Texas
A
M
University
N - M - R
Newsletter
February, 1977

R. J. Cushley and B. J. Forrest
Cholesterol Esters and Membrane Permeability. A $^{31}$P LIS Study. ............ 1

G. J. Martin and M. L. Martin
Pseudo-Dynamic $^{15}$N Spectroscopy ............ 3

E. J. Fendler and S. N. Rosenthal
Concentration Dependence of $^{13}$C Chemical Shifts of Methyl Cholate in CDCl$_3$. ............ 5

D. W. Overnall, H. H. Hoehn and T. K. Wu
$^{13}$C Additivity Parameters for Aliphatic Ketones and the Microstructure of Ethylene-Carbon Monoxide Copolymers ............ 7

L. W. Reeves and F. Fujiwara
Orientation of Lyomesophases in a Magnetic Field ............ 10

P. L. Pauson, G. A. Munro and P. Bladon
Fluxional Manganese Hydride Complexes ............ 11

P. Granger, G. J. Martin, F. Metras and B. Rogues
GERM, April 16-18, 1977 ............ 13

J. A. G. Drake, D. W. Jones and H. Pakdel
Shifts in 220 MHz $^1$H Spectra of Fluorenone-9-one; Sulphur-Containing Amino Acids ............ 16

E. Santoro
Stereoisomers of 2,6-Decalindicarboxylic Acid ............ 17

G. E. Dorman and J. W. Paschal
Use of $^{15}$N NMR and CONGEN in Structure Elucidation ............ 19

J. T. Clerc and H. Sommerauer
A Program for the Estimation of $^{13}$C NMR Chemical Shifts ............ 21

C. Crocker and R. J. Goodfellow
Heteronuclear INDOO Spectra of Some Tetrahedral Fluorophosphine Complexes ............ 23

N. V. Riggs
A Problem of Locks, Anti-Locks and Pseudo-Locks ............ 27

W. B. Smith
An HA-100 + or - ............ 28

J. M. Miller
WP-60 Quadrature Detection Retrofit ............ 29

B. Egan and J. Cohen
$^1$H Scalar and Dipolar Decoupled $^{13}$C Spectra of Sickle Cell Erythrocytes ............ 30

M. Thorpe
Proton-Coupled $^{13}$C Spectrum of Mesityl Oxide ............ 32

J. A. Ladd
Exchange Phenomena in the Hydrogen-Bonded Picric Acid/Triethylamine System ............ 34

E. Berman
Optimum Conditions in FT NMR Measurements ............ 36

D. Jardetzky and W. W. Conover
Phase Shifting of Broadband Transmitter ............ 38

H. A. Resing and A. N. Darrow
High Resolution $^{13}$C Spectra in Oil Shale ............ 40

G. C. K. Roberts, J. Feeney and J. O'Neill
Selectively Deuterated Enzymes: Identification of Ligand Resonances by Transfer of Saturation ............ 41

G. E. Maciel
Magic-Angle Spin-Rate Monitor ............ 44

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.
**CHART PAPER**

Finest grade NMR Chart Paper made to be used in every model spectrometer. All charts have been updated to coincide with the newest instrument techniques...Fourier Transformation, Hetero-Decoupling, and Time Averaging.

**NOTE:** All charts packaged 500 sheets to a box except roll charts or as otherwise noted.

### CATALOG NUMBER | INSTRUMENT | TYPE | PRICE PER BOX
--- | --- | --- | ---
VARIAN WCV-100 (CFT-20) | HA-100, HA-100A, and D | Cal. | $36.00 $34.50 $34.00 $33.50
WCV-60 (S-60C) | A-60, A-60A and D | Cal. | $35.00 $34.50 $34.00 $33.50
WCV-60EL | H-60EL and 1L | Cal. | $37.50 $37.00 $36.50 $36.00
WCV-XL (XL-100) | XL-100 (Standard) | Cal. | $35.00 $34.50 $34.00 $33.50
WCV-XL-100F | XL-100 (Fourier) | Cal. | $31.50 $31.00 $36.50 $36.00
WCV-200 (CFT-20) | H-200 | Cal. | $37.50 $37.00 $36.50 $36.00
WCW-60 (S-60A) | A-60/60 | Cal. | $37.50 $37.00 $36.50 $36.00
WCW-90K-10 | EM-360 | Cal. | $30.00 $29.50 $29.00 $28.50
WCW-20 (CFT-20) | EM-300 or (330) (2) | Cal. | $14.40 $13.80 $13.00 $12.50
WCW-EM-300F (330X10) | EM-300 (Flatbed) | Cal. | $28.00 $27.50 $27.00 $26.50
WCW-EM-300T (S-60T) | T-60 (two color) | Cal. | $20.00 $19.50 $19.00 $18.50
WCW-60T | T-60 (two color) | Cal. | $17.50 $17.00 $16.50 $16.00
WCW-60U (S-60U) | T-60 (multi-nuclei) | Cal. | $20.00 $19.50 $19.00 $18.50
WCW-60UTS | T-60 (no gridded, fixe) | Blank | $16.00 $15.50 $15.00 $14.50
WCW-BL | 11" x 16" | Blank | $13.00 $12.50 $12.00 $11.50
WCW-CFT-20X-11 | Blank | Blank | $13.00 $12.50 $12.00 $11.50
WCW-3600L | 11" x 16" | Blank | $13.00 $12.50 $12.00 $11.50

**JEO**

| CATALOG NUMBER | INSTRUMENT | TYPE | PRICE PER BOX
--- | --- | --- | ---
WCJ-604 | C-604, H-100, (9.00 ppm) | Cal. | $37.50 $37.00 $36.50 $36.00
WCJ-600H | C-600H, H-100, (10.0 ppm) | Cal. | $37.50 $37.00 $36.50 $36.00
WCJ-4HC | M-100, PS-100 (10.0 ppm) | Cal. | $37.50 $37.00 $36.50 $36.00
WCJ-4HI | M-100, PS-100 (8.0 ppm) | Cal. | $37.50 $37.00 $36.50 $36.00
WCJ-4HE | PFT-100 (standard) | Cal. | $37.50 $37.00 $36.50 $36.00
WCJ-PFT-100 | PFT-100 (Fourier) | Cal. | $37.50 $37.00 $36.50 $36.00
WCJ-60FX-2 | FX-60 | Blank | $37.50 $37.00 $36.50 $36.00
WCJ-60FX-2 | FX-60 (para only) | Blank | $19.00 $18.50 $18.00 $17.50
WCJ-PFT-100FX-2 | Blank | Blank | $15.00 $14.50 $14.00 $13.50

**BRUKER**

| CATALOG NUMBER | INSTRUMENT | TYPE | PRICE PER BOX
--- | --- | --- | ---
WCB-100C | HH-90, HFX-10 | Cal. | $40.00 $39.50 $39.00 $38.50
WCB-6L | 12-1/2" x 20" | Cal. | $17.00 $16.50 $16.00 $15.50
WCB-WH-90 | WH-90 | Cal. | $35.00 $34.50 $34.00 $33.50
WCB-BX-F | HK-270 | Cal. | $40.00 $39.50 $39.00 $38.50

**PERKIN-ELMER**

| CATALOG NUMBER | INSTRUMENT | TYPE | PRICE PER BOX
--- | --- | --- | ---
WCPE-2000 | R-20, R-20A | Cal. | $37.50 $37.00 $36.50 $36.00
WCPE-2001 | R-20 | Cal. | $37.50 $37.00 $36.50 $36.00
WCPE-462-1075 | R-12, R-12A (8 rolls/box) | Cal. | $35.00 $34.50 $34.00 $33.50
WCPE-435-0066 | R-24 (9 rolls/box) | Cal. | $35.00 $34.50 $34.00 $33.50
WCPE-435-72504 | R-24A (rect.) (1000 sh./box) | Cal. | $7.00 $6.50 $6.00 $5.50
WCPE-441-1880 | R-22 (rect.) (100 sh./box) | Cal. | $8.00 $7.50 $7.00 $6.50
WCPE-435-7022 | R-32 (10 rolls/box) | Cal. | $36.00 $35.50 $35.00 $34.50
WCPE-202BFL | Blank | Blank | $15.00 $14.50 $14.00 $13.50
WCPE-201BFL | 11" x 17" | Blank | $15.00 $14.50 $14.00 $13.50
WCPE-201F | 11" x 17" | Blank | $15.00 $14.50 $14.00 $13.50
WCPE-526-1102 | R-26 (rect.) (100 sh./box) | Blank | $7.00 $6.60 $6.50 $6.00
WCPE-435-92600 | R-24A (rect.) (100 sh./box) | Blank | $4.00 $3.90 $3.80 $3.70
WCPE-441-188000 | R-22 (rect.) (100 sh./box) | Blank | $4.50 $4.25 $4.00 $3.75

**NMR SPECIALTIES**

| CATALOG NUMBER | INSTRUMENT | TYPE | PRICE PER BOX
--- | --- | --- | ---
WCN-60/100 | A-60, HA-100, A-56/60 | Cal. | $36.00 $34.50 $34.00 $33.50

---

**WILMAD GLASS COMPANY, INC.**

U.S. Route 40 & Oak Road • Buena, N.J. 08310, U.S.A. • (609) 697-3000 • TWX 510-687-8911
For those who expect more in FT NMR Spectrometers . . . it's JEOL.

Low Cost — Routine 13C System

The FX60 features:

- 13C/H Dual Frequency 10, 5, 2mm V.T. Probes
- (LPCS) Light Pen Control System
- Built-in Proton-HOMO/HETERO decoupler
- RF crystal filter detection system
- 12 bit AD/DA for increased dynamic range
- INTERNAL and EXTERNAL locking modes
- 8, 16 and 32K word data collection
- Built-in Read/Write Cassette System
- 1F, 1P, 1N extensions are available

For FREE technical brochures, phone or write:

JEOL Analytical Instruments, Inc.
235 Birchwood Ave., Cranford, NJ 07016
201-272-8820
January 6, 1976

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

TITLE: Cholesteryl Ester and Membrane Permeability. A $^{31}$P LIS Study.

Dear Barry:

The addition of paramagnetic $\text{Pr}^{3+}$ to preformed phospholipid vesicles results in a downfield shift for the outside phosphorus nuclei, while the phosphorus nuclei on the inside of the closed vesicles remain unaffected. The permeability of model membrane systems with incorporated Vitamin E, phytol, phytanic acid, and palmitic acid to $\text{Pr}^{3+}$ has been studied by observing the rate of disappearance of the inside phosphorus resonance (1) after a suggestion by Bystrov (2).

We have recently studied the effect of cholesteryl palmitate on the permeability of egg lecithin bilayers using LIS $^{31}$P NMR. It was found that the incorporation of 5 mole % cholesteryl palmitate increases the permeability of phospholipid bilayers by approximately 13 times. In addition, these mixed vesicles are instantaneously permeable to EDTA. This is in direct contrast to pure egg lecithin vesicles which are relatively impermeable to this complexing agent.

In the accompanying figure, the upper trace represents the spectrum of a 3 ml sample of the mixed vesicles immediately after the addition of 150 $\mu$L of 0.1 M $\text{Pr}^{3+}$. The middle trace is of the same sample after 3044 minutes showing the progressive disappearance of the upfield "inside" resonance. The lower trace represents the spectrum immediately after the addition of 300 $\mu$L of 0.1 M EDTA. EDTA complexes not only with the $\text{Pr}^{3+}$ on the outside of the closed vesicles, but also is able to traverse the membrane to complex with the "inside" $\text{Pr}^{3+}$ resulting in a single upfield peak. Subsequent addition of a 500 $\mu$L aliquot of $\text{Pr}^{3+}$ again results in two $^{31}$P resonances with the relative areas of these resonances identical to that given by the upper trace, confirming that this phenomenon is not due to vesicle rupture.

A complete discussion of our results will form the basis of a forthcoming publication.

Sincerely,

[Signatures]

R. J. Cushley
Associate Professor

B. J. Forrest

$^{31}$P spectrum of 10% w/v egg lecithin vesicles containing 5 mole % cholesteryl palmitate after addition of Pr$^{3+}$. Time = 7 minutes.

Sample after 3044 minutes.

Sample immediately following EDTA addition. Time = 3103 minutes after Pr$^{3+}$ addition.
Dear Barry,

We have found that natural abundance $^{15}$N spectroscopy may provide a good, simple alternative to conventional DNNR methods for evaluating the activation energy $E_a$ of C-N rotational processes (1).

Providing that: i) the $\sigma$ framework of the nitrogen atom of a N-C fragment remains unmodified in the series of compounds under investigation, ii) the excited state levels do not significantly change, a good correlation between the $E_a$ and $^{15}$N values can be computed.

For example, the conjugated N,N-dimethyl derivatives obey the relationship.

$$E_a(\text{kcal-mole}^{-1}) = 80 + 0.217 \delta^{15}\text{N}(\text{ppm}/N\text{O}_3).$$

This correlation has been applied to the prediction of $E_a$ values in compounds for which conventional DNNR methods are unapplicable or dubious:

a) fortuitous equivalence of diastereotopic nuclei ($^1\text{H}, ^{13}\text{C}$)
b) C-N rotation masked by intermolecular processes
c) very high (>25 kcal-mole$^{-1}$) or very low (<7 kcal-mole$^{-1}$) activation energies.
Thus, it is difficult to estimate the barrier of C-N rotation in the adduct between (CH$_3$)$_2$N-CO-N(CH$_3$)$_2$ and SbCl$_5$ since an intermolecular exchange of ligands precludes the measurement of barriers (2).

$^{15}$N spectroscopy gives the following results:

$\delta^{15}$N (adduct) = -304.8 ppm/NO$_3^-$ and Ea = 13.9 kcal-mole$^{-1}$ (case b).

Very high Ea values may be anticipated for Mannich-type iminium salts (CH$_3$)$_2$N = CH$^+$, but the symmetry of the molecule prohibits any DNMR study. We have measured a Ea value of 46.3 kcal-mole$^{-1}$, which agrees with ab initio calculations (3).

The case of the simple enamine (CH$_3$)$_2$N-CH=CH-CH$_3$ is also interesting to consider since no peak separation occurs in the $^1$H or $^{13}$C spectrum down to 140 K, and since the barrier is expected to be very low. The nitrogen chemical shift is -349.3 ppm/NO$_3^-$ and the corresponding activation energy Ea = 4.2 kcal-mole$^{-1}$ (case c).

Finally, the problem of the rotational barrier in tetramethylurea can be discussed. The two methyles of a (CH$_3$)$_2$N group are isochronous in the whole accessible temperature range in both $^1$H and $^{13}$C spectroscopies. However the $^{15}$N signal at -315.3 ppm/NO$_3^-$ leads to a Ea value of 11.6 kcal mole$^{-1}$. This behaviour suggests a fortuitous equivalence of the signals (case a).

1) G.J. MARTIN, J.P. GOUESNARD, J. DORIE, Ch. RABILLER and M.L. MARTIN
J. Amer. Chem. Soc. in press

2) G. OLOFSSON, P. STILBS, T. DRAKENBERG and S. FORSEN
Tetrahedron 27, 4583 (1971)

3) P.A. KOLLMAN, W.F. TRAGER, S. ROTHENBERG and J.E. WILLIAMS
October 8, 1976

Title: Concentration Dependence of $^{13}$C Chemical Shifts of Methyl Cholate in CDCl$_3$

Dear Barry,

In our preliminary investigations of bile salt systems, unusually large rate enhancements (up to 10 million-fold) have been exhibited for the reactions of a variety of organic "substrates". Consequently, we have initiated investigations of the properties of these bile salt systems and of the interactions responsible for the remarkable catalyses. In order to elucidate the structure and nature of the bile salt aggregate, we have begun a study of these systems using $^{13}$C nmr spectroscopy. Experiments on methyl cholate (1) in CDCl$_3$ revealed that the $^{13}$C chemical shifts of this compound were sensitive to its concentration.

As the concentration of methyl cholate is increased the chemical shifts move upfield. Additionally, plots of chemical shifts versus concentration for a number of carbons show discontinuities in the vicinity of 0.3 M and indicate that methyl cholate self-associates forming bilayered or reversed type aggregates. A typical chemical shift (the example is for C-21) versus methyl cholate concentration plot is given in the accompanying figure.
We have also carried out solubilization and interaction studies of "substrates" (e.g., p-nitrophenyl sulfate, p-nitrophenyl phosphate, and 2,4,6-trinitro-N-t-butyl-benzamide) in sodium cholate/DMSO-d\textsubscript{6} systems using \textsuperscript{1}H nmr spectroscopy. The results suggest strong hydrogen-bonding between the "substrate" and the hydroxyl groups of the aggregated sodium cholate "catalyst" as well as other interactions between the two entities and with the solvent DMSO-d\textsubscript{6}.

Sincerely yours,

Eleanor J. Fendler

Steven N. Rosenthal
January 19, 1977

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

Dear Barry:

\[ ^{13}C \text{ Additivity Parameters for Aliphatic Ketones and} \]
\[ \text{the Microstructure of Ethylene-Carbon Monoxide Copolymers} \]

Recently we have been studying the microstructure of ethylene-carbon monoxide (E/CO) copolymers by \(^1\text{H}\) and \(^{13}\text{C}\) nmr. To aid in assigning the \(^{13}\text{C}\) spectra we have derived additivity factors from data in the literature and from some spectra of our own, for a total of 17 aliphatic ketones. Starting from the \(^{13}\text{C}\) chemical shifts of the alkanes containing the same carbon skeletons as the ketones, five additivity parameters were required. These are given in Table I and they reproduce the \(^{13}\text{C}\) chemical shifts of the 17 ketones with a standard deviation of about 0.3 ppm.

E/CO copolymers consist mainly of linear structures of the form \(-E\_mCO\_nCO\_p-\) where \(n, m,\) and \(p\) are integers \(\geq 1\). Both the \(^1\text{H}\) and \(^{13}\text{C}\) spectra have been analysed to give the compositions of the copolymers and the percentage of the ethylene which is present in 1,4-dione, i.e., \(-COECO-\) structures.

A model in which the ethylenes are distributed randomly between the CO units, no two CO units being adjacent, gives for the 1,4-dione content:

\[ \%[1,4\text{-dione}] = 100 \left(\frac{\%CO}{\%E}\right)^2 \]

This expression is in quite good agreement with our nmr data.

Sincerely,

Derick W. Ovenall
Harvey H. Hoehn
Ting Kai Wu (1)

dew - 7

(1) Plastic Products and Resins Department, Du Pont Experimental Sta.
### Table I

<table>
<thead>
<tr>
<th>Parameter</th>
<th>No. of Observations</th>
<th>Mean Value</th>
<th>Standard Deviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₁</td>
<td>5</td>
<td>15.78</td>
<td>.33</td>
<td>methyl in 2-one</td>
</tr>
<tr>
<td>B₂</td>
<td>4</td>
<td>11.68</td>
<td>.05</td>
<td>methylene, methine or quaternary β-shift in 2-one</td>
</tr>
<tr>
<td>B₂'</td>
<td>12</td>
<td>12.73</td>
<td>.34</td>
<td>methylene, methine or quaternary β-shift in 3-one or above</td>
</tr>
<tr>
<td>C</td>
<td>11</td>
<td>-5.65</td>
<td>.34</td>
<td>γ-shift for straight chain methyl or methylene</td>
</tr>
<tr>
<td>C'</td>
<td>6</td>
<td>-4.10</td>
<td>.50</td>
<td>γ-shift for methine, quaternary or branch methyl</td>
</tr>
</tbody>
</table>

### Table II

<table>
<thead>
<tr>
<th>Structure</th>
<th>Carbon-13 Chemical Shift</th>
<th>Triads</th>
</tr>
</thead>
<tbody>
<tr>
<td>COCH₃CH₂CH₂CH₂₃-</td>
<td>42.7 (Predicted) 42.5 (Observed)</td>
<td>COEE</td>
</tr>
<tr>
<td>COCH₂CH₂CO-</td>
<td>37.0 (Predicted) 37.3 (Observed)</td>
<td>COECO</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CH₂CH₂₃-</td>
<td>30.0 (Predicted) 29.6 (Observed)</td>
<td>EEE</td>
</tr>
<tr>
<td>COCH₂CH₂CH₂₃-</td>
<td>24.3 (Predicted) 23.8 (Observed)</td>
<td>COEE</td>
</tr>
</tbody>
</table>

1. The carbon of interest is underlined.
Before you order a Fourier transform accessory for your nmr spectrometer you should consult Transform Technology Inc. The name is new but the personnel have many years experience in the spectroscopy field. Write or call collect to discuss your requirements.

Remember this ad?

We ran this ad in mid-1972 when six of us, including myself, formed Transform Technology Incorporated with the help of Nicolet Instrument Corporation. Now, less than four years later we have over three dozen employees and are now a Nicolet operating division, known as Nicolet Technology Corporation.

What has happened since our first ad? Well, we don't mind tooting our horn by pointing out that NTC has become established as a leader in the development of FT NMR equipment. We have developed, produced and installed scores of FT accessories for use on instruments such as the XL-100, HR-220, T-60, R-12 and R-32. In fact, for over a year we have been the leader in U.S. sales of FT data systems. Now we're working on becoming the leader in overseas sales as well.

Why the success story? We feel it's because we're responsive to customers' needs. Being a relatively small group of dedicated souls we can move quickly in the development of equipment which utilizes the latest techniques.

Consider some of our "firsts" in commercial equipment:

FIRST to employ a single sideband crystal filter for improved signal-to-noise ratio,
FIRST to provide phase shifted rf pulses for high resolution T₂ studies,
FIRST to use Quadrature Phase Detection,
FIRST to provide plots of relaxation recovery curves with data points, and
FIRST to develop a complete software package which includes provision for five methods of measuring T₁ values and three methods for T₂ values.

You can be sure that we are actively working on new "firsts." For example, we'll be demonstrating a complete Fourier Transform Mass Spectrometer very soon. To repeat the closing statement from our original ad—write or call collect to discuss your requirements. Maybe we can work together to add another "first."

NTC
Nicolet Technology Corporation
145 East Dana Street
Mountain View, California 94041
Phone: 415/389-2070
(formerly Transform Technology Inc.)
Thank you for the reminder. We thought it might be a good idea to take up a study of the velocity of orientation of lyomesophases in the magnetic field, one of many loose ends that we have noticed in our "try it and see" experiments of the past. [Ph.D. Thesis of D.M. Chen, Waterloo, 1975.] Studies have been made by Geoffrey Luckhurst, John Lindon, Jim Emsley and D. Shaw (1) based on the so called Leslie equations (2) for the thermotropic liquid crystals. Looking to our NMR spectrometer, as our professor, we realized that two basic problems were accessible (a) The orientation rate of the mesophase directions in the field (b) The randomisation effect (somewhat similar to $T_2$ in NMR) on the directors once oriented and rotated out of the field direction. We immediately verified for lyomesophases two effects described in the previous work for thermotropic nematics (1, 2).

Consider a lyomesophase of type I, which orients with the directors all in the field direction, as for all thermotropics. We have shown that some lyomesophase systems which are oriented and spinning in the appropriate magnet type, give residual simple line widths at times down to 0.5 Hz even if removed a great deal from the centre of the spectrum. This indicates a really homogeneous alignment of directions in the bulk of the mesophase. It is evident, however, that for a simple dipole-dipole on nuclear quadruple doublet any error in the exact alignment of all directors in the mesophase becomes magnified at 45° where the derivative with respect to angle $\Omega$ of $\frac{1}{2}(3\cos^2\Omega-1)$ becomes a maximum. The contribution of error in exact alignment to the line width is:

$$\frac{\Delta\nu}{\nu} = (\Delta\Omega) \sin 2\Omega \times \text{constant} \quad [1]$$

where $\Omega$ is the angle between the centre of the director distribution and the static applied magnetic field: we have verified this and shown that at $\Omega = 0^\circ$ the line width is determined only by natural relaxation and magnet inhomogeneity. $\Delta\Omega$ is a parameter describing the distribution of director angles.

We have also in static experiments verified the expression:

$$\ln(\tan \Omega) = kt \quad [2]$$

for $\Omega < 45^\circ$ where $k$ is a velocity constant. (1 - 3).

It appears that so far the lyotropic and thermotropic liquid crystals are magnetohydrodynamically similar in their behaviour. That's all for now. With kind regards.

Sincerely,

L.W. Reeves

P. Fujiwara

References:


Professor B. L. Shapiro,  
Texas A and M University,  
College of Science,  
College Station,  
Texas 77843,  
U.S.A.

Dear Barry,

Fluxional Manganese Hydride Complexes

Some recent work of the organometallic group has produced interesting n.m.r. results.

Prolonged LAH treatment of cyclohexadienyl manganese tricarbonyl ([I]) has yielded a compound which can best be formulated as ([II]). The n.m.r. spectrum in C₇D₈ at -30° is consistent with this structure (see table) but as the temperature is raised, firstly the peaks due to H1, H2 and H3 coalesce at 35°, then at 45° the peaks due to H3, H3', and H4 merge and finally above 85° a single peak due to H4 results. The endo proton H4 and the hydride protons H1, H2 form a separate pool simultaneously coalescing but distinct from the first group.

This fluxional behaviour can be rationalized by invoking an intermediate structure ([III]). That the two groups of protons separately become equivalent is confirmed by the variable temperature study of deuterium labelled derivatives in which only one proton is present in the 'top' pool or two protons are present in the 'bottom' pool. No exchange occurs between the two pools. These deuterated derivatives should also be amenable to spectral simulation.

Yours sincerely,

P. L. Pauson  
P. A. Munro  
P. Bladon
Note - these may be up to 3 stereoisomers of II due to different arrangements of ligands round the octahedral Mn

Spectra of II

$\delta$ at $-30^\circ$

- $H_1$: 4.47 t, 5.5 Hz
- $H_2$: 4.01 dt, 5.5, 3.4 Hz
- $H_3$: -0.88 dm, 15.6 Hz
- $H_4$: -0.05 m
- $H_A$: 0.17 m
- $H_B$: -6.17 broad

$\delta$ at $110^\circ$

- 2.5
- -3.9
Dear BARRY,

NMR groups flourish in countries which are active in the field of magnetic resonance applications. These countries are primarily English-speaking and French-speakers are unfortunately somewhat handicapped for this reason. Some French-speaking chemists are, at the moment, trying to set up a NMR discussion group - the GERM. The first GERM meeting will be held in VICHY on the 16, 17, 18 April 1977 and will be devoted to some aspects of Molecular Dynamics in relation with Nuclear Magnetic Resonance. Fundamental aspects of this subject will be treated. Plenary lectures and discussion panels will take place on the following topics:

- Dynamic processes and time scale in molecular physics NMR
- Relaxation mechanisms in NMR; experimental determinations of $T_1$, $T_2$ and $T_1^f$
- Mathematical models for molecular dynamic studies
- Molecular motions in liquids; relation between relaxation and molecular motion
- Examples of applications (simple molecules, paramagnetic species, biological molecules).

Ch. BREVARD (Wissembourg), J.J. Delpuech (Nancy), J. KINTZINGER (Strasbourg), J. REISSE (Bruxelles), J.B. ROBERT (Grenoble), P. SICOU (Nice), F. WEHLRI (Zürich) and K. WÜTRICH (Zürich) have agreed to give lectures or conduct discussions.

Yours very sincerely,

The organization committee

P. GRANGER (Rouen) G.J. MARTIN (Nantes) F. METRAS (Pau) S. ROQUES (Paris)
Mon Cher Collègue,

Un grand nombre de chercheurs utilisant les techniques de résonance magnétique en France et dans les pays de langue française et appartenant à différents secteurs d'activité (chimie, chimie-physique, biochimie...etc...) se sont inquiétés du manque de coordination et de rencontres entre les différents utilisateurs.

Ayant ressenti la nécessité de constituer un groupe d'étude en résonance magnétique comme il en existe déjà dans la plupart des pays voisins, nous proposons, MARTIN (Nantes), BÉVARD (Bruker), DELPUECH (Nancy), GRANGER (Rouen), METRAS (Pau), REISSÉ (Bruxelles), ROBERT (CEN Grenoble) et ROQUES (PARIS V), la constitution d'un tel groupe dont les buts seraient :

- d'assurer une réflexion sur le développement des méthodes et techniques de résonance et leurs applications,
- de contribuer à renforcer les liens et les échanges entre les utilisateurs (diffusion de l'information, aide aux rencontres...etc...),
- d'élargir en collaboration avec des chercheurs d'autres disciplines le champ d'application des techniques de résonance,
- d'organiser annuellement une rencontre de travail avec conférences, discussions...etc...

Dans ce but, nous suggérons la création d'une structure permanente sous la responsabilité d'une équipe renouvelable.

Pour cette année, nous proposons une réunion qui se tiendrait à VICHY du 16 au 18 avril inclus et dont le thème général serait :

"RMN ET DYNAMIQUE MOLECULAIRE DANS LES LIQUIDES".

Ces trois journées comprendraient des exposés généraux avec analyses de résultats expérimentaux ainsi que deux tables rondes de discussions.
A titre d'information, les thèmes développés par les différents conférenciers pourraient être :

- Processus dynamique et échelle de temps en physique moléculaire (cas particulier de la RMN).

- Mécanismes de relaxation en RMN.

- Mesures expérimentales des différents temps de relaxation.

- Rappel des éléments mathématiques nécessaires en dynamique moléculaire.

- Mouvements moléculaires dans les liquides.

- Relation entre relaxation et mouvements moléculaires.

- Exemples d'applications (dynamique de molécules simples, d'espèces paramagnétiques et de molécules biologiques).

Pour des raisons matérielles, le nombre des participants est limité à 40. Le prix de la journée (chambre individuelle, trois repas, boissons comprises, taxes incluses) est de 150 F., soit 450 F. pour les trois jours prévus.

Les personnes intéressées par la réunion de VICHY sont priées de répondre avant le 31 Décembre à :

G. MARTIN
Chimie Organique Physique
UNIVERSITE DE NANTES
U.E.R. de Chimie
38, Boulevard Michelet
B.P. 1044 - 44000 NANTES.

Les personnes ou laboratoires intéressés par le G.E.R.M. mais ne pouvant participer cette année à la réunion sont priés de se faire connaître afin de faciliter les contacts futurs.

Nous espérons que notre initiative recueillera l'écho le plus large afin que notre réunion permette de préciser et d'enrichir les objectifs de ce groupe.

Nous vous prions, cher Collègue, d'agréer l'expression de nos sentiments les meilleurs.

Comité d'Organisation :

MARTIN (Nantes)
GRANGER (Rouen)
METRAS (Pau)
ROQUES (PARIS V).

Professor Bernard L. Shapiro,
TAMU NMR Newsletter, Dept. of Chemistry,
College of Science, Texas A. & M. University,
College Station,
Texas 77843, U.S.A.

Dear Dr Shapiro,

SHIFTS IN 220 MHz 1H SPECTRA OF FLUORENE-9-ONE; SULPHUR-CONTAINING AMINO ACIDS

220 MHz 1H NMR spectra of fluorene-9-one (I) in CS₂ and CDCl₃ solutions recorded over the temperature range 228-323K have been analysed by J.A.G.D. with the aid of the LAOCOON program. In the (ABMX)₂ spin system, \( A = H₄ = 7.53 \), \( B = H₃ = 7.48 \), \( M = H₂ = 7.30 \), \( X = H₁ = 7.67 \) ppm (shifts at infinite dilution in CDCl₃). Thus \( \delta₄ > \delta₃ > \delta₂ > \delta₁ \) and \( \delta₃ \approx \delta₄ \approx \delta₅ \approx 7.53 \) Hz; the three \( J₃₄ \) orthocoupling constants are similar, as are the corresponding C-C bond lengths in the crystal structure of I. In CS₂ solution, \( \delta₂ \) is the least concentration-dependent, while in CDCl₃ solution \( \delta₄ \) shows the biggest concentration dependence; the shift of CHCl₃ from TMS is independent of concentration.

\[ \text{Eu(fod)}_3 \] induces an appreciably bigger shift in \( H₁ \) of I than in the other protons, presumably because complexing involves the carbonyl group; induced shifts are in the same sequence, \( H₁ \approx H₄ > H₃ > H₂ \), as when the solvent is changed from CS₂ to CDCl₃. Application of the lanthanide-induced shifts and the crystal-structure atomic co-ordinates of I (planar) to the LISCA stereochemistry program led to a geometry (agreement, \( R = 1.44 \)) between experimental shifts calculated as dipole-induced with the metal below the (extended) plane of I. An analogous treatment of the solvent shifts could imply preferential location of CDCl₃ along the \( C = O \) axis.


Yours sincerely,

J.A.G. Drake
D.W. Jones
H. Pakdel
Title: Stereoisomers of 2,6-decalindicarboxylic acid.

Dear Prof. Shapiro,

Our Bruker WH/90 arrived about two months ago and we have been concerned with $^{13}$C and $^1$H runs as fast as possible. We are well satisfied of the spectra and also of the performances of the instrument: we currently obtain $S/N = 150/1$ for the standard 10 mm $^{13}$C sample. As application of $^{13}$C n.m.r. we wish to report some preliminary results on the stereoisomers of the 2,6-decalindicarboxylic acid, a problem which remained unsolved by $^1$H n.m.r. The product is obtained by hydrogenation of the corresponding naphtalene dicarboxylic acid. The reaction product shows a melting range of 216°C±228°C in agreement to the fact that it is a mixture of stereoisomers. Keeping somewhat the substance at high temperature (250°C±300°C) the resulting product shows a big change in the melting point. The $^{13}$C n.m.r. spectra of samples obtained at increasing times at 250°C let us establish the presence of at least four stereoisomers A, B, C, D whose relative abundances change with time. The $^{13}$C chemical shifts and the initial and final abundances after 5 hours at 250°C, are reported in the following table:
<table>
<thead>
<tr>
<th>Isomer</th>
<th>Initial concentr. %</th>
<th>Final concentr. %</th>
<th>(^{13}\text{C chem. shifts (ref. TMS)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7</td>
<td>83</td>
<td>37.1; 34.3; 34.1; 28.8; 24.5;</td>
</tr>
<tr>
<td>B</td>
<td>58</td>
<td>2</td>
<td>42.9; 33.7; 30.5; 27.7; 23.0;</td>
</tr>
<tr>
<td>C</td>
<td>7</td>
<td>12</td>
<td>42.4; 40.7; 35.3; 31.9; 28.5;</td>
</tr>
<tr>
<td>D</td>
<td>29</td>
<td>3</td>
<td>41.5; 38.5; 34.1; 31.2; 28.9; 28.3; 27.3; 27.3; 23.3; 22.5</td>
</tr>
</tbody>
</table>

We can expect that 2,6-decalindicarboxylic acid has three couples of cis interconverting conformational isomers and three trans isomers which cannot interconvert. Considering the \(^{13}\text{C chemical shifts of cis and trans deca}l\text{in, and the substituent effects of the COOH, COOMe groups}\), one should conclude that the isomers A, B, D are probably cis and the isomer C is probably trans. But this conclusion is not in agreement with what can be derived considering the possible steric interactions in the isomers: butane-gauche, 1,3 diaxial, ... On these bases one can expect that the most stable stereoisomer should be the trans one with both carboxylic group equatorial\(^2\). Further work is in progress to completely clarify the situation.

Sincerely yours,

E. Santoro

1) N.K. Wilson and I.B. Stothers in "Topics in Stereochemistry" vol. 8, pag. 26, Edited by E.L. Eliel and N.L. Allinger, John Wiley and Sons N.Y., 1974

January 12, 1977

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

Dear Professor Shapiro:

**Use of $^{15}$N nmr and CONGEN in Structure Elucidation**

Among our most enjoyable tasks here at the Lilly Research Laboratories are the very challenging structure elucidation problems brought to us by the isolation chemists. Of course, any new method which aids or expedites this work is of particular interest to us. We would like to share one example in which $^{15}$N nmr spectroscopy and a computer program named CONGEN provided important help in structure elucidation.

On chemical and chromatographic evidence, one of the fermentation products isolated by Dr. D. H. Berg was believed to be a dithiodiketopiperazine. After extensive spectroscopic examination of this compound and one of its degradation products, we proposed structure 1.

![Structure Diagram]

This structure includes an N-O bond which some of our chemists found unlikely. To support our proposed structure, we measured the $^{15}$N nmr spectrum which showed two resonances: a relatively strong resonance at 82.5 ppm (downfield from ext. NH$_4$Cl) and a weaker peak at 164.5 ppm. The approximately 80-ppm difference observed here corresponds reasonably well with the chemical shift differences observed in the following model compounds:

---

While structure 1 was consistent with all the $^1$H and $^{15}$N nmr data, some of the $^{13}$C chemical shifts seemed unusual. We therefore decided to seek an alternative structure which would better fit these data, using the program CONGEN written by Ray Carhart and co-workers [J. Am. Chem. Soc., 97, 5755 (1975)]. CONGEN assembles inferred partial structures in all possible ways, utilizing user-supplied constraints to eliminate undesired structural features. In the present case, we were surprised to find that there were 12 structures consistent with the data supplied to the computer. Visual inspection of these structures suggested further experiments; and after a little more work, including some nice mass spectrometry by John Occolowitz, 9 of these structures were excluded. The remaining alternatives 2, 3, and 4 all fit the $^{13}$C data better than 1, and structure 4 appears to fit it best. We hope to confirm this choice in continuing experiments.
Dear Professor Shapiro,

We have developed a conversational program for the estimation of $^{13}$C-NMR chemical shifts by simple additivity rules\(^1\). The program runs on a Bruker BNC 28 minicomputer with 8 K memory. The current version is limited to aliphatic carbon atoms in acyclic compounds with various functional groups.

To enter a structure, the skeleton is first defined by connecting chains (command K). All atoms are assumed to be carbons connected by single bonds. Then, the skeleton is modified by introducing heteroatoms (command H) and multiple bonds (command B).

The program then outputs the numbering scheme and the linearized structure, followed by the estimated chemical shift values. An example is given in Figure 1.

Figure 1

C13NMR ESTIMATION

- K 1.8
- K 9 9.4
- K 10 10.7
- K 0.2
- B 2 4 9
- H N 7

STRUCTURE
1 2 3 4 [ 9 ] 5 6 7 [ 10 ] 8
CH3-CH2-O-CH2-CH2-NE-CH3-CH3

CALC SPECTRUM

<table>
<thead>
<tr>
<th>ATOM NR</th>
<th>SHIFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.6</td>
</tr>
<tr>
<td>2</td>
<td>59.1</td>
</tr>
<tr>
<td>5</td>
<td>33.5</td>
</tr>
<tr>
<td>6</td>
<td>53.7</td>
</tr>
<tr>
<td>8</td>
<td>41.2</td>
</tr>
<tr>
<td>10</td>
<td>41.2</td>
</tr>
</tbody>
</table>

The program has proved to be quite useful in practical applications, even though the increments used are not yet fully optimized. We are currently developing extended versions of the program which eventually will handle cyclic compounds and multiply bonded carbons. Also further optimization of the increments is planned.

Yours Sincerely,

J. T. Clerc
H. Sommerauer

PS: Please credit this contribution to the subscription of Prof. Simon.
Dear Professor Shapiro,

Heteronuclear INDO\textsuperscript{R} Spectra of some Tetrahedral Fluorophosphine Complexes

In contrast to the wealth of data on the coupling between the phosphorus nuclei of mutually cis or trans phosphine ligands in square planar or octahedral transition metal complexes, the information on tetrahedral complexes is restricted to a few nickel complexes of fluorophosphines\textsuperscript{1} and in no case has the sign been determined. We have used $^{19}$F($^{31}$P) INDO\textsuperscript{R} spectroscopy to determine the relative signs and assist in the analysis of the spectra of four tetrahedral fluorophosphine complexes. The matrix elements and general features of an $[AX]_4(T_d)$ spin system with large $J(AX)$ have been described by Lynden-Bell.\textsuperscript{2} The lines of the strong doublet in the $X^{(19)}$ spectrum ($J(AX) + 3J(AX)$) arising from $M(A)=\pm 2$ states were used for the INDO\textsuperscript{R} experiments. There are only eighteen A transitions (Table 1) related to each of these - a considerable reduction compared to the total A spectrum. Four of the $A_I$ transitions form a series, $v_A + \frac{1}{2}N + n\frac{1}{2}[J(AA) + J(XX)] - J(AX)$ where $n$ is 0 to 3 whilst the remaining four occur on the other side of $v_A$ with spacings of $\frac{1}{2}[J(AA) + J(XX)] + J(AX)$. Identification of these leads to $[J(AA) + J(XX)]$ and $J(AX)$ with relative signs whilst (9) and (18) give the sign and magnitude of $J(XX)$.

The figure shows one half of the directly observed $^{31}$P F.t. spectrum with the relevant halves of the INDO\textsuperscript{R} spectra obtained from the two strong $^{19}$P lines. We did not observe lines (4), (7), (13) and (16) which are almost forbidden when $J(AA)>>J(XX)$. The parameters were refined by fitting spectra computed by LACX to the proton decoupled phosphorus spectrum. The results are given in Table 2. The signs are on the basis that $^{1}J(PP)$ is negative.\textsuperscript{4}

Yours sincerely,

C. Crocker R.J. Goodfellow

Table 1

Transitions of the A nuclei of an \([AX]_4 (T_d)\) spin system which are related to the X line at \((\nu_X + \frac{1}{2}N)\) (with approximations following from \(J_{AX}\) being large).

<table>
<thead>
<tr>
<th>(m_X)</th>
<th>Symmetry</th>
<th>Approximate Energy (+\nu_A)</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(A_1)</td>
<td>(\frac{1}{2}N) (-J_{AX}^+ + \frac{1}{2}J_{AA} + \frac{1}{2}J_{XX})</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>(A_1)</td>
<td>(\frac{1}{2}N) (-J_{AX}^+ + \frac{1}{2}(5J_{AA} - 3J_{XX} - R))</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>(T_2)</td>
<td>(\frac{1}{2}N) (-J_{AX}^+ + \frac{1}{2}(5J_{AA} - 3J_{XX} + R))</td>
<td>(\frac{1}{2}(9 + 3g))</td>
</tr>
<tr>
<td>4</td>
<td>(A_1)</td>
<td>(\frac{1}{2}N) (-2J_{AX}^- + J_{AA} + J_{XX})</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>(T_2)</td>
<td>(\frac{1}{2}N) (-2J_{AX}^- + J_{AA} + J_{XX})</td>
<td>(3(1 + h))</td>
</tr>
<tr>
<td>6</td>
<td>(T_2)</td>
<td>(\frac{1}{2}N) (-2J_{AX}^- + \frac{1}{4}(6J_{AA} + J_{XX} - S))</td>
<td>(3(1 - h))</td>
</tr>
<tr>
<td>7</td>
<td>(T_2)</td>
<td>(\frac{1}{2}N) (-3J_{AX}^- + \frac{1}{2}(3J_{AA} + 3J_{XX}))</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>(T_2)</td>
<td>(\frac{1}{2}N) (-3J_{AX}^- + \frac{1}{4}(3J_{AA} + J_{XX}))</td>
<td>3</td>
</tr>
</tbody>
</table>

\(R = [(J_{AA} + J_{XX})^2 + 8(J_{AA} - J_{XX})^2]^\frac{1}{2}\), \(S = [(2J_{AA} - J_{XX})^2 + 8J_{XX}^2]^\frac{1}{2}\),

\(g = [(J_{AA} + J_{XX}) + 8(J_{AA} - J_{XX})]/R, h = [2J_{AA} - J_{XX}]/S, N = J_{AX} + 3J_{AX}^+\).

Transitions 10 to 18 are obtained by reversing the signs of \(\frac{1}{2}N\) and the \(J_{AX}^-\) term and correspond to the reverse sign of \(m_x\). The transitions related to \((\nu_X - \frac{1}{2}N)\) (1' to 18') are obtained by reversing the signs of the terms in \(J_{AA}\) and \(J_{XX}\). Total intensity on this scale is 1024.

Table 2

<table>
<thead>
<tr>
<th>(\delta_F)</th>
<th>(\delta_P)</th>
<th>(1_{FF})</th>
<th>(2_{FF})</th>
<th>(3_{FF})</th>
<th>(4_{FF})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(FPOC,H,0)(_4)</td>
<td>14.0</td>
<td>-158.1</td>
<td>-1288</td>
<td>+29.2</td>
<td>+17.7</td>
</tr>
<tr>
<td>Ni(FP(OPh)(_2)(_4)</td>
<td>29.9</td>
<td>-140.2</td>
<td>-1206</td>
<td>+34.7</td>
<td>+21.7</td>
</tr>
<tr>
<td>Pt(FPOC,H,0)(_4)</td>
<td>13.8</td>
<td>-117.4</td>
<td>-1359</td>
<td>+34.2</td>
<td>+100.7</td>
</tr>
<tr>
<td>Pt(FP(OPh)(_2)(_4)</td>
<td>22.5</td>
<td>-106.7</td>
<td>-1269</td>
<td>+40.3</td>
<td>+102.5</td>
</tr>
</tbody>
</table>

Shifts to high field of CFCl\(_3\) and H\(_3\)PO\(_4\) respectively.
INDOR spectrum using low frequency $^{19}F$ line

Low frequency half of $^{31}P$ spectrum of $[\text{Pt}(\text{PPFOC}_{6}H_{4}O)_{4}]$

INDOR spectrum using high frequency $^{19}F$ line

Low frequency half of $^{31}P$ spectrum of $[\text{Pt}(\text{PPFOC}_{6}H_{4}O)_{4}]$
New breakthroughs in EPR instrumentation

ER-200 Compact Spectrometer
A compact EPR system for routine measurements with research performance.

- Built-in reference arm
- Push-button tuning
- 3 Detection channels
- 1st or 2nd Derivative Detection
- Built-in LN$_2$ VT unit
- He temp accessory
- Double resonator accessory

ER-420 Research Spectrometer
A modular system which can be tailored to your exact requirements for the most demanding applications.

- Variable temperature operation from 1.9° K to 1200° K.
- Rectangular, cylindrical, large access, optical transmission, dual sample and high temperature resonators.
- Choice of magnet systems and power supplies.
- Microwave systems for UHF, S-band, X-band and Q-band.

ER-10 Minispec
A small analytical system with automated operation and high sensitivity at a price you can afford.
Title: A Problem of Locks, Anti-Locks, and Pseudo-Locks

In Newsletter No. 212, p.37, I described preliminary experiments on conversion of our HA60-IL spectrometer for pulse-modulated lock operation. To retain the convenience of a single +5V supply together with compactness and versatility, we have more recently replaced the LM339 quad comparator with an LM311 (single) comparator, and SN74122 (single) and SN74123 (dual) one-shots and, with a few external components, we can control independently the transmitter-, delay-, and receiver-pulse widths over wide ranges, and the threshold voltage (thence audio-phase) of the comparator. In the standard crossed-coil configuration of the V4333 probe, none of these is critical (we can even operate the receiver c.w.) and, with a 19p sample at 56.000 MHz (generated coherently from the 1 MHz output of our GR1164 synthesizer), the standard "lock-box" circuits produce very strong and effective locking signals over a range of at least 20° on either side of the optimum RF reference-phase setting on the V4311 transmitter unit.

BUT - I now wish to use your pages to describe and ask for possible solutions to our present problem: in single-coil mode (using, naturally, the receiver coil), we have so far discovered no combination of pulse-widths and/or RF or audio phases that produces a field-frequency locking condition with the standard HA60-IL circuits. As in crossed-coil mode, the major variable seems to be the RF reference phase but, where in crossed-coil mode we can easily select locking conditions, in single-coil mode we have been able to select only neutral (unlocked) or anti-locked conditions. By the latter term, I mean that the field is driven away rapidly (and by a large amount) from the resonant value. An RF phase shift of 180° causes rapid driving of the field in the opposite direction, whereas either intermediate setting (90° phase shift) produces an unlocked condition. In the anti-locked condition, there is apparently a large DC output (whose source we have not discovered (divined?) from the audio-phase detector in the lock box; it is outside the range of the DC offset adjustment provided, but the "driving" effect may be counteracted by a range of settings of the slow-sweep unit to produce a pseudo-locked condition. Sisyphus was condemned to rolling his stone uphill for eternity, but the mercury batteries in the slow-sweep unit do not share his eternal life. In any case, we would prefer to obtain (and hold) a genuine lock.

Do any of your readers know the origin and solution of our problem and, if so, would they be prepared to write to me directly (and perhaps submit their answer as a Newsletter in case others have the same problem).

Yours sincerely,

N.V. RIGGS
January 21, 1977

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

Dear Barry:

An HA-100 + or -

Since the arrival of our FT instrumentation we have relegated our HA-100 to a standby position and for use on F19 and B11. Recently, we found that one pole of the high impedance magnetic had shorted out to a cooling coil. We are now faced with five alternatives. 1. Junk it totally; 2. Try to sell off V-4311's, lock box, scope, super stabilizer, C-13 (CW) unit, etc., to people for spare parts; 3. Pay an outsized repair bill to replace the pole; 4. Try to find someone who could tell us how to repair it; or 5. Identify someone who would sell or give us a high impedance magnet or a low impedance magnet plus supply.

The latter would be the most desirable course from my point of view, and I would ask the NMR community if anyone could help us out. Persons who might be interested in option 2 or could help via 4 are also asked to please step forward.

Sincerely,

W. B. Smith,
Chairman

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

Dear Professor Shapiro:

Re: WP-60 Quadrature Detection Retrofit

Your pink notice arrived just after we had our two year old WP-60 retrofitted by Bruker for quadrature detection. The conversion took a couple of days, but would be less for anyone with dual ADCs in their computer already. Except for a loose contact and a power supply chip that required replacement the retrofit went smoothly and without difficulty. It is certainly something that should be seriously considered by anyone with a WP or WH spectrometer, since especially for carbon-13 the instrument throughput can be doubled. Unlike the single side band crystal filter method which is normally set up for a single sweep width, the 40% S/N enhancement of quadrature detection is available at all sweep widths. We observed 40% or better S/N enhancement for all our nuclei, and by optimizing filter widths for the particular sample considerably in excess of 40%. We will probably alter the values of some of the filters to correspond more closely to some commonly used sweep widths. We have also observed that shimming on the sample FID is easier, presumably because the pulse is in the centre of the spectrum and close to sample peaks, and slight changes are more readily visible to the eye. Both spectral expansion and decoupler offset settings are simpler once one is used to pulsing in the centre of the spectrum, which also should give less distortion on very wide sweep widths.

External Lock

We have had our $^{19}$F probe fitted with a deuterium external lock channel for use in very low temperature studies as the common deuterium lock solvents don't have low enough melting points. Resolution was a few hertz over an hour, but the trick with its use appears to be the use of very low lock power levels.

Jack M. Miller, Professor,
Chairman.
Dr. Bernard L. Shapiro  
Department of Chemistry  
College of Science  
Texas A&M University  
College Station, Texas 77843

Scalar and Dipolar Decoupled $^{13}$C Spectra of Sickle Cell Erythrocytes

Dear Barry:

Sickle cell anemia is due to a genetic mutation that results in the replacement of Glu 6 with Val in the $\delta$ chains of hemoglobin. This replacement drastically reduces the solubility of deoxy HbS, with the result that it forms a fibrous precipitate in the erythrocyte; a tubular, helical structure for these fibers has been proposed by Finch, Perutz, Bertles and Döbler (1). We hope to be able to gain some insight into the nature of the interactions between the individual HbS molecules in the precipitate by examining its dipolar decoupled $^{13}$C spectrum.

The accompanying Figure shows the scalar and dipolar decoupled spectra of sickled erythrocytes. A large intensity change in the region between ca. 0 and 40 ppm, due primarily to side chain carbon atoms, is evident. Since dipolar decoupling alters the spectrum, a number of carbon atoms reorient slowly ($R < 10^5$ sec$^{-1}$) in certain directions; however, since spectra are obtained using a relatively short delay time between pulses (2 sec), reorientation of these carbon atoms over other directions is rapid ($R > 10^6$ sec$^{-1}$). Whether the spectral changes are due to particular side chain carbons (e.g., those on the surface) is not yet known. A series of experiments, in collaboration with Alan Schecter and Bill Sutherland (Laboratory of Chemical Biology, National Institute of Arthritis, Metabolism and Digestive Diseases), to obtain quantitative data about the interactions between hemoglobin molecules in the gel and to quantify the effects of certain agents on the gelation are now in progress.

With best wishes,

Bill Egan and Jack Cohen  
Reproduction Research Branch  
National Institute of Child Health and Human Development

(1) J. T. Finch, M. F. Perutz, J. F. Bertles and J. Döbler,  

Figure 1. 15.09 MHz $^{13}$C spectra of sickled erythrocytes at $37 \pm 2^\circ$C (8192 transients, 1K data points, 20 KHz spectral window, 2 sec recycle time, 4 usec (90\(^\circ\)) pulse width). The top spectrum (a) was acquired using scalar decoupling ($\gamma H_2/2\pi \sim 4$ KHz) and the bottom spectrum (b) using dipolar decoupling ($\gamma H_2/2\pi \sim 60$ KHz). The FID's were exponentially multiplied so as to produce an additional 10 Hz line broadening in the transformed spectrum. Chemical shifts are in ppm and relative to external TMS.
Title: Proton-coupled $^{13}$C spectrum of mesityl oxide

Dear Barry:

We recently had occasion to examine the proton-coupled $^{13}$C spectrum of mesityl oxide, of which I am enclosing a copy.

![Chemical Structure](image)

The most interesting feature of this spectrum is the lack of any measurable $J_{C_1H_3}$. The complexity of $C_3$ makes it impossible to be sure from this spectrum, but it appears that $C_3$ is showing the expected three-bond couplings with the protons on $C_1$ as well as those at $C_5$ and $C_6$.

Here are the coupling constants that we did derive:

- $^1J_{C_6H_2} = 127.4 \pm 0.6$ Hz
- $^3J_{C_6H_2} = 4.2 \pm 0.6$ Hz
- $^3J_{C_6H_3} = 8.0 \pm 0.6$ Hz
- $^1J_{C_1H_1} = 126.3 \pm 0.6$ Hz
- $^3J_{C_1H_1} = 153.7 \pm 0.6$ Hz

In addition, $C_4$ appears to be a septet, which implies two-bond couplings to the protons at $C_5$ and $C_6$, but not that at $C_3$. $^3J \approx 6$ Hz.

The $C_2$ multiplet is at least a quartet, showing $^3J_{C_2H_1}$ of 4–6 Hz, but it is not clear whether there is also coupling with $H_3$.

Sincerely,

[Signature]

Martha Thorpe
Senior Chemist

MT: jkw

Enclosure
$^1$H-Coupled $^{13}$C Spectrum of Mesityl Oxide at 25.2 MHz. Approximately 50% (v/v) in DMSO-d$_6$. 

* solvent peak
Exchange phenomena in the hydrogen-bonded picric acid/triethylamine system.

Dear Professor Shapiro,

Para studies of various mixtures of picric acid/triethylamine in different solvents show that a strongly hydrogen-bonded complex is formed. When the acid is in slight excess, this is evidenced by the observation of a broad NH resonance at 9.35-9.50 ppm together with an additional 4.5Hz splitting of the methylene signal of the amine (see Figure). When the amine is in excess, this splitting disappears and the NH resonance sharpens and moves upfield.

The evidence points to a complex of the type

\[ \text{O}_2N \text{---} \text{H}^+ \text{NET}_3 \]

and, in the presence of excess amine, of an exchange process of the type

\[ \phi_A \text{--} \text{HNET}_3 + \phi_B \text{--} \text{H}^+ \text{NET}_3 \iff \phi_A \text{--} \text{H}^+ + \phi_B \text{--} \text{HNET}_3 \]

By judicious choice of solvent and concentration a coalescence point at 36°C can be observed for the additional methylene splitting and this leads to a value of \( \Delta G^{\circ} = 16.7 \text{ kcal/mol} \) for the exchange of triethylamine molecules.

Yours sincerely,

J. A. Ladd
Decoupled NH

Decoupled CH₃
Optimum Conditions in FTNMR Measurements.

January 25, 1977

Dear Prof. Shapiro,

In order to obtain "good" spectra in FTNMR measurements, an optimization of several factors is needed, some of which do not depend directly on the intrinsic properties of the compound under study. Such factors call for some form of systemization; this may sound trivial in nature but nevertheless can be very useful and time saving. Two such factors are the observation carrier position $F_1(01)$ and the decoupler carrier position $F_2(02)$.

The choice of $F_1(01)$ or $F_2(02)$ offsets are functions of both the nature of the lock signal used and the sample signal range. In the case of hetero-nuclear decoupling the optimization of the $F_2(02)$ carrier position is essential in order to obtain good decoupled spectra; and of great importance in Single Frequency Off-Resonance Decoupling (SFORD) experiments. With this in mind we have calibrated our two new FTNMR spectrometers for both $F_1(01)$ in $^1$H-NMR work and $F_2(02)$ in $^{13}$C-NMR work.

Since TMS is commonly used as a reference in both $^1$H- and $^{13}$C-NMR, we have used its signal as a reference for the $F_1(01)$ and $F_2(02)$ positions in the spectrum for a given lock signal. The Table summarizes the data for eight deuterated compounds commonly used to supply the locking signal. In addition we have tabulated the lock signal chemical shifts relative to TMS.
Table of Lock Offsets at room temperature, for 02 (TMS) in WH-90.

<table>
<thead>
<tr>
<th>Type of lock</th>
<th>$\delta^H$ from TMS $\pm$ 0.1 ppm</th>
<th>$\delta^{13}C$ from TMS $\pm$ 0.3 ppm</th>
<th>02 for TMS* $\pm$ 5 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDCl$_3$</td>
<td>7.3</td>
<td>77.05</td>
<td>2924</td>
</tr>
<tr>
<td>C$_6$D$_6$</td>
<td>7.2</td>
<td>128.0</td>
<td>2928</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>5.3</td>
<td>53.6</td>
<td>3101</td>
</tr>
<tr>
<td>CD$_2$OD</td>
<td>3.3</td>
<td>48.5</td>
<td>3279</td>
</tr>
<tr>
<td>(CD$_3$)$_2$SO</td>
<td>2.5</td>
<td>39.6</td>
<td>3350</td>
</tr>
<tr>
<td>(CD$_3$)$_2$CO</td>
<td>2.05</td>
<td>29.9</td>
<td>3393</td>
</tr>
<tr>
<td>CD$_3$COOD</td>
<td>2.0</td>
<td>21.1</td>
<td>3393</td>
</tr>
<tr>
<td>C$<em>6$D$</em>{12}$</td>
<td>1.4</td>
<td>26.1</td>
<td>3453</td>
</tr>
</tbody>
</table>

*02(TMS)$_{270} = 5x02$ (TMS)$_{90}$; these 02 values are given when the lock compound is used as solvent; The errors include deviations due to the use of a mixture of solvents and concentration effects.

As $\delta^H$ for the lock signal is a function of $F_2$(02), a plot of $\delta^H$ vs. $F_2$(02) will necessarily yield a straight line; it is true of course for $F_1$(01) as well. Such a plot may be used to derive the carrier positions for any other type of lock signal, provided $\delta^H$ for this signal is known. With this information the operator can easily optimize the $F_1$(01) position, and the spectral width under QPD mode of operation, or to choose the best $F_2$(02) position in SFORD experiments, without the need for frustrating and time consuming experiments every time different lock signal is used.

Please credit this modest contribution to the account of Dr. R. Poupko.

Sincerely,

Elisha Berman
January 28, 1977

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

RE: Phase Shifting of Broadband Transmitter

Dear Barry:

We have recently replaced the transmitter of our HXS-360 with a broadband scheme utilizing a Fluke radio frequency synthesizer and a Rockland audio frequency synthesizer. The mixing scheme is neither new nor unique but is very straightforward. The Fluke is single side band mixed with the Rockland (operating at 1.9 MHz) using broadband Merrimac quad hybrids. The final frequency is selectively amplified using an HP 230 tuned amplifier. This provides enough power for CW work. An ENI broadband power amplifier provides pulse power for FT. The system is now in use and works very well.

The feature I wished to bring to the attention of the newsletter readers is the versatile capabilities of the Rockland Model 5100 Frequency synthesizer. First, it has resolution to the nearest millihertz over its 0.001 to 2 MHz range. This feature combined with its ability to be programmed in binary by a computer provides the nmr system with a highly selective computer controlled frequency offset for FT work. Also, since the synthesizer has phase coherence from one programmed frequency to the next programmed frequency, computer controlled digital frequency sweeps are a simple matter of programming. In fact, the Rockland is so fast that the time limiting factor for the sweep is the computer.

Another great advantage of the Rockland is that a small modification allows the computer to control 90° and 180° phase shifts. This allows easy inclusion of the popular baseline correcting schemes and of quadrature detection image cancelling routines which are extremely convenient. Also T₂ measurements employing phase shifts (Modified Carr-Purcell Method) and echo cancelling T₁ measurements become readily available.
Dr. Bernard L. Shapiro
January 28, 1977

After getting the hardware and software together and debugged, the system has been doing very well. In the FT mode, quadrature detection images are never a problem and the baselines are considerably flatter.

In the CW mode, the correlation spectroscopy is working out very well. Fast reproducible sweeps of any sweep width are possible. Also a similar setup on the decoupling channel allows computer controlled decoupling.

In summary, our relatively simple-minded approach to a broad-banded transmitter is very versatile due to the capabilities of the Rockland synthesizer. Since the Rockland frequency is mixed onto a base rf frequency, the phase shifting is available even at 360 MHz, a frequency where phase shifting is normally more complicated than at lower frequencies.

Sincerely yours,

Oleg Taredzky

Woodrow W. Conover
Dr. B. L. Shapiro  
Department of Chemistry  
Texas A & M University  
College Station, Texas 77843 USA

Dear Dr. Shapiro:

High Resolution $^{13}$C Spectra in Oil Shale

Some time last spring we completed construction of our magic-angle-spinning proton enhanced $^{13}$C spectrometer. As evidence thereof we are pleased to submit the spectra, both with and without 2 kHz spinning, of a Laramie oil shale spinner; the spinner was machined directly from a lithic specimen. The best that could be done was to resolve the aromatic and aliphatic regions; this allows the fraction of each hydrocarbon component to be determined. The aromatic fraction is thus 0.24 ± .03; this fraction was found to be quite independent of cross polarization time between 0.1 and 10 msec for Hartmann-Hahn matching at rf fields of 40 kHz. The $T_1$ for the oil shale protons is about 100 msec, and $T_{1p}$ ~ 6 msec. Please credit this as Bill Moniz's subscription payment.

Sincerely,

A. N. Garwray

OIL SHALE

[Diagram showing spectra with ppm scale]
Professor Bernard L. Shapiro,
Department of Chemistry,
Texas A & M University,
College Station,
Texas 77843, U.S.A.

Dear Barry,

Selective deuterated enzymes: identification of ligand resonances by transfer of saturation

Our WH-270 has been operational for about six months now, and we have been continuing our studies of substrate and inhibitor binding to L-casei dihydrofolate reductase. In order to be able to describe the binding process in detail, we must be able to resolve as many resonances of individual amino-acid residues as possible. To this end, we have prepared a number of selectively deuterated analogues of the enzyme.

The spectrum shown is of an analogue in which all protons of the Phe, Trp and His residues had been replaced by deuterium, as had the 3,5-protons of the tyrosine residues. The sample contained two molar equivalents of the tightly-binding inhibitor trimethoprim; apart from the resonances of the excess free inhibitor, the only resonances visible in the aromatic region of the spectrum are five sharp lines, each corresponding to the 2,6-protons of a single tyrosine residue. As has been seen in other proteins, a single resonance is seen for both the 2- and 6-protons of each tyrosine residue, indicating relatively rapid rotation (or, more probably, 'flipping' through 180°) of the aromatic rings about their Cα-Cγ bonds. A paper describing the effects of ligand binding on the tyrosine residues, together with one on the histidine residues, is in press in the Proceedings of the Royal Society (ser.B) - preprints are available.

A further potential advantage in the use of selectively deuterated enzymes is that they should make it easier to observe the resonances of ligands bound to the enzyme when - as for trimethoprim - the exchange of the ligand between the free and the bound states is slow on the nmr timescale. Although the resonances of H6 and H2, + H6 of free trimethoprim are clearly seen in the spectrum, the corresponding resonances of bound trimethoprim are not obvious. Even a comparison with the spectrum of a similar sample containing 2',6'-deuterated trimethoprim did not allow us to identify the resonances of bound trimethoprim with any certainty. However, this
could be achieved by a transfer of saturation experiment. Thus irradiation at the frequency indicated by the arrow for 0.4 s immediately before the observing pulse led to a decrease of about 50% in the intensity of the $H_2^+ + H_4^-$ resonances of free trimethoprim. Similarly, the $H_6$ resonance of bound trimethoprim could be shown to lie under the highest-field tyrosine resonance. Both these resonances of bound trimethoprim, particularly that of the 2',6'-protons are thus substantially broadened. It is interesting that, while the resonance of $H_2^+ + H_4^-$ is shifted upfield 0.76 ppm on binding, the resonances of the nearby CH$_2$ and OCH$_3$ protons show essentially no shift.

For a system such as dihydrofolate reductase, where many of the ligands bind sufficiently tightly to be in slow exchange, we have found transfer of saturation to be extremely valuable for the identification of the resonances of bound ligands.

Yours sincerely,

G.C.K. Roberts  J. Feeney  J. O'Neill


The aromatic region of the 270 MHz $^1$H spectrum of a selectively deuterated analogue of L.casei dihydrofolate reductase in the presence of 2 molar equivalents of trimethoprim (1 mM enzyme, 0.35 ml, 2000 transients, 55°C). The H$_{6}$ and H$_{2}$+H$_{6}$' resonances of free trimethoprim are labelled; the remaining five sharp resonances are those of the 2,6-protons of the five tyrosine residues.
Dr. B.L. Shapiro  
Department of Chemistry  
Texas A and M University  
College Station, Texas  77843  

Dear Barry:  

During the past several months, we have been working here on 13C spectra of solids, using Proton Enhanced Nuclear Induction Spectroscopy and magic-angle spinning. Our spectrometer, home-built by Vic Bartuska, is based on an old HR-60 magnet.

One of the problems we have encountered in this work is measuring accurately and conveniently the spin-rate of the magic-angle spinner. Not only does one like to know the spin rate for which each 13C spectrum is obtained, but one wishes to be able to monitor progress in the development of magic-angle spinner designs. With the strobes available to us, even this last capability was neither convenient nor reliable. Vic solved this problem by using a Fairchild FPA 104 Light Reflection Emitter/Sensor Array, whose ir beam is modulated at the spinning rate of a rotor painted with a black mark. The modulated signal from the phototransistor is amplified, and the spinning rate is monitored either on a scope or on a counter. Use of a scope permits one to observe undesirable periodic motions.

Watch this space for further developments at the MHPL!

Sincerely,

Gary E. Maciel  
Professor  

Arrangement for Bench Testing  

Circuit Diagram
New 18-mm Probe for the XL-100

13C Spectra
10 Times Faster

Now Varian XL-100 users can run natural abundance 13C spectra at millimolar concentrations. Varian's new V-4418 Variable-Temperature Probe accommodates 18-millimeter sample tubes and boosts sensitivity to over three times that of the standard 12-mm probe. Compare the two spectra of 10 mM sucrose—clearly this new probe could extend the application of 13C NMR to entirely new areas of chemical research.

The V-4418 is Varian's latest offering to the scientist who needs 13C spectra of samples of limited solubility or limited molarity, or who studies certain equilibria and requires low concentration; or who works with relaxation properties that are best studied at low concentration. The V-4418 lets him use samples less concentrated by a factor of 3, or reduces the time required for an experiment by a factor of 10—with results second to none.

Not only is the absolute sensitivity of the V-4418 Probe outstanding, it also offers excellent sensitivity per milliliter of solution, an important asset if you study scarce or expensive (most often both) macromolecules. The Probe develops its full sensitivity potential with 6 milliliters, a volume only three times that required with the standard 12-mm probe!

And that's not all. When the V-4418 Probe is used together with the recently introduced single-sideband filter, overall sensitivity of the XL-100 increases by a factor of 5. Or, in terms of time savings, these combined capabilities reduce a formerly 24-hour experiment to a routine 1-hour run.

Compare these two broadband proton-decoupled carbon spectra of 10 mM sucrose in D2O, one using an 18-mm sample, the other the standard 12-mm sample. Data were accumulated for 4096 transients, with a one-second acquisition time and a 90° pulse.
The Record Proves ... For those who expect more in FT NMR Spectrometers ... it's JEOL

Low Cost — Routine 13C System
The FX60 features:
- 13C/H Dual Frequency 10, 5, 2mm V.T. Probes
- (LPCS) Light Pen Control System
- Built-in Proton-HOMO/HETERO decoupler
- RF crystal filter detection system
- 12 bit AD/DA for increased dynamic range
- INTERNAL and EXTERNAL locking modes
- 8, 16 and 32K word data collection
- Built-in Read/Write Cassette System
- 1H, 31P, 13N extensions are available

JEOL
Analytical Instruments, Inc.
235 Birchwood Ave., Cranford, NJ 07016
201—272—8820

Comprehensive 60 and 100 MHz Systems
The FX60Q & FX100 features:
- (DQD) DIGITAL Quadrature Detection System
- Dual Frequency variable temperature probes
- 4-channel DIGITAL phase shifters (DPS)
- Comprehensive auto-stacking system
- Computer based pulse programmer
- CPU Expandable to 65K words (MOS)
- 2-channel 12 bit AD/DA
- Tri-spin locking system
- Disc storage systems
- Multi-Frequency HOMO/HETERO decoupling capabilities
- Multi-Frequency observation

For detailed brochure, demonstration or information, phone or write ...