounds. We use as our standard aqueous 2M Na$_2$MoO$_4$ at pH 11, which is stable, gives a narrow line, and can be observed in a single pulse.

Two spectra are presented to illustrate some of the applications of $^{95}$Mo NMR. (i) The quartet as the result of $^{95}$Mo-$^{31}$P coupling allows the ready identification of this coupling constant in Mo(CO)$_3$[P(OMe)$_3$] whereas identification of this coupling constant from the $^{31}$P spectra is complicated by coupling of phosphorus to $^{95}$Mo ($I=5$) and $^{97}$Mo ($I=5/2$). (ii) The $^{95}$Mo spectrum of a mixture of a number of different substituents in the aromatic ring shows a separate signal from each compound. The identification of the components in such a mixture is trivial from the $^{95}$Mo spectrum compared to the complexity expected for the $^{13}$C or $^1$H spectrum.

Please credit this contribution to the Monash University group (Dr. M. Heffernan) who are kind enough to share the newsletter with us.

Yours sincerely,

R.T.C. BROWNLEE
M.J. O'CONNOR
A.G. WEDD
A.F. MASTERS
March 11, 1981

Dear Barry:

In response to your note here is some news from Columbus.

Hindered rotation in tin compounds: We have been interested in highly substituted allyllithium compounds which we generate by cleaving the corresponding tin compounds with butyllithium. At least one of these tin compounds, \( \Phi_3\text{SnCH}_2\text{t} \), \( \Phi_3\text{SnLi} \), exhibits time-dependent NMR behavior which we ascribe to very slow interconversion among rotamers. Compound \( \Phi_3\text{SnCH}_2\text{t} \) is purified by distillation giving a clear liquid. This analysis correctly in every way except that the sample, in CDCl\(_3\), immediately on isolation, gives rise to two \( ^{13}\text{C} \) NMR spectra, in ratio 3/1, with very similar shifts. Over about two days at room temperature (25°) the lower intensity spectrum disappears. After this no amount of cooling or heating (at different rates) changes the spectrum. We can only imagine that the formation reaction generates some unstable conformer(s) which convert slowly into the most stable one by rotation about the \( \text{CH}_2\text{C}= \) single bond. Steric hindrance keeps this slow. The thermodynamically unstable conformer(s) could give \( \Phi_3\text{Sn} \) gauche to \( \text{t}-\text{butyl} \); in the stable form these groups would be further apart. Similar explanations have been invoked for the IR data on organotin compounds. ¹ ²

A useful non-polar NMR solvent: A non-polar \( ^{13}\text{C} \) NMR solvent with a window in the hydrocarbon region is toluene-\( \text{d}_5\)-\( \alpha\)-C\(_{12}\). Since he needed a few grams of this stuff, Dr. Rainer Stumpe, who spent a year in our lab, made it himself. Interested readers should apply for more information.

The price of isotopically enriched compounds continues to increase faster than most people's grants so it is incumbent on those of us who need these materials to develop cheap, fast, easily carried out syntheses and to share the information.

Best wishes.

Yours sincerely,

Gideon Fraenkel
Professor, Ohio State University

Superior sensitivity is only one of the features we put into our Supercons...

...but it takes a great deal more to qualify for excellence.

Bruker continuously succeeds in building supercons with performance characteristics and features that exceed those of any other commercially available system. Here are just a few:

**A Data System providing**
- true multitasking including simultaneous multiple processing
- 24-bit word length for highest dynamic range
- virtual memory capability for acquisition and processing of up to 512 K data
- high-density disc systems from 24 to 95 megabyte storage capacity

**Optional Satellite Terminal** for simultaneous processing, plotting and display

**A Pulse Programmer of unparalleled flexibility and operator simplicity**

**Correlation NMR capability**
- A range of Probeheads
  - broadband observe — broadband decouple
  - dual-frequency computer-switchable — triple resonance — CIDNP — and many others.
- A wide selection of Magnet Systems from 1.9 to 11.7 T (80 — 500 MHz ¹H frequencies)
- 300 KHz ADC for spectral widths up to 150 KHz

The broad range of Bruker high-resolution high-field and high-power NMR systems is illustrated in the selection chart. For a hands-on demo or detailed documentation on the right system for you, simply call or write Bruker Instruments, Inc., Manning Park, Billerica, MA 01821, (617) 667-9580.

In high-field NMR there is simply no alternative.
More evidence:

62.8 MHz $^{13}$C lineshape:
80% CH$_4$, 10 mm tube;
linewidth at 0.55% peak height: 2.24 Hz

62.8 MHz $^{13}$C sensitivity:
single pulse 10% ETB,
10 mm tube; S/N > 200:1

(quod erat demonstrandum)
Radio Frequency Field Strengths and Rotor Impurities in Cross Polarization in Solids

Normal spin locked cross polarization NMR in solids has the advantage of being rather forgiving of the exact amplitude, time and phase of the pulses. Signal to noise may suffer, but adequate spectra can usually be obtained. There are experiments where quantitation is desired and the Hartmann-Hahn condition must be carefully met and a knowledge of the amplitude of the decoupling field is desired. High Q probes and non-linear amplifiers usually give pulse envelopes which look something like:

Since estimation of $\gamma B_1$ from the time of a 180° pulse (~6-15µs) is in the most nonlinear portion of the rf response it is a highly inaccurate means of determining the decoupling field which exists say 2-100ms later.

We have been using a spin tickling technique which gets around this problem. We use a liquid sample of $^{13}$C enriched CH$_3$OH sealed in glass and inserted in a rotor. Using a very low level coherent frequency decoupling we vary the proton frequency to find the exact proton resonance. Then we offset the decoupler by 60 kHz and perform a "normal high resolution experiment" with high powered proton decoupling. i.e.:

```
  13C
    \[ \text{tickling} \]
  1H
```

with a low duty cycle. The Fourier transform is a quartet, the splitting of which is proportional to $\gamma B_1$. Martin, Delpuech and Martin$^2$ have described off resonance calibration of rf fields but in our particular case, the equation of interest is:

$$J_r = [(\Delta v + J/2)^2 + (\gamma B_1)^2]^{1/2} - [(\Delta v - J/2)^2 + (\gamma B_1)^2]^{1/2}$$
where $\delta$ is the decoupler offset (60 kHz in our case), $J$ is the $^1$H-$^13$C splitting in the absence of decoupling (142 Hz for methanol) and $J'$ is the residual splitting. In Figure 1, we have plotted the channel separation for a 60 kHz offset, 100 $\mu$s dwell, 8K Fourier transform experiment with methanol and the rf amplitude can be easily read off the graph. An estimate of $B_1$ homogeneity over the sample can be made using the same equation and measuring the linewidth difference between the tickling experiment and high power on-resonance decoupling.

To measure $\gamma B_1$ for the carbons, the decoupler frequency is reset, the methanol is replaced by a rotor full of adamantane and the $^13$C rf level is adjusted for a maximum in the cross polarization signal using a contact time $\leq$ 1 ms. The relatively small C-H dipolar coupling in adamantane make it a good choice for setting the Hartmann-Hahn condition. The short cross polarization contact time is needed for an accurate match of the carbon and proton fields. We can see intensity differences in the amplitude of the adamantane FID with a 0.2 dB mismatch between the carbon and proton fields.

It is worth mentioning that we find it necessary to retune our probe matching circuits both when changing samples and when moving the decoupler frequency by 60 kHz. Clearly probe efficiency and rf field strengths are a function of the probe tuning and impedance match.

As an aside we would also like to reiterate a problem which was mentioned by de Wit et. al. (TAMU Newsletter, Sep. 1980), impurities in rotor materials. On our 1.4 T magic angle sample spinning instrument we use polychlorotrifluoroethylene rotors and have seen no cross polarization peaks due to impurities. On our 4.7 T instrument we have been using deuterated PMMA rotors which have enough protons to give a cross polarization signal and polyoxymethylene rotors which have impurity peaks and side bands as seen in Figure 2. These can interfere with detection of weak resonances.

Sincerely,

William L. Earl
Center for Fire Research

David L. VanderHart
Center for Materials Science


FIGURE 2
CPMAS spectrum of polyoxymethylene (Delrin) at 4.7 T.
ssb=spinning sideband
I = Impurity
The impurity peaks are each approximately 2% of the total intensity.
Dear Prof. Shapiro,

Our second contribution to TAMU is devoted to:

Use of Analysis of Variance for the Determination of Experimental Conditions of NMR Quantitative Measurement

The value of aromaticity \( f_a \) - the ratio of aromatic carbon atoms to all carbons in measured sample is an interesting characteristics of the most petrochemical products. The conditions of the measurement of quantitative \(^{13}\text{C}\) NMR spectra can be evaluated theoretically if \( T_1 \) and NOE are known.\(^1\) The analysis of variance can be used for the determination of reproducibility of integral intensities and by this way for checking of the experimental conditions. The Table 1 shows the results of analysis of variance of measurement of \( f_a \) of the one sample of crude oil. The parameter \( C_1 \) is a parameter characterizing experimental method of measurement (\( C_1 \) - gated decoupling with delay time 10 s, \( C_2 \) and \( C_3 \) - broad band decoupling with 10 s and 0.6 s delay times, resp.), \( B \) is a parameter of three independent measurements and parameter \( A \) means the three independent integration for each measurement were performed (replicative factor).

If the calculated F criterion is greater than the theoretical one, the difference between compared methods is signi-
ificant. It follows from the Table, that significant differences exist for all ones or \( C_1 \) and \( C_2 \) - methods, but does not exist for \( C_2 \) and \( C_3 \) - methods.

**Table 1.** Calculated and theoretical (in parentheses) \( F \) criteria

<table>
<thead>
<tr>
<th>Comparison of: ( C_1 ),( C_2 ),( C_3 )</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( C_2 ),( C_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor A</td>
<td>1.0039</td>
<td>1.0039</td>
<td>1.0039</td>
</tr>
<tr>
<td>B</td>
<td>0.3470(3.555)</td>
<td>0.5617(3.885)</td>
<td>1.902(3.885)</td>
</tr>
<tr>
<td>C</td>
<td>33.8671(3.555)</td>
<td>47.9316(4.451)</td>
<td>0.015(4.451)</td>
</tr>
</tbody>
</table>

The result indicate the existing influence of NOE on the measurement of \( f_a \). The difference among independent measurements \( (B_1 , B_2 , B_3) \) is in the range of random errors. These statistical results can provide interesting information, even though the measurement requires a lot of time. We performed some of these statistical experiments at the end of last year during the installation of our new FT NMR spectrometer Tesla operating for \( ^{13}\text{C} \) at 25 MHz.

Yours sincerely

Milan Hájek
Petr Traska
Prague Institute of Chemical Technology

**Literature**

2. System IBM 360, Scientific Subroutine Package
Dear Professor Shapiro

Supercon Installation and Helium Recovery

At last the superconducting age has come to Marburg University. We have recently installed a Bruker WH-400 spectrometer and wish to communicate some installation details which might be useful for other people who are planning to set up a supercon.

A central helium liquification system was already present in our institute with a connection to the laboratory where the supercon was to be installed. Therefore it seemed reasonable to connect the magnet to the recovery line and save the annual helium costs of about DM 4000. However, we measured some pressure oscillations in the recovery line which were caused by the activities of other helium users. We decided, therefore, to connect the magnet to a balloon of 2 m³, which seemed to be a good compromise between the helium diffusion rate through the balloon surface, the helium evaporation rate of the magnet, available laboratory space and cost of the balloon. The content of the balloon is transferred to the recovery line 2-3 times a week using a lab pump. This arrangement has, in our opinion, the advantage of being completely independent from all events or mishaps in the central helium liquifier system.
The Bruker magnet power supply B-CN-70 only has the positions "fast" and "slow" for the helium level measurement. It is said that removing the helium level probe would reduce the helium evaporation. We found it very inconvenient always having to either remove the rod or disconnect the cable after measuring the helium content. We therefore disconnected the 18 megohm-resistance on print 2 (Dwg. No. 4-3S-3308) in the power supply, which changes the position "slow" to "off". With this minor modification our magnet (Oxford coil and dewar) has a weekly evaporation rate of 12% with both cable and helium level probe always installed.

Besides some very minor starting problems, working with this 400 Mhz instrument is an extreme pleasure.

Sincerely yours

Dr. S. Berger

McNEIL PHARMACEUTICAL
SPRING HOUSE, PA 19477 (215) 628-5000

GROUP LEADER SPECTROSCOPY

McNeil Pharmaceutical is seeking an experienced NMR Spectroscopist to head the Spectroscopy Group of the Research Division.

The primary responsibilities of this senior staff position will be to supervise the provision of all spectroscopic service (IR, UV, NMR, MS), to conduct and participate in research projects with members of the Chemical Research and Biological Research Departments primarily involving applications of NMR spectroscopy, to maintain or supervise the maintenance of all spectroscopic instrumentation, and to manage and administer the other members of the spectroscopy group.

The successful candidate will possess a Ph.D. degree, have a strong spectroscopic background with emphasis on NMR (experience in biological applications of NMR is preferred), have at least five (5) years experience, be a general instrumentalist with maintenance experience, and be a good communicator with proven management abilities.

If interested, you may contact Richard S. Egan, Ph.D. at (215) 628-5508.
March 6, 1981

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

SUBJECT: An NMR Comparison of Shale Oils Produced by the Fischer Assay and the IGT Hytort Process

Dear Barry:

As you probably know, there is becoming an increased interest in the development of synthetic liquid fuels to replace or supplement the ever dwindling supplies of petroleum. Liquid fuels from oil shales represent an alternative to this problem. The major interest in oil shale development in the United States thus far, has focused on the oil shales of the Green River Formation in Colorado, Utah and Wyoming. However, a substantial portion (nearly 250,000 square miles) of the Eastern United States is underlain by the Devonian Black Shales, and in principle, represents a sizeable potential resource. These shales, however, yield less than half as much liquids upon heating as do the Green River Formation oil shales, because of the lesser hydrogen contents of the Devonian shales. Therefore, processes to extract liquids or improve recovery ratios from the Devonian shales must necessarily deal with recovery techniques for hydrogen deficient materials. One such candidate process is the Institute of Gas Technologies Hytort process\(^1\), which retorts oil shale under hydrogen pressure with the dramatic result that oil yields of Devonian shales are increased 2.5 times over those obtained by the standard Fischer assay. Characterization of the materials that are produced by the IGT process would be beneficial toward a) assessing the quality of the product oils, b) understanding the retort process and c) providing information for optimizing the process.

In this letter we report some preliminary results of our NMR studies of shale oils produced by the IGT Hytort process and shale oils produced by the Fischer assay.

Previous solid state \(^{13}\text{C}\) NMR measurements\(^2\) on raw oil shales have shown that the kerogen in Kentucky oil shales is much more aromatic than Colorado oil shales; hence significant differences in the amount and type of organic material converted to liquids is expected. Thus, it is not surprising that
the carbon distribution and composition of shale oils from the two types of materials are different. The major differences between the two oils produced during Fischer assay, as shown by the spectra, are: 1) the greater carbon aromaticity of the Kentucky shale oil and 2) the higher degree of branched alkanes and/or short chain length aromatic substituents in the Kentucky shale oil. The aromatic region of the Kentucky oil shale shows a more asymmetric pattern in the aromatic region, which is probably due to a larger number of substituted aromatic carbons in this shale oil. An NMR comparison of the liquids derived from the Fischer assay and Hytort processes should reveal some of the differences attributable to the hydrogen. The $^{13}$C spectra of Fischer assay and Hytort oils from Colorado and Kentucky are shown in Figure 1(a-d).

The $^{13}$C NMR spectra of the Kentucky - Fischer assay and Hytort shale oils are somewhat more revealing than the analogous ones for the Colorado shale oil. The major difference is the reduction in the olefins from the Hytort process. Whether retorting these materials in the presence of $H_2$ prevents olefins from forming, or saturates them once formed, is not clear at this time.

We are in the process of applying NMR to investigate this aspect of oil shale retorting.

1. Feldkirchner, H. L. and Janka, J. C. Proc. of the IGT Symposium on Synthetic Fuels from Oil Shale Dec 3-6, 1979, Atlanta, GA., p. 489.

Sincerely,

[Signatures]

F. P. Miknis

D. A. Netzel
Carbon-13 NMR

**Colorado Shale Oil**
Fischer Assay

![Graph](a)

200 ppm

**IGT Hytort Process**

![Graph](b)

200 ppm

---

**Kentucky Sunbury Shale Oil**
Fischer Assay

![Graph](c)

200 ppm

**IGT Hytort Process**

![Graph](d)

200 ppm
Getting 90°-pulse widths is a perennial problem facing NMR spectroscopists. This is especially annoying when one is doing relaxation experiments of samples with widely varying dielectric constants. In such cases, the pulse width can alter drastically.

The usual methods of getting pulse widths are time-consuming and tedious, at best. For instance, observing spectra intensities (after FT) for 90° pulses necessitates waiting enough time between pulses for recovery to equilibrium. Trying to null out the FID with a 180° pulse is difficult, at best, with dilute samples. Finally, the phase-error detection method has the same problem at the first-mentioned method, namely, long waits between pulses.

An alternate method I stumbled on recently while working hard on my new FX-90Q was to find the null point in the FT spectrum after applying a rapid train of 360° pulses. What is done is to apply pulses at the rate of one per second, or so. When you are near to the true 360° pulse, the spectrum nulls out. Close to the correct width gives spectra of large amplitude (but of opposite sign in intensity); as the width goes further from the correct 360° value, you encounter saturation. Thus, the method is easiest to apply when you are close to the desired pulse width; this is not true with other methods.

If the pulse width parameter can be stacked, as is the case with the FX90Q computer system, this method is very easy to do. You can find the correct width in ten minutes or so by merely stacking spectra during a coffee break (or, in Florida, an orange juice break). The only time-consuming part would be to get a preliminary phase-corrected spectrum with a small pulse width. After getting the 360° pulse, you need only divide by four to get the 90° pulse (if anyone needs help on this part, it's too late). It is assumed, of course, that your pulse generator is good enough to have the 360° pulse exactly four times as long as the 90° pulse; if this is not true, it's back to the drawing board.

Sincerely yours,

Milton D. Johnston, Jr.
Associate Professor of Chemistry

SUGGESTED TITLE: 90°-pulses (easily)
Dear Professor Shapiro,

NMR Evidence for the Existence of $P_4S_8$

With this contribution we would like to open a subscription to the Newsletter.

We have gained evidence by means of the FT $^3$P NMR (80.76 MHz) that the primary product of the desulfuration of $P_4S_9$ by triphenylphosphine is apparently $P_4S_8$, a previously unreported phosphorus sulfide bearing the same adamantoid cage as $P_4S_9$ and $P_4S_{10}$ (Fig 1).

When a 2.5 g/l $P_4S_9$ solution in $CS_2$ was allowed to react at r.t. with an equivalent amount of $PH_3P$, the following signals were observed after 5 minutes ($\delta$ are downfield from external $H_3PO_4$):

- the typical $AB_3$ multiplet of $P_4S_9$
- two equivalent singlets $\delta$ 84.6 and 110.9 ppm assigned to $P_4S_7$ with its unique zero $\delta_{PSP}$
- two equivalent triplets $\delta$ 13.4 and 135.4 ppm, $\delta_{J}$=82.8 Hz, indicative of an $A_2X_2$ system and consistent with the assumed geometry of $P_4S_8$
- two non attributed small singlets $\delta$ 162 and 167.2 ppm
- the signal of $PH_3PS$, $\delta$ 41.9 ppm

The signals of $P_4S_8$ disappear completely after a week, owing probably to its dissociation to $P_4S_7$ and $P_4S_9$.

A more detailed report will soon be published.

J.J. BARIEUX
M. DEMARCO
\[ \text{Fig. 1} \]
\[ \text{P}_4\text{S}_9 + \Phi_3\text{P} \quad (80.76 \text{ MHz}) \]

\text{Conditions}
- PD 50 \mu s, PD 10 \times 10^\text{6} K
- Freq 12 kHz
- Obs 3,3,8 kHz
- 550 scans

\[ \text{P}_4\text{S}_8 \quad \text{P}_3\text{S}_7 \quad \Phi_3\text{P-S} \quad \text{P}_4\text{S}_9 \]

\[ \delta 155.4 \quad 44.9 \quad 44.9 \quad 134 \]

\[ J = 82.5 \text{ Hz} \] (folded peaks)
Combined COSY-NOESY Connectivity Diagram for Sequential Resonance Assignments in Extended Polypeptide Chains.

Dear Barry,

The use of two-dimensional correlated spectroscopy (COSY) for delineation of J-coupling connectivities and 2D NOE spectroscopy (NOESY) for studies of cross relaxation networks in proteins was recently described. In Fig. 1 we present a combined plot of COSY and NOESY data which was found to be particularly suitable for obtaining sequential resonance assignments in extended polypeptide chains. The plot is explained in the figure caption. The resonance assignments are based on the observation that in extended polypeptide chains the α-proton of residue i is the proton nearest to the amide proton of residue (i+1).

Two extensions of the experiment in Fig. 1 lead to additional information. Firstly, by analysis of the COSY peaks corresponding to amino acid side chain protons the nature of the amino acids assigned by Fig. 1 can be determined. As a consequence it is usually possible to locate the sequentially assigned residues in the amino acid sequence. Secondly, the experiment can be performed in H2O rather than in D2O so that its use is not restricted to polypeptide segments with slowly exchanging amide protons. In BPTI, individual assignments for a continuous segment of 20 amino acid residues were thus obtained.

Sincerely yours,

G. Wagner
K. Wüthrich


Studies of J-Connectivities and Selective $^1H-^1H$ Overhauser Effects in $H_2O$ Solutions of Biological Macromolecules by Two-Dimensional NMR Experiments.


Individual Assignments of Amide Proton Resonances in the Proton NMR Spectrum of the Basic Pancreatic Trypsin Inhibitor.

![Combined COSY-NOESY connectivity diagram for sequential resonance assignments in polypeptide chains.](image)

Fig. 1 Combined COSY-NOESY connectivity diagram for sequential resonance assignments in polypeptide chains. In this contour plot the upper left triangle comes from a NOESY spectrum of a D$_2$O solution of BPTI (basic pancreatic trypsin inhibitor, a small protein with 58 amino acid residues and a molecular weight of 6500) recorded with a mixing time of 100msec and the lower right triangle from a COSY spectrum of BPTI recorded from the same sample under identical conditions. The combination of the sequential J- and NOE-connectivities between the backbone $\alpha$ and amide protons of residues 24 to 19 indicated by solid lines has the shape of a spiral ("$\beta$-snail"). A $\beta$-snail is typical for extended polypeptide chains such as the individual strands in $\beta$-sheets. ⁴
Dear Dr. Shapiro:

* C * O * S * M * I * C *

For quite a while now we have been intrigued by the thought that Ray Freeman's and Ad Bax' "INADEQUATE" pulse sequence might in fact be quite ADEQUATE for directly arriving at the full structure (the carbon backbone, to be precise) of an unknown via an analysis of the satellites representing one-bond carbon-carbon couplings.

Our program "COSMIC" ("Computer-Originated Structure Models from "Inadequate"-derived Coupling data"), written in PASCAL for our XL-200 data system, analyses the $^{13}C$ satellite frequencies taken from an "INADEQUATE" spectrum plus the $^{13}C$ chemical shifts from a conventional noise-decoupled spectrum, establishes all pairs of matching satellites, checks for strong coupling effects, determines secondary isotope shifts and prints a list of all carbon-carbon bonds found. Reconstructing the connectivity graph and filling in the heteroatoms (if any) is all that is left for the chemist to do.

In our most challenging case tried so far, the computer gave us the full carbon connectivity matrix and hence the full two-dimensional structure of 5a-androstan-3β-ol. (With the preliminary and unrefined version of COSMIC we are presently using, some operator intervention is required to help the computer with ambiguities in cases as complex as this one, where COSMIC has to evaluate close to $10^6$ possible satellite combinations).

As a side benefit, we have measured lots of carbon-carbon coupling constants and isotope shifts that will eventually provide a wealth of additional structural information. We will just have to learn to interpret these data.

A full paper describing the details of COSMIC and discussing applications is in preparation.

Sincerely yours,

Toni Wirthlin
Reinhard Richarz
Willi Ammann
Fig. 1. Proton decoupled $^{13}$C NMR spectra (50.3 MHz) of 5a-androstanol. Saturated solution in CDC$_3$. 10 mm probe, spectral width 4000 Hz, acquisition time 2 sec, digital resolution 0.25 Hz, temperature 25°C.

Bottom trace: Conventional $^{13}$C spectrum, 6 (ppm) from TMS.
Top trace: "INADEQUATE" spectrum. The experiment was optimized for JCC = 34 Hz, N=0. 7140 transients were completed.

Sample courtesy Dr. Machinek, Göttingen (BRD).

C(10) and C(8)
(Signals no. 8 and no. 9)

Fig. 2. Expansion of partial "INADEQUATE" spectrum from Fig. 1, showing overlapping satellites of carbon 8 and 10. Assignments shown reflect the result of the "COSMIC" analysis.

Fig. 3. Data input (only partially represented, corresponding to partial spectrum shown in Fig. 2) and result of the "COSMIC" analysis. The signal numbering system (from low field to high field in the conventional $^{13}$C spectrum) has to be differentiated clearly from the standard numbering and nomenclature.
19 March 1981

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

The Release of Serotonin (5-HT) from its Storage Complex

Roché Products Limited - PO Box 8 - Welwyn Garden City - Hertfordshire AL7 4AY
Telephone Welwyn Garden 28128 Telex 262098 ROCHEW

Dear Barry

After our first "final ultimatum" from your office in some fifteen years, we hope that this contribution is acceptable, to forestall expulsion from the Newsletter.

Previous studies on tricyclic antidepressants such as imipramine (I) have demonstrated that they form stable complexes in solution with biogenic amines such as serotonin (5-HT) (IV). The formation of these complexes is characterised by large, upfield shifts in the $^1H$ n.m.r. spectrum, indicating that the complex is formed between the aromatic ring of the 5-HT and the side chain NHMe$_2$ group of the antidepressant. It is known from other studies that adenosine triphosphate (ATP) (V) forms strong complexes with 5-HT$^2$.

These studies may have some significance in the mechanism of action of these drugs. While it is a commonly held view that the action of the tricyclics is to block the re-uptake of 5-HT at the brain synapse, the alternative theory that 5-HT is held in a storage form with ATP at the presynaptic vesicle is well supported.

Further experiments were carried out with 1:1 complexes of ATP:5-HT (0.1M) in aqueous solution. Addition of a tricyclic antidepressant to this solution caused a shift of the 5-HT resonances to low field, particularly the ring protons.

Registered office at Broadwater Road Welwyn Garden City Hertfordshire Registered number 100674 London
We interpret this as reflecting the release of 5-HT from its complex. Similar observations were made for each of three different tricyclic antidepressants (I), (II) and (III), measuring the shifts for H-2 and H-6 of the 5-HT ring (Figure). It appears that in addition to the well-known inhibition of re-uptake it is possible that tricyclic antidepressants may also act by triggering the release of 5-HT from storage vesicles to the presynaptic cleft.

![Chemical structures](image)

(I) \( R = H \)  
(II) \( R = Cl \)

With best wishes.

Sincerely,

Dr W A Thomas and I W A Whitcombe  
Physical Methods Department

Figure: Plot of shift (Δδ) of H6 and H2 protons of 5-HT on addition of tricyclic antidepressant (I), (II) (III) to a 1:1 ATP/5-HT complex.
Varian’s new Zens Probes double NMR sensitivity

Varian’s new high-sensitivity probes, available in 10-mm or 16-mm sample sizes and in the frequency range from $^{14}\text{N}$ through $^{31}\text{P}$, provide double the sensitivity of any other commercial NMR system at 200 MHz.

This superior sensitivity of the XL-200 allows you in just a few hours to complete experiments that would previously have taken overnight.

Get all the facts.
For detailed information on the unique capabilities of the XL-200 and the new high-sensitivity Zens Probes, contact your nearest Varian Magnetics Sales Specialist or the Palo Alto Magnetics Product Team.

Research Magnetics Sales Specialists
East 201-822-3700
          301-772-3663
Midwest 216-281-8035
         312-825-7772
South 713-783-1800
        404-855-1392
West 415-968-8141
     Ext. 2196
        213-927-3415
           303-425-0413

Research Magnetics Products Team
Palo Alto 415-493-4000
         Ext. 3047
Cholesteryl Acetate 0.020 M
50.3 MHz 13C
200 Transients

13C Sensitivity Test: 0.02 molar cholesteryl acetate in a 16 mm tube, 200 transients.

Single Transient
Proton-Decoupled

20.3 MHz
XL-200

15N Sensitivity Test: 90% Formamide in dms-o-d6, 10 mm 20-81 MHz broadband probe. Upper trace: single-transient (with NOE) proton-decoupled. Lower trace: eight transients, coupled (with NOE) 8-second acquisition time, 20-second delay time.

15N Sensitivity Test: 90% Formamide in dmso-d6, 10 mm tube, 200 transients.
March 22, 1981

Dear Professor Shapiro:

Current vs. Field Strength Curve For Varian 15-Inch Magnet

We have run experiments on a number of nuclei at field strengths from 3 to 23.5 kilogauss using a Varian low impedance 15-inch magnet. Since there are a number of similar magnets in use with various consoles such as the Varian XL-100-15, Nicolet TT-23, Bruker SXP, and Varian HA-100D-15 we thought that this curve might be of interest to other readers. It was determined empirically by observing the resonances of eleven different nuclei at 13.56 MHz plus protons at 100 MHz. The power supply output values are expected to be similar from one system to another, but the relative coarse current settings will likely be shifted from one system to another because of resistor values and tolerances being different.

Sincerely,

Ronald E. Block
Associate Scientist

A non-profit institution for medical research and education supported by tax exempt contributions
An equal opportunity employer
March 13, 1981

Dr. Barry L. Shapiro  
Editor, TAMU NMR Newsletter  
Department of Chemistry  
Texas A & M University  
College Station, TX 77848  

"New Level of 10 mm $^{15}$N Sensitivity"

Dear Barry:

Nitrogen NMR of the spin-1/2 variety usually requires large sample tubes and sufficient sample material to obtain natural abundance spectral information. In order to reduce run times and conserve precious sample material, we have developed a 10 mm fixed frequency $^{15}$N probe which makes natural abundance $^{15}$N studies routine. Figure 1 illustrates the probe's performance on the standard 90% Formamide sensitivity test. Here the decoupled spectrum represents one 90° pulse with NOE. The coupled spectrum is the accumulation of 8 transients with NOE. These results are about a factor of two better than the results recently reported by Jakobsen, Daugaard and Ellis for an 18 mm fixed frequency probe (TAMU 269-22). Figure 2a demonstrates the probe performance on 0.10 M (114 mg/ml) Gramicidin-S using 90° pulses and a 2 sec repetition rate (total run time 4.0 hours). Figure 2b shows the spectrum obtained on the above sample in 10 minutes using refocused INEPT. Figure 2c represents an overnight run (15.1 hours) on 0.010 M Gramicidin-S (11.4 mg/ml) using the refocused INEPT pulse sequence.

Sincerely yours,

Toby Zens

Please credit to Howard Hill's account.

/bry  
Enclosure

1G. Morris, JACS, 102, 428 (1980)
FIGURE 1

\[ \frac{2}{\nu} \times 2 \]

\[ S/\nu = \frac{204 \times 25 \times 2}{2} = 113 \]

FIGURE 2

a. 

b. 

c. 
Selective population inversion of satellites of satellites

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

Dear Barry,

Although the method of selective population transfer (I) is not very appropriate as a general procedure of sensitivity enhancement it remains a powerful and versatile technique for spectral identification and the determination of relative signs of coupling constants. For example, it allows the accurate measurement of small $J^{15N \cdot H}$ coupling constants in the amide structure (I) and in the corresponding iminium salt (II).

\[
\begin{align*}
&\text{C}_6\text{H}_5\text{CH}_2\text{NICH}_2 \quad (\text{I}) \\
&\text{C}_6\text{H}_3\text{CH}_2\text{NICHOC}_3 + X^- \quad (\text{II})
\end{align*}
\]

Thus selective inversion of a non-degenerate transition in the $^{15N}$ satellite spectrum of proton $\text{H}_A$ may introduce specific polarizations in poorly resolved $^{15N}$ multiplets. These polarizations lead to narrow positive and negative components in a given submultiplet resulting from the coupling constant $2J^{15N \cdot H}$ and a value of 0.6 Hz is thus accurately determined in compound I.

As shown in the figure it is also possible, in a compound (I) enriched at a level of only 30% in $^{15N}$, to selectively invert a transition in an unobservable multiplet which corresponds to the $^{15N}$ satellite spectrum of transitions which are themselves $^{13C}$ satellite transitions of proton $\text{H}_B$. Thus by inverting the two low frequency components of the $2 \times 2 \times 2$ proton multiplet associated with the coupling constants $1J(\text{C}_B \text{H}_B), 2J(15N \text{H}_B)$ and $3J(\text{H}_A \text{H}_B) (= 2Hz)$, polarizations are observed in the $^{15N}$ satellite transitions of the carbon spectrum. Denoting the $^{13C}$ transitions of the species which contains both the $^{15N}$ and the $^{13C}$ isotopes 1 to 16 from high to low frequencies, we observe negative polarization of the quadruplet 13-14-15-16 produced by the $2J(\text{C}_B \text{H}_A) = 3J(\text{C}_B \text{H}_B)$ (= 4 Hz) coupling constants and a given spin state of $^{15N}$. The progressively connected quadruplet 5-6-7-8 is positively polarized. This result corroborates the fact that $2J(\text{N} \cdot \text{H}_B)$ and $13J(\text{C} - \text{N})$ have the same sign.

Similarly proton transitions which are $^{125}\text{Te}$ satellite transitions of a $^{13C}$ satellite spectrum can be selectively inverted at the natural abundance level of both the $^{125}\text{Te}$ and $^{13C}$ isotopes (0.08%). These experiments enable the determination of the relative signs of various $^{125}\text{Te}$-$^{13C}$ coupling constants in tellurophenes (2).

Yours sincerely,

M.L. MARTIN
H. MARTINEAU
M. TRIERWEILER


Figure Legend

a) Normal $^{13}$C spectrum of carbon C$_B$ of compound I enriched in $^{15}$N at a level of about 30%. The $^{13}$C spectrum of the labelled compound gives rise to $2 \times 4$ multiplets with 15% intensity, on both sides of each of the two main quadruplets resulting from the species which contains the $^{14}$N isotope.

b) Same spectrum as a) but exhibiting selective population transfer in the satellite $^{15}$N spectrum of C$_B$. 
March 18, 1981

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

TITLE: Strong coupling effects in rapidly exchanging weakly coupled spin systems

Dear Barry:

While testing our recently published (J. Mag. Res. 41, 463 (1980)) method for simulating NMR lineshapes for the ABC \( A'B' + C' \) exchange problem (applicable to the \( ^{31}P \) NMR of phosphoryl transfer enzyme reactions) we noticed some unusual intensity effects for rates large enough to make all exchanges fast. Using an exchange rate of \( 10^7 \) s\(^{-1} \) and the spectral parameters (NMR operating frequency = 40.3 MHz):

\[
\begin{align*}
\omega_A &= 11.0 \text{ ppm}, \quad \omega_A' = 10.4 \text{ ppm}, \quad \omega_B = 4.4 \text{ ppm}, \quad \omega_c = 4.8 \text{ ppm}, \quad \omega_c' = 2.9 \text{ ppm}, \\
J_{AB} &= J_{BC} = 15.0 \text{ Hz}, \quad J_{AC} = 0, \quad J_{A'B'} = 18.2 \text{ Hz}; \quad [ABC]/[A'B'] = 0.8, \quad [AB] = [C]; \\
(T_2A)^{-1} &= 8 \tau, \quad (T_2B)^{-1} = (T_2C)^{-1} = (T_{2A'})^{-1} = (T_{2C'})^{-1} = 10 \pi \text{ s}^{-1}, \quad (T_{2B'})^{-1} = 30 \pi \text{ s}^{-1};
\end{align*}
\]

and varying \( \omega_B \) between 14 ppm and 24 ppm, the spectra shown in Fig. 1 are obtained. Note that the intensity pattern of the \((A + A')\) and \((B + B')\) resonances is exactly like that of a strongly coupled two spin system (in Fig. 1a the exchange averaged chemical shifts of A and B nuclei are equal to each other).

We felt that the "average A" and "average B" nuclei are strongly coupled under fast exchange although the individual AB and A'B' pairs are weakly coupled \((J_{BC} \text{ is washed out of the spectrum})\). In order to verify this contention we resimulated the spectra by turning off the off-diagonal elements involving \( J_{AB} \) and \( J_{A'B'} \) in the calculation and obtained the spectra in Fig. 2. The intensity pattern in Fig. 2 is exactly that for a coupled two spin system which is incorrectly treated by ignoring the off-diagonal elements, thus verifying the above interpretation of the spectra in Fig. 1. Therefore, two weakly coupled spin systems in fast exchange can give rise to a spectrum with strong coupling features. Although this might sound somewhat unusual the explanation for the observation is straightforward in terms of the effect of the off-diagonal elements of spin-spin coupling in the presence and absence of exchange. We welcome comments from TAMU readers whether this feature was noticed earlier by other people, or better yet if there is an experimental example for it.

Sincerely yours,

K. V. Vasavada

J. I. Kaplan

B. D. Nageswara Rao
ABC \rightleftharpoons A'B'C'

OFF-DIAGONAL
\begin{align*}
J_{AB}, J'_{AB} &= 0 \\
(A+A') \quad + (B+B')
\end{align*}

\begin{align*}
\omega_B &= 18.5 \text{ ppm} \\
\omega_B &= 14 \text{ ppm} \\
\omega_B &= 24 \text{ ppm}
\end{align*}

Figure 1

ABC \rightleftharpoons A'B'C'

OFF-DIAGONAL
\begin{align*}
J_{AB}, J'_{AB} &= 0 \\
(A+A') \quad + (B+B')
\end{align*}

\begin{align*}
\omega_B &= 18.5 \text{ ppm} \\
\omega_B &= 14 \text{ ppm} \\
\omega_B &= 24 \text{ ppm}
\end{align*}

Figure 2
Dear Professor Shapiro,

We have recently completed a variable temperature $^{13}$C $\tau_1$ study of the internal methyl rotation in $\text{1-MN}$ and a similar $^2$H $\tau_1$ study of its perdeuterated analogue ($\text{1-MN-d}_{10}$). The purpose of the investigation has been to find whether the isotope effects would conform to the predictions of absolute rate theory model proposed for some time ago.

The measurements were made for 2M solutions in deuterochloroform using a XL 100 spectrometer. After demonstrating the full NOE in the $^{13}$C spectra, assuming the CH distances (1.08Å for the ring carbons and 1.09Å for the CH$_3$ group) and the deuterium quadrupole coupling constants (193 kHz for the ring deuterons, 165 kHz for the CD$_3$ deuterons) the effective correlation times for different sites in the two molecules were evaluated.

If the overall motion of the molecule is treated as isotropic small step rotational diffusion, the average ring $\tau_c$ gives the corresponding diffusion constant $D$. $\tau_c$ for the methyl group is related to $D$ and the rate, $R_1$, of random jumps between the three equivalent equilibrium positions, by the equation derived by Woessner:

$$\tau_c^{\text{eff}} = \frac{A}{6D} + \frac{B + C}{6D + \left( \frac{3R_1}{2} \right)}$$

For tetrahedral methyl groups, $A = 1/9$ and $B+C = 8/9$.

Following the procedure applied previously to $^{13}$C data, we plot the $D$ and $R_1$ values versus $1/T$ in the figure. We note that the rotational diffusion constants in $\text{1-MN}$ and $\text{1-MN-d}_{10}$ are identical at a given temperature. On the other hand, the $R_1$ values for the CH$_3$ group are a factor of more than two larger than the $R_1$ values.

Postal address
Postbox 5
S-104 05 STOCKHOLM
Sweden

Street address
Bergsåsvägen 65
Frescati
Tel. 15 06 60 (exchange)
for the CD₃ group. The activation energies for Rₐ are 9.0 ± 0.2 kJ mole⁻¹ (CH₃) and 9.3 ± 0.2 kJ mole⁻¹ (CD₃) (error limits of 1σ). According to calculations¹, the activation energy for the CH₃ group should be about 0.2 kJ mole⁻¹ lower than for the CD₃ group and the Rₐ's should provide a reasonable approximation to the threefold barrier, V₃. The combined ¹³C and ²H experiments agree qualitatively with the former prediction (we cannot claim the quantitative agreement because of experimental uncertainties) and we hope therefore that we also can trust that the V₃ value in 1-MN is about 9–9.5 kJ mole⁻¹.

Yours sincerely,

Anders Ericsson

Jozef Kowalewski

References:

1. J. Kowalewski and T. Liljefors
2. D.E. Woessner
3. A. Ericsson, J. Kowalewski, T. Liljefors and P. Stilbs
Optimal Parameters in the Convolution Difference Technique

In the Convolution Difference Technique the resolution enhancement is obtained by subtracting a portion $k$ of the original fid multiplied by a function $\exp(-n/T_2)$ from the unmodified fid. This results in a frequency domain spectrum of the type

$$J(y)_{\alpha\beta} = \frac{1}{1 + \frac{1}{1+n} (\frac{\gamma}{\omega_0})^2} - k \frac{\frac{1}{1+n} (\frac{\gamma}{\omega_0})^2}{1 + \frac{1}{1+n} (\frac{\gamma}{\omega_0})^2}$$

where $\omega_0$ is the width of the original line.

In using this technique it is important to realise that the reduction in linewidth is accompanied by a decrease in S/N ratio and some baseline distortion. In order to predict the influence of the various parameters on to the final sensitivity, resolution and line distortion Dr.Barry Kimber from the National Institute for Medical Research, London and I have investigated these effects in a short paper which we have submitted to J.Magn.Reson. Preprints are available upon request.

Yours sincerely,

(Dr.K.Roth)
Dear Barry:

In our continuing studies with lanthanide shift reagents we have encountered an example which clearly illustrates the importance of using a chemically reasonable model. Consider the following hypothetical reduction of cholestenone which could yield either (or both) of the stereoisomers A and B.

If only a single isomer were obtained from such a reaction, the verification of a stereochemical assignment by spectroscopic methods could be quite difficult.

We have studied these two stereoisomers with Eu(fod)$_3$ in CCl$_4$, and our results indicate that "traditional" methods for carrying out structure correlations with shift reagents are inadequate. While cholestanone affords a satisfactory fit only for structure A, coprostanone gives a good agreement factor for both stereoisomeric possibilities.

Table. Comparison of Experimental and Predicted LIS for Cholestanone and Coprostanone.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Agreement Factor (C-O-Eu angle)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Structure A</td>
</tr>
<tr>
<td>Cholestanone</td>
<td>0.03 (175°)</td>
</tr>
<tr>
<td>Coprostanone</td>
<td>0.03 (139°)</td>
</tr>
</tbody>
</table>

Only when the geometry of the complex is restricted so that the carbon-oxygen-europium bond angle is approximately linear is the problem resolved. When this condition is satisfied, coprostanone affords a satisfactory agreement factor only with structure B. Indeed, inspection of the table shows that the "optimum" fit of coprostanone to structure A corresponds to a complex having a C-O-Eu bond angle of 139°. We reject such a bond angle for an unhindered ketone as chemically unreasonable (J. Am. Chem. Soc., 102, 6591 [1980]). While traditional methods of fitting the LIS data would have yielded the correct assignment of isomer A for cholestanone, they would not have permitted a choice between stereoisomers A and B for coprostanone.

Best regards,

Title: LIS OF KETONES

Douglas J. Raber

THE UNIVERSITY OF SOUTH FLORIDA IS AN AFFIRMATIVE ACTION EQUAL OPPORTUNITY INSTITUTION
Professor Bernard L. Shapiro,  
Department of Chemistry,  
Texas A & M University,  
College Station, Texas,  
U.S.A. 77843  
March 23, 1981  

Dear Barry:  

"RELAXATION OF PROTEIN BOUND PHOSPHORUS NUCLEI"  

We have been studying the $^{31}$P NMR of the ATP bound to G-actin. By nitrat- 
ing Tyr-69 with TNM, we have been able to increase the concentration of G-actin in solution without incurring polymerization. This modification has no observ- 
able effects on the $^{31}$P NMR spectrum, indicating that the modified Tyr (69) is likely quite far from the ATP binding site of G-actin. We determined $T_1$ and $T_2$ values for the bound ATP resonances at 36.4, 81.0, 109.3 and 162.0 MHz in order to sort out the effects of chemical shift anisotropy (CSA) and dipole-dipole (D-D) relaxation. In the non-extreme narrowing limit ($\omega^2 \tau_C^2 >> 1$), the contribution of CSA to $1/T_2$ is proportional to $\omega^2$ (Equation 1) while the contribution of DD is independent of $\omega^2$ (Equation 2 for $^{31}$P-$^{31}$P DD interaction and Equation 3 for $^{31}$P-$^1$H DD interactions). For $\omega^2 \tau_C^2 >> 1$, the contribution of CSA to $1/T_1$ is independent of $\omega^2$ (Equation 4), while the DD contribution is inversely propor- 
tional to $\omega^2$ (Equation 5 for $^{31}$P-$^{31}$P interactions and Equation 6 for $^{31}$P-$^1$H interactions).

\[
\frac{1}{T_{2CSA}} = \frac{4}{45} \frac{\omega_P^2}{\Delta \nu} \left(1 + \frac{n^2}{3}\right) \frac{1}{\tau_C} \tag{1}
\]

\[
\frac{1}{T_{2DD}^{PP}} = \frac{9}{20} \frac{\gamma_p^2}{\tau_{PP}} \frac{n^2}{\tau_C} \tag{2}
\]

\[
\frac{1}{T_{2DD}^{HP}} = \frac{1}{5} \frac{\gamma_H^2}{\tau_{HP}} \frac{n^2}{\tau_C} \tag{3}
\]

\[
\frac{1}{T_{1CSA}} = \frac{2}{15} \frac{\omega_p^2}{\Delta \nu} \left(1 + \frac{n^2}{3}\right) \frac{1}{\tau_C} \tag{4}
\]
The observed values of $1/T_2$ for the $\alpha$, $\beta$ and $\gamma$ phosphates of ATP bound to nitrated G-actin are plotted versus $\omega^2$ in Figure 1, and the observed values of $1/T_1$ are plotted versus $1/\omega^2$ in Figure 2. Figure 1 shows that at high magnetic field strength, CSA dominates $T_2$ relaxation processes accounting for about 90% of the linewidth of all three phosphates of protein bound ATP at 162 MHz. Figure 2 shows that CSA also dominates $T_1$ relaxation processes, accounting for about 80% of the $1/T_1$ relaxation rate at 162 MHz. With the experimentally determined $1/T_{2\text{CSA}}$ and $1/T_{1\text{CSA}}$ terms, equations (1) and (4) can be combined to solve for $\tau_c$ or $(\Delta \sigma)(1 + n^2/3)^{1/2}$. The $\tau_c$ values determined were 40, 44 and 41 nsec for the $\alpha$, $\beta$ and $\gamma$ phosphates of protein-bound ATP, while the theoretical $\tau_c$ for a macromolecule the size of G-actin is 36 nsec. This indicates that each phosphate in the ATP is firmly bound to the protein. The values determined for $(\Delta \sigma)(1 + n^2/3)^{1/2}$ were 260, 260 and 240 ppm for the $\alpha$, $\beta$ and $\gamma$ phosphates; these values are higher than would be expected from model compounds and likely reflect some interaction of the protein with the bound ATP increasing the anisotropy of electron density around the $^{31}$P nuclei.

The effects of chemical exchange between free and protein-bound ATP on these $T_1$ and $T_2$ values have been considered. Published values of the dissociation rate constant of ATP from G-actin range from $10^{-5}$ to $10^{-3}$ sec$^{-1}$, indicating that we are probably in the very slow exchange limit for both $T_1$ and $T_2$ processes. We also considered the effects of cross-relaxation between $^{31}$P and $^1$H nuclei, since our spectra were taken in the absence of $^1$H decoupling. In the non-extreme narrowing limit, the calculated value of $\sigma$ is very low, since the $W_0$ and $W_2$ terms roughly cancel. The ratio of $\rho/\sigma$ is about 112, indicating that cross-relaxation of $^{31}$P nuclei with $^1$H nuclei is negligible in the non-extreme narrowing limit.

Best regards,

Dr. Manfred Brauer and B.D. Sykes

Professor of Biochemistry
March 24, 1981

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

Re: 13C NMR of Brominated Poly(phenylene oxide) (Br-PPO)

Dear Barry,

In the past year we have used 13C NMR extensively to characterize a variety of brominated poly(phenylene oxide)s. The degree of bromination can be easily determined from integration of the resonances labeled A, B and C in the Figure. The three spectra correspond to samples which were 50%, 70% and 100% brominated (a, b and c) where 100% bromination in our terminology is one bromine atom per PPO ring. Assignments are given for the Br-PPO homopolymer (C). All spectra were obtained under quantitative conditions. The resultant analyses were found to be consistent with gravimetric determinations. The data for a series of mono- and dibrominated PPO's will be published shortly.

Sincerely,

E. A. Williams  
P. E. Donohue  
Chemical & Structural Analysis Branch  
INORGANIC MATERIALS & STRUCTURES LAB

/ldr
Figure. $^{13}$C NMR spectra of (a) 50% brominated PP0, (b) 70% brominated PP0 and (c) 100% brominated PP0 (one bromine per ring).
March 16, 1981

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

Dear Barry:

The JEOL INSTITUTE is a non-profit, educational function that has been recently formed to teach short but comprehensive courses in NMR. These courses are of interest to both analytical and research scientists dealing with NMR spectroscopy in all its forms. The first course that we have formulated has been given twice, and has received outstanding critiques by the attendees. In view of these excellent responses, we plan to expand the number and nature of the courses given, and would appreciate your disseminating this information to the NMR community via the Texas A&M Newsletter.

In addition to my duties as Director of the JEOL INSTITUTE, I teach the first three sessions of the course presently in our curriculum. There are two other sessions in the same course, and these are taught by Dr. Thomas C. Farrar and Dr. John S. Waugh.

It should be emphasized that although the JEOL INSTITUTE is associated with JEOL USA INC., it is a wholly independent and non-profit organization. Instrument references from other manufacturers are treated equally and without bias. The sole responsibility of the JEOL INSTITUTE is educational in its nature.

The first session of this course deals with the physics and basic concepts of a wide variety of NMR phenomena. The signals generated by these experiments are traced through block diagrams of the instrument, through the computer, and finally to the recorder. This is a three-day session, and is designed to give in-depth concepts of the best techniques to employ so that the maximum information can be obtained from the instrument. It includes T₁ and NOE measurements, decoupling techniques, and their applications for structure determinations. In addition, this session also serves as an excellent preparation for more advanced training in troubleshooting, or for making simple modifications to perform experiments not originally planned by the instrument manufacturers.
The second session is taught by Dr. Thomas C. Farrar and deals with analysis of dynamic systems. Topics such as $T_1$-rho and spin-echoes are covered as well as some applications of these techniques in determining molecular motions.

The third session is taught by Dr. John S. Waugh and reviews the basic ideas and concepts involved with magic angle spinning, cross-polarization, two-dimensional spectroscopy and NMR imaging.

Separate courses are being planned for the future which will give considerably more details concerning the exact experimental techniques required to actually obtain 2-D spectra, spectra of solids, etc. In addition, courses in interpretation of spectra are also being considered.

The next course is scheduled for the first week of June 1981 (June 1-5, 1981). Further details may be obtained by writing:

JEOL INSTITUTE
P.O. BOX 21
CRANFORD, NEW JERSEY 07016

Sincerely yours,

BOSTON COLLEGE
CHESTNUT HILL, MASSACHUSETTS 02167

Equipment Needed

Recently some of the shim coils in our aged A-60A died, rendering it nonfunctional. We thus need a new left pole cap, but the price of a new replacement part is prohibitive. Consequently, I'd like to ask any of your readers who may have retired an A-60A and are cannibalizing it, to contact me if a pole cap were available at a reasonable price.

Sincerely,

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

Dennis J. Sardella
Associate Professor
(617) 969-0100 ext. 3612
March 24, 1981

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

Title: $^{91}\text{Zr-}\{^1\text{H}\}{^1\text{B}}$ spectrum of Zr(BH$_4$)$_4$

Dear Dr. Shapiro:

Until a short time ago, zirconium-91 NMR received little attention.$^1$ Recently it became desirable to decouple protons and boron-11 from the $^{91}\text{Zr}$ spectrum of Zr(BH$_4$)$_4$, both separately and simultaneously. Principles for retuning the decoupling coil are well known$^2$ and the method adopted here was to remove all tuning elements from inside the probe and mount new single tuned and double tuned networks inside small brass boxes which could then be attached separately, via two BNC connectors, to the base of the probe. One BNC connector is the one originally for the proton decoupling input and the other is a new one mounted at the hole vacated by a variable capacitor of the original tuning network. It should be noted that some capacitors have "tinned copper clad steel" leads and therefore should not be used. Hanging the capacitor on a string in the magnet gap while observing a lock signal is a good test for suitability.

A General Radio 1164-A frequency synthesizer (locked to a 5 MHz source from the spectrometer) and an RF Communications Inc. type 805 amplifier were used to decouple boron-11 at 28.875 MHz. A bandpass filter was required at the output of the amplifier and also a reject filter (28.875 MHz) was needed at the input to the signal amplifier. Facility for proton decoupling was already available with the Bruker WH90.

The results of these modifications appear in the accompanying figure. A fuller account will be forthcoming.

Yours sincerely,

J.I.A. Thompson, B. Sayer, Nguyen Hao, and M.J. McGlinchey

enclosure

The $^{91}\text{Zr}$ NMR spectrum of $\text{Zr(BH}_4)_4$ at 25°C: A, fully coupled; B, $^{11}\text{B}$ decoupled; C, $^1\text{H}$ decoupled; D, $^1\text{H}$ and $^{11}\text{B}$ decoupled.
Cher Monsieur SHAPIRO,

Title : "GERM"


Pour 1982, la réunion du GERM s'effectuera conjointement avec celle du comité homologue allemand et elle se tiendra toujours à Pont-à-Mousson, les 10, 11 et 12 Mars. Le comité d'organisation 1982 effectuera sans doute un rappel de cette manifestation grâce aux pages du TAMU NMR Newsletters.

Veuillez croire, Cher Monsieur SHAPIRO, en nos sentiments les meilleurs.

A. BRIGUET

P.S. Pouvez-vous attribuer cette contribution au Laboratoire de Spectroscopie Hertzienne (J. DELMAU, J.C. DUPLAN, A. BRIGUET) ?
PROGRAMME

Mardi 10 Mars au soir - Accueil des participants - Dîner à partir de 20h30

Mercredi 11 Mars

8h30 - 9h30  S. FORSEN (Lund)
"N.M.R. of magnesium, calcium and cadmium; biological applications."

9h30 - 10h30  O. LUTZ (Tübingen)
"N.M.R. of 3A and 3B group elements and of vanadium and copper."

10h30  Pause

11h00 - 12h00  C. BREVARD (Wissembourg)
"R.M.N. des noyaux de faible rapport gyromagnétique; cas de l'argent, du tungstène et du molybdène."

12h30  Dîner

16h15 - 18h15  Tables rondes TR1 & TR2

18h30 - 19h30  J.-Y. LALLEMAND (Paris)
"Philosophie de l'emploi et de l'adaptation des calculaturs."

20h00  Dîner

Jeudi 12 Mars

8h30 - 9h30  I.V. CAMPBELL (Oxford)
"N.M.R. experimental techniques for the investigation of biomolecules"

9h30 - 10h30  J. PARELLO (Montpellier)
"Structure et dynamique de protéines."

10h30  Pause

11h00 - 12h00  G. WEIL (Strasbourg)
"R.M.N. des macromolécules synthétiques."

12h30  Dîner

16h15 - 18h15  Tables rondes TR3 & TR4

18h30 - 19h30  B. LAMOTTE (Grenoble)
"R.M.N. in vivo"

20h30  Dîner
Vendredi 13 Mars 1981

8h30 - 9h30  M. CHARVOLIN (Orsay)
"R.M.N. des milieux hétérogènes non biologiques."

9h30 - 10h30 J. TABONY (Grenoble)
"Surfaces et molécules adsorbées."

10h30  Pause

11h00 - 12h00 A. BRIGUET
"Imagerie R.M.N."

12h30  Déjeuner

Dispersion des participants.

TABLES RONDES

TR1 : Milieux hétérogènes
      Modérateur : J. COURTIEU (Orsay)

TR2 : Techniques expérimentales dans les milieux biologiques.
      Modérateur : J. PARELLO (Montpellier)

TR3 : Sur l'utilisation et l'adaptation des calculateurs.
      Modérateur : W. VON PHILIPSBOHN (Zurich)

TR4 : Polymères.
      Modérateur : D. BESSERE (Clermont-Ferrand)
March 4, 1981

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

"Positions Available - Post Doctoral Fellowship, NMR Spectroscopist/Natural Products Chemist"

Dear Dr. Shapiro:

I have two openings for research scientists in our Corporate Research Laboratories in Manhattan, New York.

A post doctoral fellowship position for 1 to 2 years. Suitable candidate should have working experience in the isolation of natural products by chemical and chromatographic methods, and a strong background in structure elucidation using high field NMR spectroscopy.

We are also looking for an NMR spectroscopist/natural products chemist, an experienced Ph.D. with a proven track-record in the isolation and identification of natural products. The successful candidate will be familiar with all useful chromatographic and spectroscopic techniques and will be expert in the use of ¹H and ¹³C NMR instrumentation.

Interested candidates should send to me a complete resume, including the names of two people to whom reference may be made on their behalf.

Sincerely,

William V. Rosemberger  
Personnel Manager

WDR:dp
March 9, 1981

Prof. B. L. Shapiro
Dept. of Chemistry
Texas A and M University
College Station, Texas  77843
U.S.A.

"An Accustomed Level of 10 mm C-13 Sensitivity"

Dear Prof. Shapiro,

We were somewhat puzzled to read of Dr. Toby Zens' enthusiastic introduction of a 'new generation' of probes from our worthy competition (TAMU 269-49). Our puzzlement centres mainly around what it is, exactly, that is new.

We enclose a couple of spectra recorded as part of day to day operations in Mississauga. The only unusual treatment was to use Dr. Zens' 3.5 Hz line broadening in the ASTM test. Normally, and so as not to mislead customers, we employ (natural linewidth notwithstanding) a line broadening equal to data point resolution achievable with a given sweepwidth and data table size. The spectra were obtained on our 18 month old WM-250 using our 10 mm 1H, 31p broadband probe.

We should perhaps welcome Dr. Zens to the new generation. Would that we had been able to do so in 1979!

Sincerely yours,

Martin Smith
Charles Rodger
Alex Bain

/df

Encl.
WM250: 62.8 MHz $^{13}C$ spectra (10 mm broadband probe)

10% ethyl benzene in CDCl₃

Single 1/2 pulse (25 ms)

Line broadening 0.7 Hz

S/N ≈ 120:1

13C ASTM test sample

Single 1/2 pulse (25 ms)

Line broadening 3.5 Hz

S/N ≈ 245:1
Dear Barry,

LONG-RANGE COUPLING IN ESTERS

Nearly 13 years ago, Dr (now Professor) S.M. Verma and I reported (1) several proton-proton coupling constants of up to 0.9 Hz through four or five bonds including the central C-O-C bonds of esters, and suggested that the couplings could all be ascribed to transmission through planar-W or extended-W σ-bond systems, the function of the ester group being to maintain the necessary degree of planarity.

I have recently had a senior undergraduate student, Mr Dennis O'Shea, make calculations of coupling constants on various conformations of simple esters by my current DEC20 descendant of the QCPE program, FINITE.

Dennis began with various ab initio geometries of methyl formate (2) and showed that minor local variations were not significant but changes of configuration about the O-C bond and of Me-group conformation certainly were. In particular, for the Z-configuration (Me group cis to carbonyl O) with the Me group staggered about the O-C bond, the four-bond planar-W formyl-methyl H-H coupling as calculated by the INDO approximation is 2.62 ± 0.02 Hz, only slightly smaller than three times the observed 0.9 Hz, and the CNDO/2 value (2.31 Hz) is only a little smaller again. Neither the Z eclipsed-Me conformation, nor either conformation for the E-configuration give values remotely near the above, so we believe the earlier experimental conclusions and the argument that σ-π interactions are not significant in these long-range couplings have now been substantiated theoretically.

For methyl acetate, the Z-configuration with both Me groups staggered about the O-C bond gave $^5J$ (planar, extended-W) values of 0.58 Hz (INDO) or 0.43 Hz (CNDO/2), both considerably smaller than three times the observed value (0.25 Hz). No other conformations for the Z-configuration gave values remotely near these, but some conformations for the E-configuration gave values in the range, -0.25 to -0.87 Hz; the E-configuration may, however, be discounted in view of its much higher energy (15-22 kJ/mol).

Yours sincerely,

Noel V. Riggs

Uncompromising performance, limitless adaptability.

Our spectrometer systems have been conceived and designed to provide optimum performance while being fully adaptable to new techniques with minimal cost and difficulty. More than just a collection of instruments, they represent a completely modular approach to FT-NMR instrumentation that allows the user to expand his system as his research needs grow and to easily accommodate new experimental techniques as they develop.

Outstanding Nicolet features include these:
- A full range of superconducting magnets from 4.7T to 11.7T (200MHz to 500MHz proton frequency range), in both wide-bore and narrow-bore configurations.
- Multinuclear observation with a wide variety of fixed-tune and broadband probes.
- Simultaneous acquisition, processing, and plotting for greater sample throughput.
- Simplified control of spectrometer operations and parameters by using easy keyboard commands.
- Advanced Nicolet 1180E Data System with 128K/20-bit memory, 256-step pulse programmer, and the most comprehensive FT-NMR software package available.
- Extended dynamic range performance with 40-bit acquisition and floating-point processing.
- An expandable pulse-sequence library, including T1, T2, Redfield, INEPT, homo- and hetero-2D-FT, etc.
- Convenient computer control of field shimming, observe and decoupling frequencies, sample temperature, and probe-tuning.
- Precise digital plotting with full annotation of spectral parameters and flexibility of hardcopy format.

The versatile Nicolet spectrometers provide the user with the ability to easily adapt to the newest techniques and experimental configurations. Some of these are:
- High resolution studies of solids with Waugh-Pines cross-polarization and magic-angle spinning.
- High sensitivity wide-bore 13C studies of high molecular weight polymers.
- Automated T1 and T2 measurements.
- Chemical dynamics studies.
- Temperature-programmed experiments.
- 31P experiments on living organs.

NICOLET MAGNETICS CORPORATION
A NICOLET INSTRUMENT SUBSIDIARY
145 East Dana
Mountain View, California 94041
TWX: 910-379-6589
Telephone: 415-969-2076
FX SERIES
OF
FT NMR SYSTEMS

FX Features

- Light Pen Control System
- Bilevel Software Package
- 2-D Spectroscopy
- Auto T<sub>i</sub>, T<sub>2</sub> Meas./Calculation
- FX Series Work Station
- Programmable Multi-Pulser: INEPT, Selective Excitation, Cross Polarization, Bilevel Decoupling, etc.

- Digital Quadrature Detection
- Oxford SCM Systems
- Programmable Variable Temperature
- Double Precision (32 bit word length)
- Floppy; Moving Head Disc Systems

FX-60QS:
- CP/MAS
- 13C, 31P, 29Si (examples)
- Routine Liquids/Solid State

FX-270:
- Dual Frequency Probes
- Broad-Band Probes
- "Tilt" Micro Probe

FX-90Q:
- OMNI Probe™ System
- 10mm, 5mm Micro Inserts
- Wide Band (1H to 103Rh)

FX-200:
- Dual Frequency Probes
- Broad-Band Probes
- CP/MAS Extension

JEOL
USA Inc., Analytical Instruments Div.
235 Birchwood Ave., Cranford, NJ 07016
201-272-8820