TEXAS A&M UNIVERSITY

# NMR NEWSLETTER

NO. 311

AUGUST 1984



continued on page (i)

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TEXAS A&M UNIVERSITY

NMR NEWSLETTER

All Newsletter Correspondence
Should be Addressed to:

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

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No. 313 -------- 1 October 1984

No. 314 -------- 5 November 1984

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**AUTHOR INDEX ------ TAMU NMR NEWSLETTER NO. 311, AUGUST 1984**





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ABBOTT

Abbott Laboratories
North Chicago, Illinois 60064

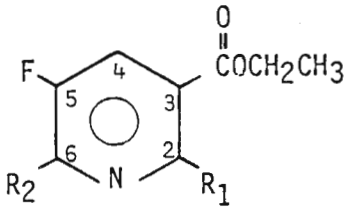
May 7, 1984

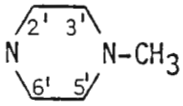
Dr. B.L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843

Structure Assignment of Three Related Compounds by $^{13}C$ NMR

Dear Barry:

Three compounds came through the NMR laboratory recently for structure assignment:




1 $R_1$ = Cl, $R_2$ = 

2 $R_1$ =  , $R_2$ = Cl

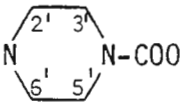
3 $R_1$ = Cl, $R_2$ = 

Table I shows the carbon chemical shifts for the three compounds and the carbon-fluorine coupling. Assignments were made by comparison with model compounds and with each other. In compounds 1 and 3, C-2' and C-6' show carbon-fluorine coupling which aided in the assignment. These two compounds were run at a different field strength to confirm that it was indeed four bond carbon-fluorine coupling and not non-equivalence as was originally suspected.

Sincerely,

R. Stanaszek
E. Gracey
Abbott Laboratories

RS:EG:dmh

Table I

| Carbon | Chemical Shift ppm | | | $^{13}C$-$^{19}F$ Coupling Hz | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 |
| O ‖ C | 163.4 | 165.0 | 163.2 | ----- | ----- | ----- |
| O ‖ C | ----- | ----- | 155.3 | ----- | ----- | ----- |
| C-2 | 143.6 | 155.0 | ----- | ----- | ----- | ----- |
| C-3 | 114.2 | 112.7 | 114.9 | ----- | ----- | ----- |
| C-4 | 127.6 | 129.0 | 128.5 | 23.2 | 22.0 | 23.2 |
| C-5 | 145.8 | 147.5 | 146.0 | 255.1 | 251.5 | 255.1 |
| C-6 | 148.9 | 138.5 | 148.8 | 7.3 | 19.5 | 7.1 |
| $OCH_2$ | 61.2 | 61.5 | 61.6[a] | ----- | ----- | ----- |
| $OCH_2$ | ----- | ----- | 61.4[a] | ----- | ----- | ----- |
| C-3', C-5' | 54.9 | 54.7 | 43.5 | ----- | ----- | ----- |
| C-2', C-6' | 46.6 | 49.4 | 46.6 | 8.6 | ----- | 7.3 |
| $N\text{-}CH_3$ | 46.0 | 46.0 | ---- | ----- | ----- | ----- |
| $CH_3$ | 14.3 | 14.2 | 14.7[b] | ----- | ----- | ----- |
| $CH_3$ | ---- | ---- | 14.3[b] | ----- | ----- | ----- |

a and b = Assignments may be interchanged.

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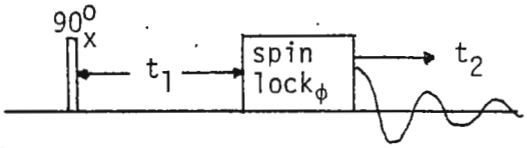
Dr. Bernard L. Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A&M University
College Station, Texas 77843

Dear Barry:

One experiment that has not yet received the attention it deserves is the two-dimensional CAMELSPIN experiment, proposed by Aksel Bothner-By and co-workers (1). This experiment measures cross-relaxation in the rotating frame. As the rotating frame cross relaxation effect is positive for all motional correlation times, the method is especially well suited for the study of compounds that have a near-zero normal NOE effect.




However, there are two potential dangers connected to this experiment. First, the obvious risk is to overheat the probe by the long spin-lock pulse. It appears, however, that a rather low rf power can be used; $\gamma H_1/2\pi$ on the order of the spectral width turns out to be sufficient if quadrature detection is used. The less obvious danger comes from coherent transfer. For very short durations of the spin-lock pulse, the experiment is identical to the familiar COSY experiment. Naively, one might assume that for durations of the spin-lock pulse greater than 10 ms, all coherent transfer is defocused by rf inhomogeneity. However, we all know that in the COSY experiment the data for the $90^\circ_x$-$t_1$-$90^\circ_x$-Acq. and $90^\circ_x$-$t_1$-$90^\circ_{-x}$-Acq. are co-added with identical receiver phase. Since, in principle, the effect of a $90^\circ_{-x}$ and a $270^\circ_x$ pulse is identical, this already suggests that the sign of the transferred magnetization must be identical for a $90^\circ_x$ and a $270^\circ_x$ pulse. More general, magnetization transferred from A to X by an $\alpha$ mixing pulse is proportional to $\sin^2\alpha$. Therefore, an inhomogeneous "$100\pi$" mixing pulse in the COSY experiment causes $\overline{\sin^2\alpha} = 0.5$ of the cross-peak intensity seen in a normal 90°-$t_1$-90°-Acq COSY. The way to distinguish COSY and cross-relaxation effects in a CAMELSPIN spectrum (or in a regular 2D NOE experiment) is simple: the spectrum should be recorded in the 2D absorption mode, and the phase-sensitive integral over the cross multiplet should be taken. The COSY multiplet has zero total intensity due to the antiphase nature of the multiplet components and does not contribute to the phase-sensitive integration. Other ways to suppress coherent transfer in a CAMELSPIN experiment and a more detailed account of the whole story will appear at the usual place.

Just as an example, the accompanying figure shows some cross sections through the 2D absorption CAMELSPIN spectrum, obtained with a 600 ms spin-lock pulse. The cross-peaks have an intensity of only several % of the diagonal peaks, and small phase errors cause relatively large baseline anomalies. Therefore it is difficult to visualize cross peaks lower than 0.5% in a 2D contour plot presentation, whereas in cross-sections they are easily recognized.

Kindest regards,

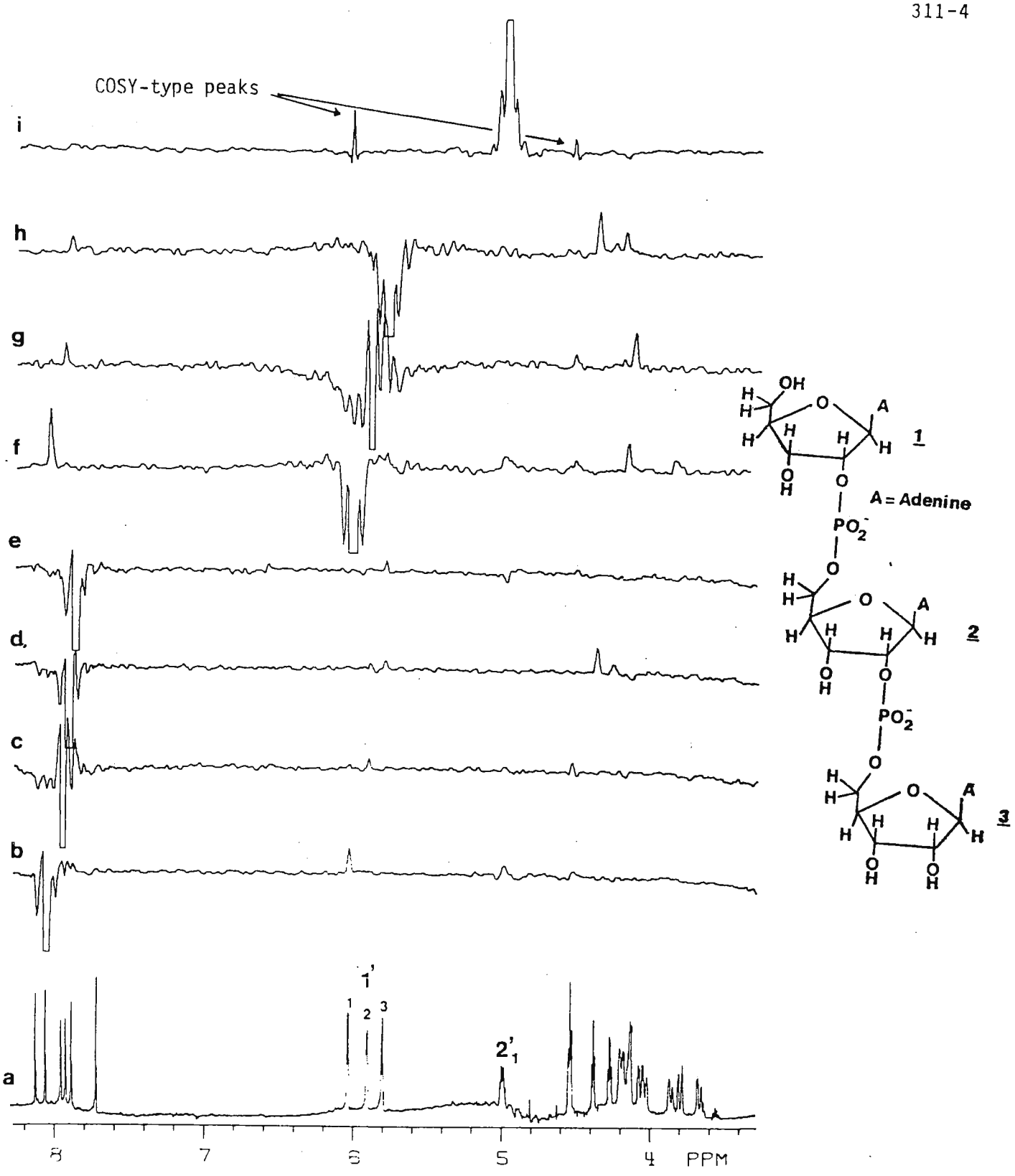
Ad

Ad Bax

R. Tschudin

Rolf Tschudin

(1) A. A. Bothner-By, R. L. Stephens, J. Lee, C. D. Warren and R. W. Jeanloz, J. Am. Chem. Soc. 106, 811 (1984).




(a) The regular $^{1}H$ spectrum of A2'-5'A-2'-5'A. (b-h) Cross-sections parallel to the F1 axis through the 2D absorption CAMELSPIN spectrum taken at the chemical shifts of H8(1), H8(3), H8(2), 1'(1), 1'(2) and 1'(3). For example, (b) shows the NOE effect between H8 of the adenine connected to ribose 1 and proton 1' of this ribose unit. (i) A cross-section taken through 2'(1) of a CAMELSPIN spectrum obtained with a 30 ms spin lock, showing the cross-peaks, with 1'(1) and 3'(1), which are due to coherent transfer.

GRIFFITH UNIVERSITY

**Nathan, Brisbane, Queensland, Australia, 4111.**

**Telephone (07) 275 7111. Telegrams Unigriff Brisbane Telex AA40362**

**Brisbane NMR Centre**

**Ref:** PFB:ss
**Please Contact:**
**Telephone:** 2757636

11th July, 1984.

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

Dear Prof. Shapiro,

$^{29}$Si NMR of 2:1 Phyllosilicates

As part of our continuing work on the 2:1 layer silicates by $^{29}$Si and $^{27}$Al NMR we have recently looked at the sepiolite and palygorskite minerals. The structures are based upon an octahedral magnesium layer sandwiched between two silicate sheets. However, these minerals differ in that the sheets are in fact ribbons as they are continuous in only one dimension and have a set width in terms of number of silicate units across in the other dimension. A representation of the structure of sepiolite, in which the ribbon is twelve silicate and eight magnesium units wide, is shown in the attached figure. These ribbons are inter-connected via inverted Si-O-Si linkages which results in the presence of open channels containing hydrogen bonded water.

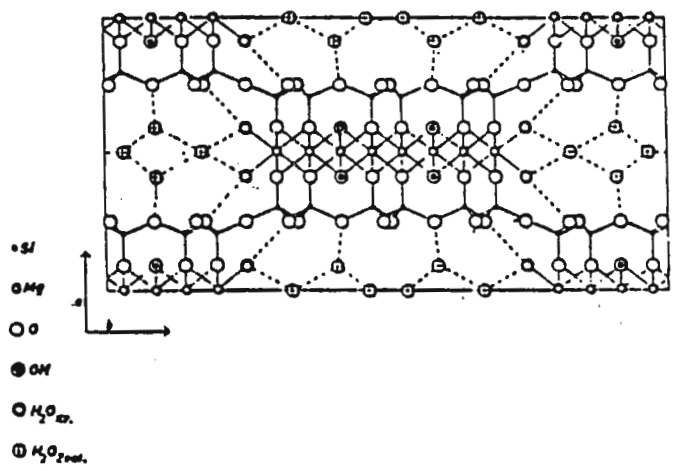
This structure has three distinct types of silicate units across the ribbons and hence three $Q^3(0Al)$ $^{29}$Si resonances are observed at -93, -95 and -98 ppm. This corresponds well with the range observed for $Q^3(0Al)$ resonances in normal 2:1 layer magnesium silicates, i.e. -98 ppm for talc and -92 ppm for vermiculite with moderate degree of tetrahedral Al substitution. The shifts to lower field in sepiolite relative to talc can't be due to the effect of Al substitution and are more likely to be the result of the presence of hydrogen bonded water and/or unusual bond angles or distances. Removal of the interchannel water, except for those molecules at the edge of the octahedral sheet, by heating results in the shift of the central resonance to -97 ppm. The effect on the other two resonances is much smaller. As the residual water molecules are hydrogen bonded to the basal oxygens between the two outermost

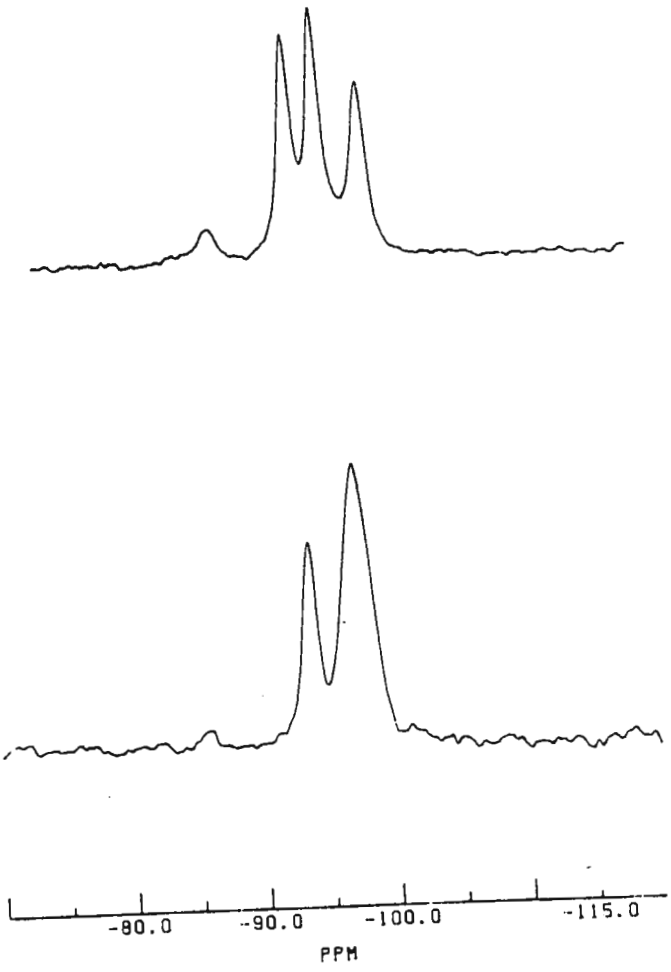
silicate units of adjacent ribbons, the central unit is likely to be most affected by dehydration and can thus be assigned to the -95 ppm resonance. The remaining two resonances can be assigned by noting the slightly lower intensity of the highest field signal and the presence of a weaker signal at -85 ppm. This small resonance is due to $Q^2$ SiOH groups at crystal defects and edges of ribbons. Hence the resonance at -98 ppm of slightly reduced intensity is due to the ribbon edge silicate units.

A detailed discussion of the spectra of sepiolite and palygorskite are the subject of a recently submitted paper. One further point worth noting is that the presence of the channel water molecules results in a dipolar contribution to relaxation and an observable $^{1}H$-$^{29}Si$ NOE. Please credit this contribution to David Doddrell's account.

Yours faithfully,

Peter Barron.


Si
Mg
O
OH
$H_2O_{str.}$
$H_2O_{zeol.}$
a
b


-80.0
-90.0
-100.0
-115.0
PPM

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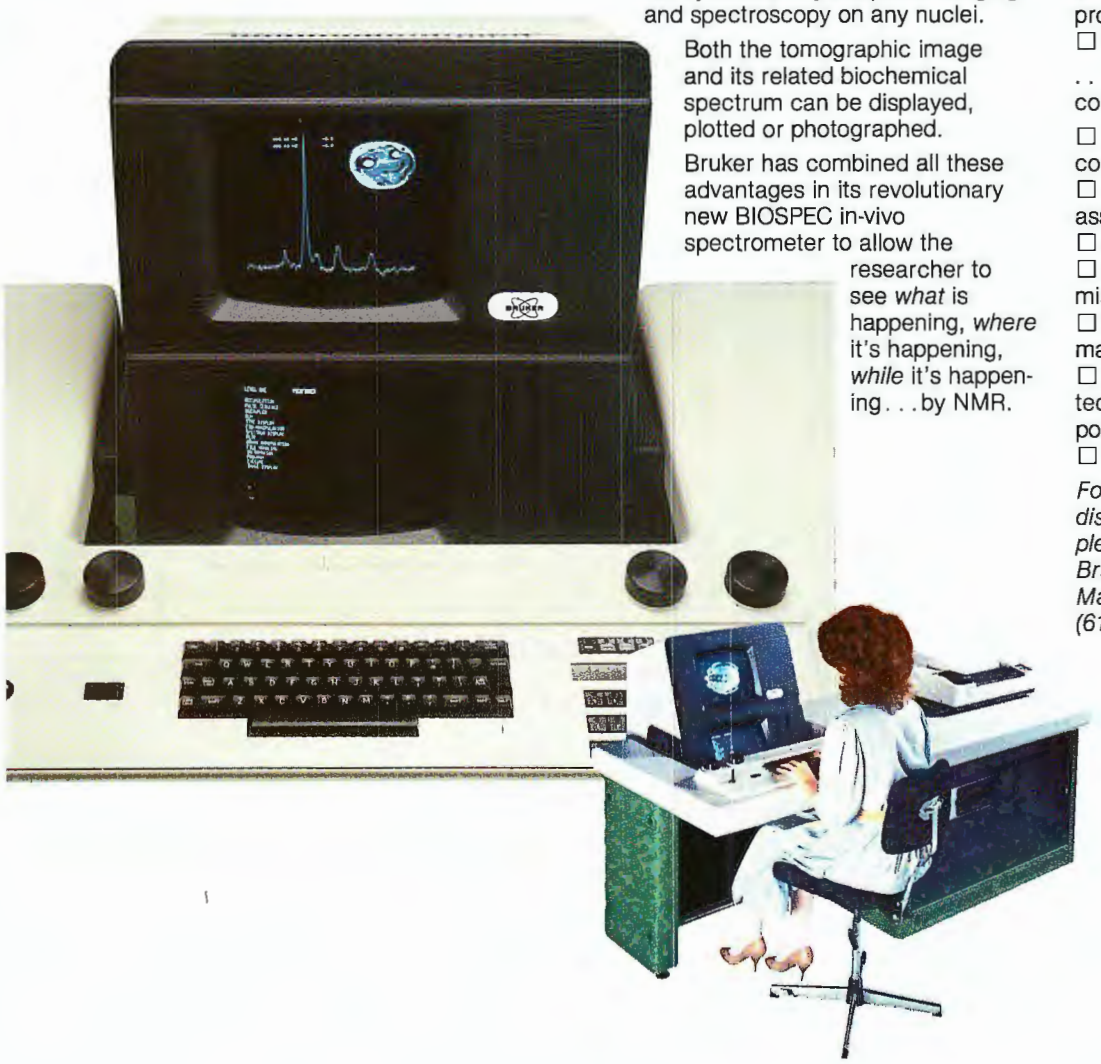

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# Oklahoma State University

*Department of Chemistry / (405) 624-5920 / Stillwater, Oklahoma 74078*

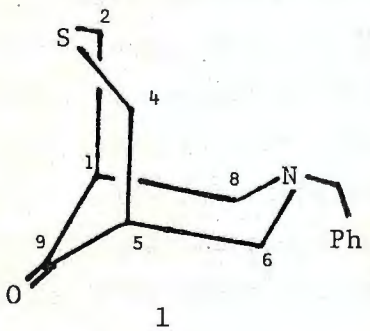

June 21, 1984

Dr. B. L Shapiro
Department of Chemistry
Texas A & M UNiversity
College Station, TEXAS 77843-3255

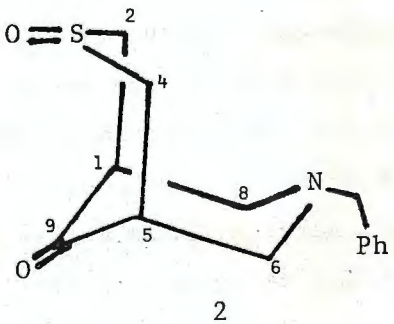
TITLE: Chair-Boat N-Alkyl-3-thia-7-azabicyclo[3.3.1]nonan-9-ones: shielding Characteristics on the 9-Position

Dear Barry:

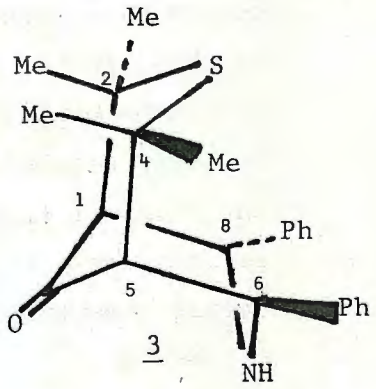
We have been investigating the $^{13}C$ NMR characteristics of the title compounds and have discovered some very interesting features regarding the shifts of C(9). For example in 1, the shift for C(9) was 212.8 ppm [$DCCl_3$, from TMS][1] while we have found that 2 and 3 upfield. The S=O bond in 2 is in particular probably the single




1




2




3

most important influence upon the C(9) resonance in the boat conformer. This type of affect is expected but rarely documented. In fact, we have not found any examples in the literature in these systems. In 3, the thianone system is a chair but the boat piperidone system does cause some shielding of C(9) compared to that observed in 1. We suspect that the C(9) signal in 3-thia-7-azabicyclo[3.3.1]nonan-9-ones can be of diagnostic value in determining the presence of a boat form. We are continuing our work in this field.

Sincerely yours,

Darnell

K. D. Berlin
Regents Professor

Reference

B. R. Bailey and Co-workers, J. Med. Chem. 1984, 27, 758.

311-11

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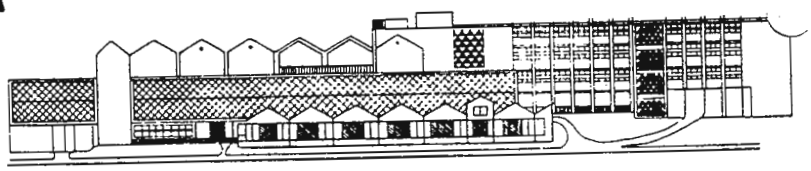

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26th June 1984.

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

Dear Professor Shapiro,

Palmitoleic Acid in the Triglycerides of Palm Oil

The common oil palm trees planted in Malaysia is of the tenera type (species Elaeis guineensis) and the oil from the fruit of this species contains only an average of 0.1% of palmitoleic (cis-9-hexadecenoic) acid (C16:1), an amount which is too small for easy detection in the $^{13}C$ spectrum of the oil. However, in the palm oil from the fruit of the species Elaeis oleifera, which is indigenous to South America, palmitoleic acid is present in larger amounts, about 2%, an amount no less than that found in cotton oil.

Figure 1 shows that the two olefinic carbons of palmitoleic (PO) acid in the triglycerides of palm oil appear at $\delta$ 129.51 and 129.42, in between the resonances of C-10 and C-9 of oleic acid at $\delta$ 129.60 and 129.29, respectively. The PO peaks are not sufficiently well resolved to permit assignment of the PO chains to the glycerol positions.

Yours sincerely,

Soon Ng

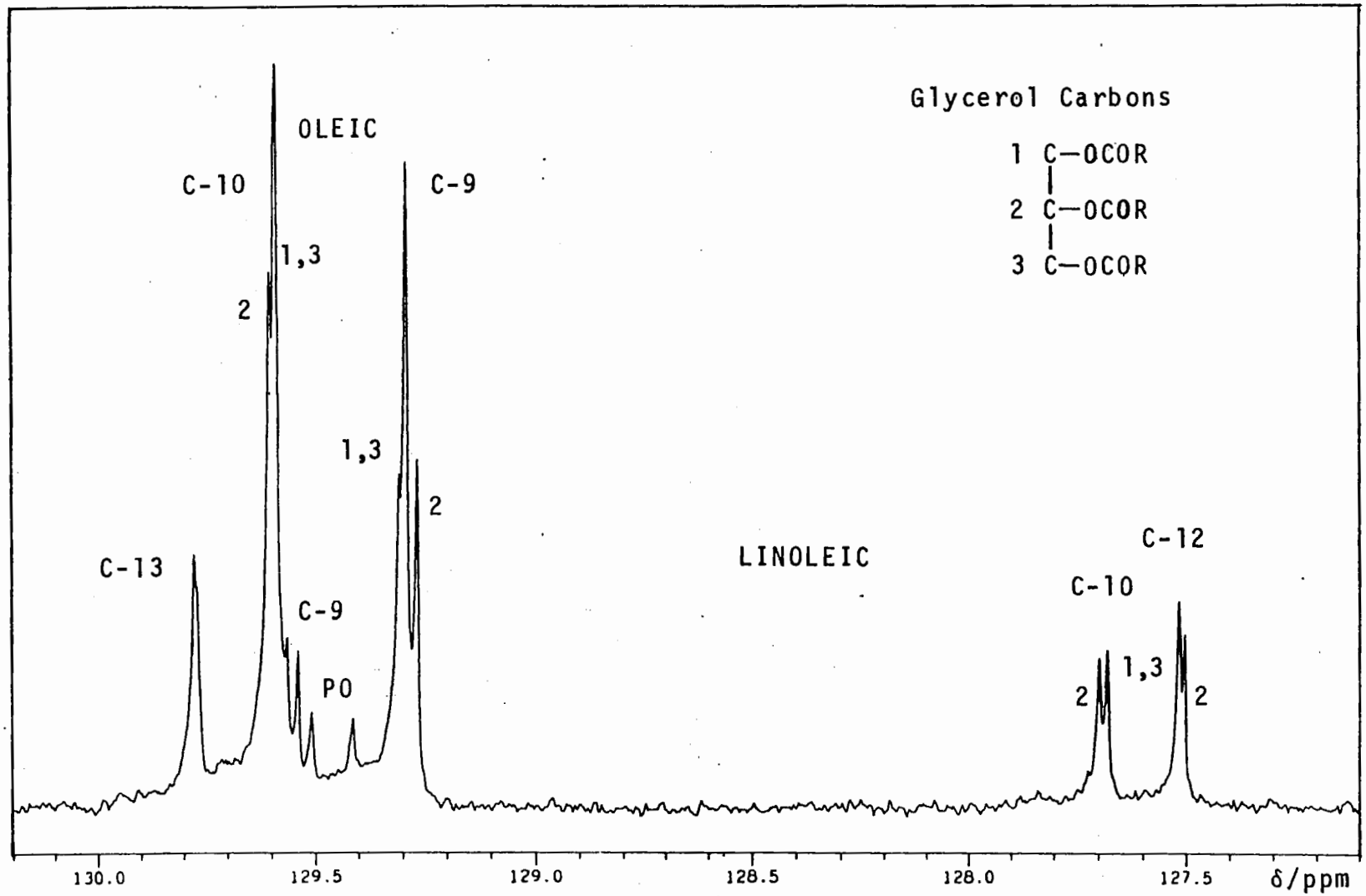


Fig. 1. 100 MHz $^{13}C$ nmr spectrum of the olefinic carbons of the fatty acids in the triglycerides of the palm oil from the fruit of the species Elaeis oleifera. The olefinic carbon of the fatty acid chain (oleic or linoleic) attached to the 2-glycerol carbon can be distinguished from that of the chain attached to the 1- and/or 3-glycerol carbons (labelled 2 and 1,3 respectively). For details refer to paper in Lipids 19, 56-59 (1984). The C-10 and C-9 signals from the palmitoelic acid are labelled PO.

DEPARTMENT OF ORGANIC CHEMISTRY
THE ROBERT ROBINSON LABORATORIES P.O. BOX 147 LIVERPOOL L69 3BX
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The University of Liverpool

28th June, 1984

RJA/AS

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

Dear Barry,

CHARGE CALCULATIONS AND N.M.R. SHIFTS

In reply to your green reminder, TAMU NMR readers may be interested in some of our recent results on charge calculations.

The question of N.M.R. shifts and their correlation (or lack of it) with electron densities is bedevilled, not only by the possibility of other mechanisms affecting the chemical shifts, but also by the lack of any accepted method of obtaining the required partial atomic charges, particularly for $\sigma$ electrons. The Mulliken population analysis, on which most of the quantum mechanical charges are based, has been repeatedly questioned, and the estimation of charges from the electrostatic potentials does not always lead to convincing results.

Thus, we have been developing a scheme of partial atomic charges, mainly for use in M.M. calculations, based on chemical concepts (e.g.[1], inductive effects) and parameterised on the observed dipole moments.[2] Recently we have extended this scheme to include resonance effects[3] and charged atoms,[3] so that it is now capable of handling any peptide or protein fragment. As a by-product of these calculations, we find that both the $^{13}C$ and also more interestingly the $^{1}H$ chemical shifts in amino-acid residues show a very good correlation with the calculated partial atomic charges.

For the atoms of amino-acids side-chains in $D_2O$, we obtain

$\delta_C = 233q + 39.5$ st.dev 5,94, corr.coeff 0.92

and $\delta_H = 100q - 2.52$ st.dev 0.38, corr.coeff 0.95

over ranges of 10 - 70 $\delta$ ($^{13}C$) and 1 - 5 $\delta$ ($^{1}H$), where q is the partial atomic charge in positions. The corresponding standard deviations and correlation coefficients using CNDO charges are for the carbon atoms 9.75 and 0.77. For the hydrogens the CNDO charges show no correlation whatsoever.

These results support those of Gasteiger and Marsili for alkyl halides using a similar scheme based on orbital electronegativity, they obtained $\delta_H \approx 106.4 q_H$ in surprisingly good agreement.

With best wishes,

Yours sincerely,

pp Surpass (Secretary)

pp DR. R.J. ABRAHAM


1. R.J.Abraham, L.Griffiths and P. Loftus, *J.Comp.Chem.*, 3, 407 (1982).
2. R.J.Abraham and B.Hudson, *ibid.*, (in press).
3. R.J.Abraham and B.Hudson, manuscript in preparation.
4. J.Gasteiger and M.Marsili, *Org.Mag.Res.*, 15, 353 (1981).


---

**NMR SPECTROSCOPIST**

The NSF Regional Instrumentation Facility in NMR at the University of South Carolina is seeking qualified applicants for the position of Facility Manager. Applicants should have a Ph.D. in chemistry with extensive hands-on experience in the applications of high field, high resolution FT nmr. Successful candidates should be knowledgeable with a variety of 2-D nmr techniques and the nmr of non-routine nuclei (for example Cd-113, Se-77, Li-7, etc.)

The principle instrument at the RIF is a fully multinuclear Bruker WH400. Experience with the current version of DISNMRP is therefore highly recommended. Salary is commensurate with experience in the $19-23k range. Position available Sept. 1, 1984.

Send resumé and three letters of recommendation to:

Dr. P. D. Ellis
South Carolina Magnetic Resonance Laboratory
University of South Carolina
Columbia, South Carolina 29208

**DEPARTMENT OF HEALTH & HUMAN SERVICES** Public Health Service

National Institutes of Health
Bethesda, Maryland 20205
Building : 30
Room : 106
(301) 496- 4563

June 28, 1984

Professor Bernard L. Shapiro
Editor, TAMU NMR Newsletter
Department of Chemistry
Texas A&M University
College Station, Texas 77843-3255

Dear Professor Shapiro,

We are using $^{19}F$ NMR at 470 MHz to study phenylalanine ring dynamics in solid p-fluoro-D,L-[2,3,5,6-$^{2}H_4$]phenylalanine. The room temperature spectrum, Fig. 1A (obtained by a phase cycled Hahn echo, EXORCYCLE, pulse sequence) is an axially asymmetric chemical shift powder lineshape having $\sigma_{33} - \sigma_{11} = 120$ ppm. At 143°C, Fig. 1B, the lineshape has narrowed, $\sigma_{33} - \sigma_{11} = 100$ ppm, since molecular motion averages the static values of $\sigma_{33}$ and $\sigma_{11}$. The motion leaves $\sigma_{22}$ unchanged. Although $^{2}H$ spectra show that the ring undergoes rapid 180° flips along the $C_1$-$C_4$ axis at 143°C, this motion will not affect the chemical shift $^{19}F$ powder pattern since single crystal $^{2}H$ and $^{19}F$ NMR spectra show that the $^{19}F$ shift tensor is orientated as shown in Figure 2. The reduction of the $^{19}F$ powder linewidth at 143°C, therefore, results from small amplitude ($\theta_{rms}$ ~17°) orientation of the ring about the 1-4 symmetry axis.

$^{19}F$ spectra were obtained with a home-built probe on a NIC-500 high resolution spectrometer interfaced to a Nicolet 2090 explorer scope. The probe contains 4 mm or 5 mm (I.D.) solenoid coil (5 turns) with two variable capacitors. In the course of this experiment we found an audio frequency stage ring down lasting about 6 μs whenever the receiver gate was turned on. In order to overcome this problem we have to put the data acquisition command "A" in a pulse sequence as early as possible.

Sincerely yours,

Dennis A. Torchia

Dennis A. Torchia, Ph.D.

Yukio Hiyama

Yukio Hiyama, Ph.D.
Mineralized Tissue Research Branch
National Institute of Dental Research

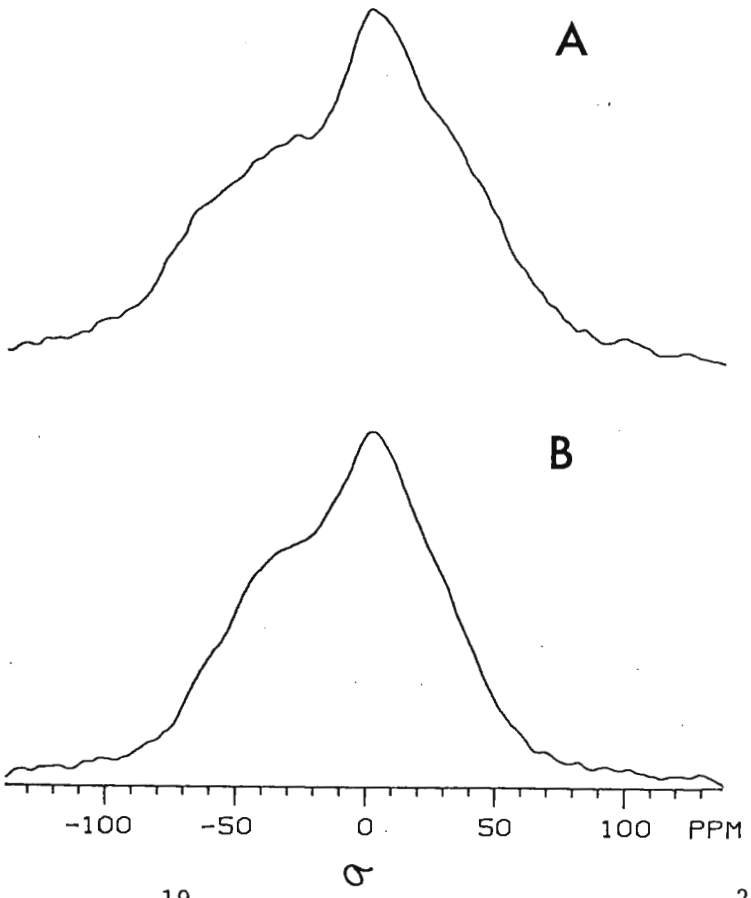



Fig. 1. Powder $^{19}F$ NMR spectra of p-fluoro-[2,3,5,6-$^{2}H_4$]D,L-phenylalanine. A: room temperature, B: 143°C. 90° pulse ~2.5 μs.

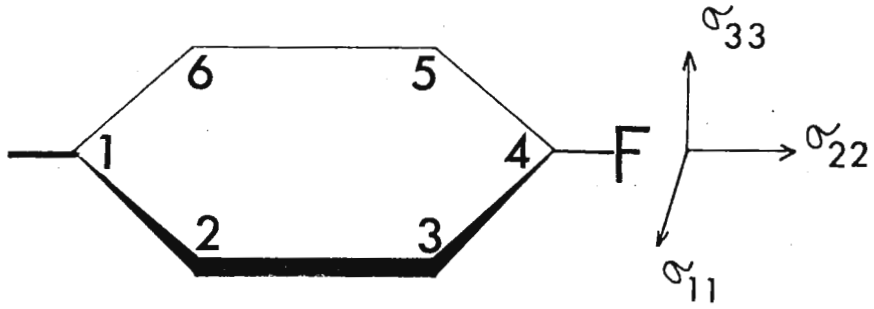



Fig. 2. Orientation of $^{19}F$ chemical shift tensor in p-fluoro-D,L-phenylalanine. $\sigma_{33} > \sigma_{22} > \sigma_{11}$.

311-17

**Varian** / 611 Hansen Way / P.O. Box 10800 / Palo Alto / California 94303 / U.S.A.
Tel. (415) 493-4000
Telex 348476

varian

June 27, 1984

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

Frequency Cycling In NOE Difference Spectra On XL-Series Spectrometers

Dear Barry,

XL-Series users may be interested in using frequency-cycled irradiation for NOE difference experiments (as recently described by Kinns and Sanders - J. Magn. Reson. 56, 518 (1984). In this experiment the decoupler is rapidly cycled through a table of user-enterable decoupler frequencies during the saturation period. The advantage is that lower powers may be used, producing better saturation of the desired multiplet and minimal saturation of nearby resonances.

As an example of this, Figure 1 show the normal power level necessary to saturate $H_b$ using only one decoupler frequency setting. This power is necessary for covering a multiplet spreading over 25Hz. Unfortunately, this partially saturates the other protons, complicating the real NOE observed for $H_a$. A small NOE for $H_c$ is totally obscured. It is necessary to attenuate the power to 21 db to avoid this neighbor saturation, but this only partially saturates $H_b$, giving poor sensitivity in the NOE difference spectrum (figure 2). At the same power level frequency cycling gives good saturation of $H_b$ and a good NOE difference spectrum (figure 3).

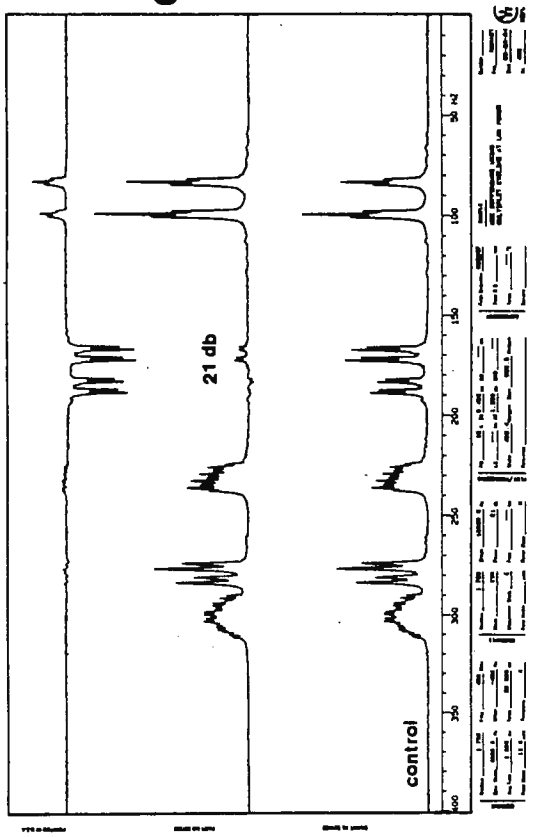
The pulse sequence source code is given for the case of 4 frequencies. The user may increase this, if desired, by modifying the code before compiling. The flag VARDO allows the cycling of decoupler offset when set to 'Y' and normal operation when set to 'N'. The parameter "N" determines the number of cycles during the saturation delay. The "OFFRES" parameter should be set far enough away for no NOE. Since DO is still available as a decoupler frequency offset during acquisition, it is possible to homodecouple some other proton during both acquisitions to simplify overlapping multiplets for a more accurate NOE determination.

Sincerely yours,

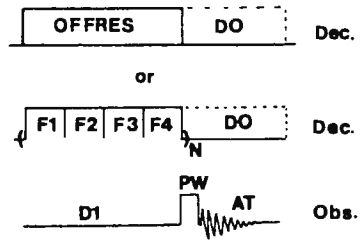
George

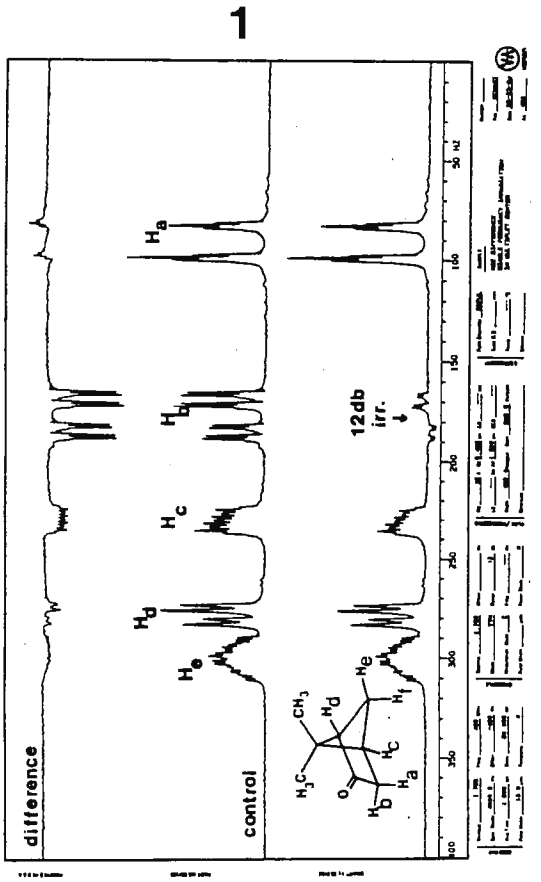
George Gray
NMR Applications Laboratory

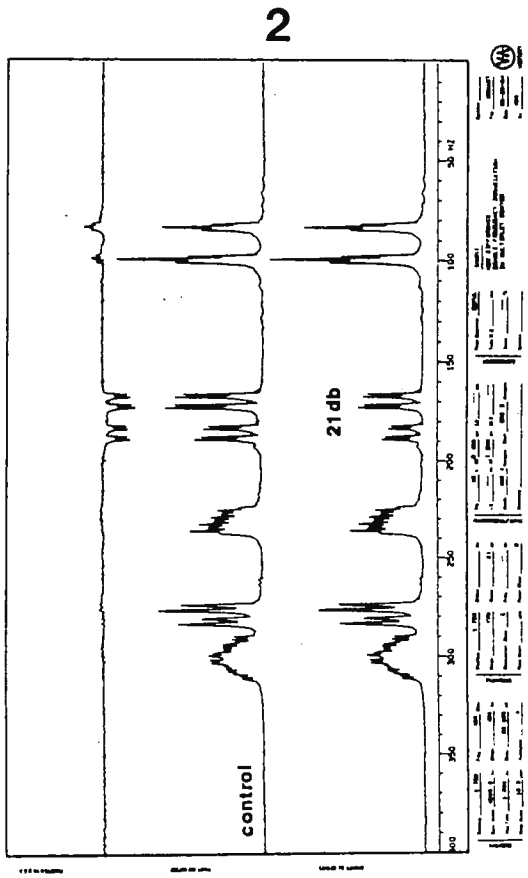
GG/tt
Enclosures




```
"NOE DIFFERENCE WITH DECOUPLER OFFSET CYCLING
 WITHIN A MULTIPLET. SET F1,F2,F3,F4 TO MULTIPLET
 FREQUENCIES FOR UP TO QUARTETS. VARDO FLAG ALLOWS
 ARRAYING BY VARDO(i)='Y',N TO PROVIDE UNPERTURBED
 SPECTRUM FOR SUBTRACTION"
"G.GRAY, 6/21/84. BASED ON M.KINNS AND J.K.M.SANDERS,
 J.MAGN.RESONANCE,56,518(1984)"

PROCEDURE PULSESEQUENCE;
   VAR OFFRES,F,N,F1,F2,F3,F4:REAL;
       VARDO:TEXT4;

BEGIN
   GETVAL(OFFRES,'OFFRES');
   GETVAL(N,'N      ');
   GETVAL(F1,'F1     ');
   GETVAL(F2,'F2     ');
   GETVAL(F3,'F3     ');
   GETVAL(F4,'F4     ');
   GETVAL(VARDO,'VARDO ');
   F:=D1/(4.0*N);
"CHOICE OF SEQUENCE"
 IF VARDO[1]='Y'
  THEN BEGIN
    STATUS(A);
    LOOP(i,N,VI);
     OFFSET(F1,i);
     DELAY(F);
     OFFSET(F2,i);
     DELAY(F);
     OFFSET(F3,i);
     DELAY(F);
     OFFSET(F4,i);
     DELAY(F);
    ENDLOOP(i);
   OFFSET(DOR,i);
 END  ELSE
    BEGIN
     OFFSET(OFFRES,i);
     DELAY(D1);
     OFFSET(DOR,i);
    END;
"OBSERVE PERIOD"
 STATUS(B);
 OBSPULSE;

END;
```



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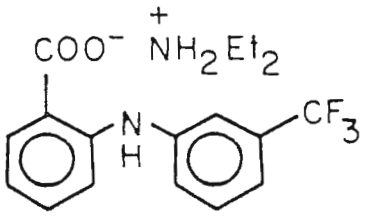
ISOTOPE DEPARTMENT מחלקת איזוטופים
Direct phone : (054)8 טלפון ישיר : (054)8

July 12, 1984

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

Dear Barry:

Recently we became interested in deuterium NMR studies of lyotropic mesophases formed by uncommon amphiphiles.[1] The present letter is concerned with the mesophases formed in mixtures of diethylammonium flufenaminate (DEAF) and water.




Eckert and Fischer[2] have shown that such mixtures form lyomesophases over a wide concentration (2.5 to 60 wt.% DEAF) and temperature (up to ~60°C) ranges. Depending on the concentration, two different mesophases are formed which were suggested by Eckert and Fischer to consist of spherical lamellae (below 20 wt.% DEAF) and planar lamellae (above 20 wt.% DEAF). We used deuterium NMR of specifically deuterated DEAF to confirm these findings and to study the ordering characteristics of the DEAF-water lyomesophases. The spectra shown in Fig. 1 are of a 30 wt.% solution containing deuterated DEAF as indicated in the figure. The assignment is based on comparison with spectra of various specifically labelled molecules. As may be seen sharp doublets are obtained for each deuteron with splittings ranging between 5 kHz and 60 kHz. These results and additional experiments support the suggested lamellar structure of Eckert and Fischer and indicate that the phase is uniaxial of type I, with a high degree of molecular orientation.

When the concentration of the solution is gradually decreased, there is a sudden change in the spectral lineshape at around 20 wt.% DEAF. This is demonstrated in the series of spectra shown in Fig. 2, which correspond to a singly labelled DEAF molecule ($5d_1$) at 30°C. It may be seen that between 20 and 15 wt.% DEAF the simple sharp peak spectrum (labelled p) is transformed into a powder-like spectrum (labelled s) which exhibits both parallel and perpendicular features. Such spectra are indeed expected from large micelles whose rate of reorientation is slow on

the NMR timescale. It may be seen that the relative intensities of the parallel and perpendicular features depend on the DEAF concentration apparently due to a concomitant change in the shape of the micelles. A more detailed description of this work will soon be submitted for publication in collaboration with Z. Luz and H. Zimmermann.

Yours sincerely,

I. Kustanovich R. Poupko


1. D. Goldfarb, M.M. Labes, Z. Luz and R. Poupko, Molec. Cryst. Liq. Cryst. 87, 259 (1982).

2. T. Eckert and W. Fischer, Colloid and Polymer Sci. 259, 553 (1981).

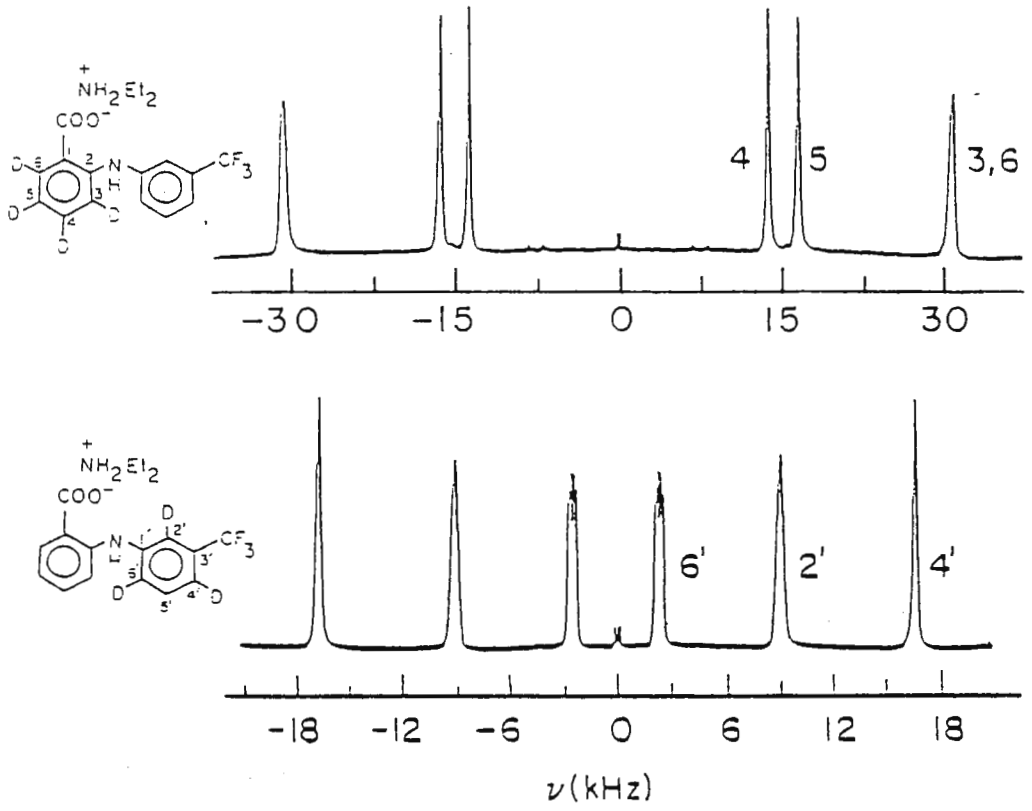




Figure 1. Deuterium NMR of deuterated DEAF (30 wt.%). The two spectra were taken at 50°C and correspond to the isotopic species indicated in the figure.

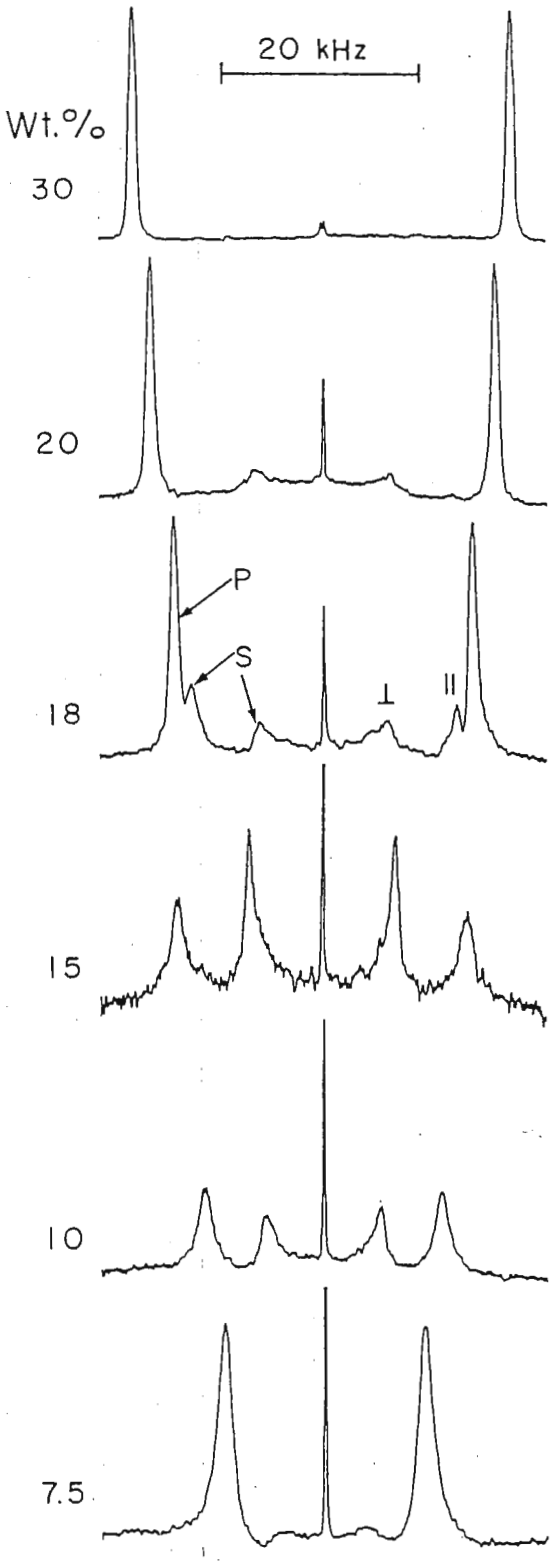
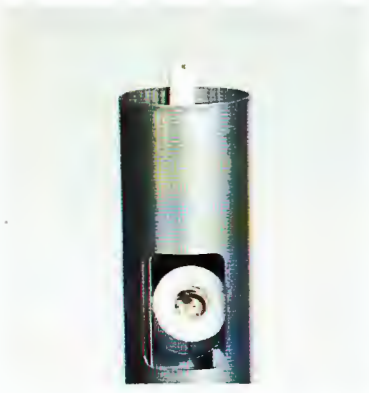



Figure 2. Deuterium NMR of DEAF-5$d_1$ in mesophases containing different DEAF concentrations as indicated in the figure. The letters p and s label the spectra from the two forms of the mesophases.



# m-100S:

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$^{13}C$ CP/MAS OBSERVATION IN A 54 mm BORE
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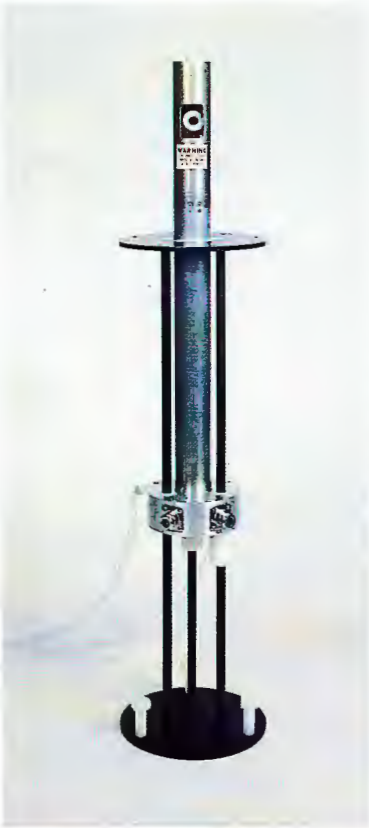

**SPECIFICATIONS:**

**He Refill Time:** >60 Days.
**$N_2$ Refill Time:** >8 Days.
**Resolution:** $^{13}C$ Adamantane CP/MAS Observation.
<8 Hz (1/3 ppm) for Narrow Bore Magnet.
<5 Hz (1/5 ppm) for Medium Bore Magnet.
**Sensitivity:** $^{13}C$ Hexamethylbenzene.
>90:1, 12 Scans
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Southern Research Institute

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2000 NINTH AVENUE SOUTH
BIRMINGHAM, ALABAMA 35255
TELEPHONE 205-323-6592

August 2, 1984

Professor Bernard L. Shapiro
Department of Chemistry
Room 120, Chemistry Building
Texas A & M University
College Station, Texas 77843

Dear Professor Shapiro:

We would appreciate your running the following advertisement in the next issue of the Newsletter. Martha tells me we might make the issue coming out next week.

NMR Position Available

We have an opening starting Oct. 1, 1984, for a NMR spectroscopist at Southern Research Institute. Applicants should have a Ph.D. in chemistry with experience in modern pulse techniques. Some knowledge of infrared, electronic, and mass spectroscopy would be a plus. SRI has a Nicolet 300NB, an XL-100, and a T-60A. The primary responsibility is to run and interpret spectra for our synthetic organic chemists. With suitable grant support a research program could be developed. Submit resume' and salary requirements to: Personnel Office, Southern Research Institute, P. O. Box 55305, Birmingham, AL 35255-5305. U. S. citizenship is required. SRI is an affirmative action/equal opportunity employer.

Sincerely yours,

W. C. Coburn Jr.

W. C. Coburn Jr., Ph.D., Head
Molecular Spectroscopy Section

WCC/cpm

311-25

THE UNIVERSITY OF ILLINOIS AT CHICAGO

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July 6, 1984

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

Subject: Improved response with T^P on the Nicolet Spectrometers and modification of our April 6, 1983 letter on floor vibration.

Dear Dr. Shapiro:

Our Nicolet 360 and 200 spectrometers came equipped with a tuning procedure that enabled us to readily adjust the match and tune of the probes while observing the response on the raster. The procedure worked well except when tuning H-1 on either instrument. For H-1 the output from the tuning bridge was too low, resulting in a display as in Fig.1. To improve the procedure, Mike added a DC Amplifier (Gain 0.5 to 3000) after the output of the tuning bridge using the +/- 15 Volt supplied in the probe interface box.

Now to tune from H-1 to at least N-14 on either instrument the user simply adjusts the gain on the DC Amp to get the display as in Fig.2.

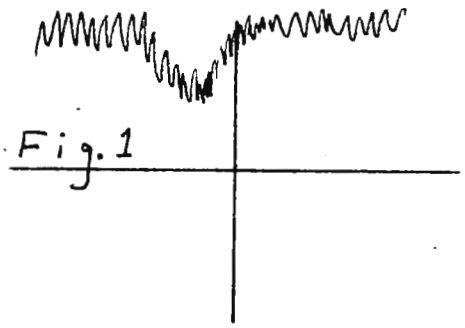
In our letter of April 6, 1983 we stated that we had reduced floor vibration problems by a factor of 100. Subsequent tests have shown great variation in the results but the more accurate reduction in the problem is by a factor of 5 not 100.

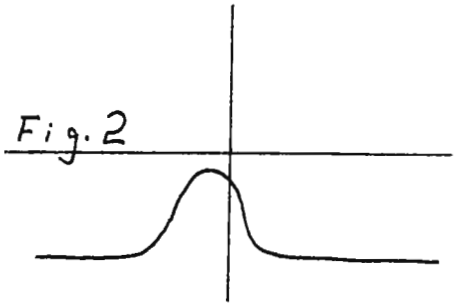
Sincerely,

Mike Mutaw
Biomedical Engineer

Robert A. Kleps
Senior Spectroscopist

RAK:kam

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The University of Alabama in Birmingham
Comprehensive Cancer Center
NMR Core Facility / CHSB B-31
205/934-5696

July 11, 1984

POSITION OPEN: Manager, NMR Core Facility

The UAB Comprehensive Cancer Center has an immediate opening for a Manager of the NMR Core Facility. The job duties include overseeing the day-to-day operations, trouble shooting and routine maintenance, software update, training and advising users etc. A knowledge of rf and digital electronics will certainly be an asset. The NMR Core Facility currently consists of two supercon systems (Bruker WH-400 and CXP-300/200) and an iron magnet system (HX-90). Excellent opportunities exist for collaborative research work in some of the ongoing molecular and in vivo NMR spectroscopy, and NMR imaging research projects. Interested candidates should send a resume and two or more letters of recommendation to:

Dr. N.R. Krishna
Director, NMR Core Facility
CHSB-B31, Comprehensive Cancer Center
University of Alabama in Birmingham
University Station
Birmingham,AL 35294

OSU

The Ohio State University

Campus Chemical
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116 Johnston Laboratory
176 West 19th Avenue
Columbus, Ohio 43210

Phone 614 422-3446

6 July, 1984

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

Homonuclear Proton NOE Difference Spectra in $H_2O$: Ribosomal 5S RNA

Dear Barry,

We are using selective homonuclear proton NOE difference spectra of the downfield imino base-pair protons in 5S RNA to identify the base-pair type (AU, GC, GU) and sequence (e.g., AU followed by GU followed by...). However, because sample concentrations are low (ca. 0.5-1 mM), extensive signal averaging may be required (ca. 8,000 scans on- and 8,000 off-resonance). Moreover, the large $H_2O$ signal is excited to a different degree by the on- and off-resonance irradiations. Usually, one would acquire the on- and off-resonance data sets separately--in that way, a single off-resonance spectrum can be used to reference any number of different on-resonance irradiation experiments. However, even when alternating-delayed acquisition is used to reduce the $H_2O$ signal, the results are not especially satisfactory (see Figure 1c).

We have found the best results with the experimental sequence shown below, in which the excitation is a modified Redfield sequence ($2P_2$-$P_2$-$P_1$-$P_2$-$2P_2$). The second and fourth pulses are phase-shifted 90°. $P_1 \cong 4P_2$, and $P_1$ and $P_2$ are adjusted for optimal water-nulling in each new sample. Alternating delayed acquisition is not necessary. Quadrature detection is on, but with no other phase cycling, and the double-resonance irradiation frequency is alternated between on- and off-resonance in successive scans. With the NT-500, it also helps to attenuate the preamp (10 dB), and to use minimal rf receiver gain.

| Step | Decoupler phase | Transmitter phase | Receiver phase | |
|---|---|---|---|---|
| 1 | 0 | 0 | 0 | on-resonance |
| 2 | 0 | 180 | 0 | off-resonance |
| 3 | 0 | 180 | 180 | on-resonance |
| 4 | 0 | 0 | 180 | off-resonance |

The transmitter alternation (steps 1 & 2, or 3 & 4) gives the NOE difference spectrum; xmit/receive alternation in steps 1 & 3 (or 2 & 4) eliminates the center glitch. The $F_2$/receiver alternation (1 & 2 vs. 3 & 4) helps to correct for unequal excitation of $H_2O$ by the on- and off-resonance $F_2$. This sequence performs well, even when the on-resonance frequency is relatively near to $H_2O$ and the off-resonance frequency is far from $H_2O$ (see Fig. 1b).

We are presently combining NOE-difference experiments with $Mg^{++}$ titrations, temperature variation, and selective enzymatic cleavage fragments, in order to deduce partial base-pair sequences in ribosomal 5S RNA's based solely on NMR experiments.

Sincerely,

Lee-Hong Chang, Charles E. Cottrell,
Shi-Jiang Li, and Alan G. Marshall

Lee-Hong Chang Shi-Jiang Li
Charles Cottrell Alan Marshall

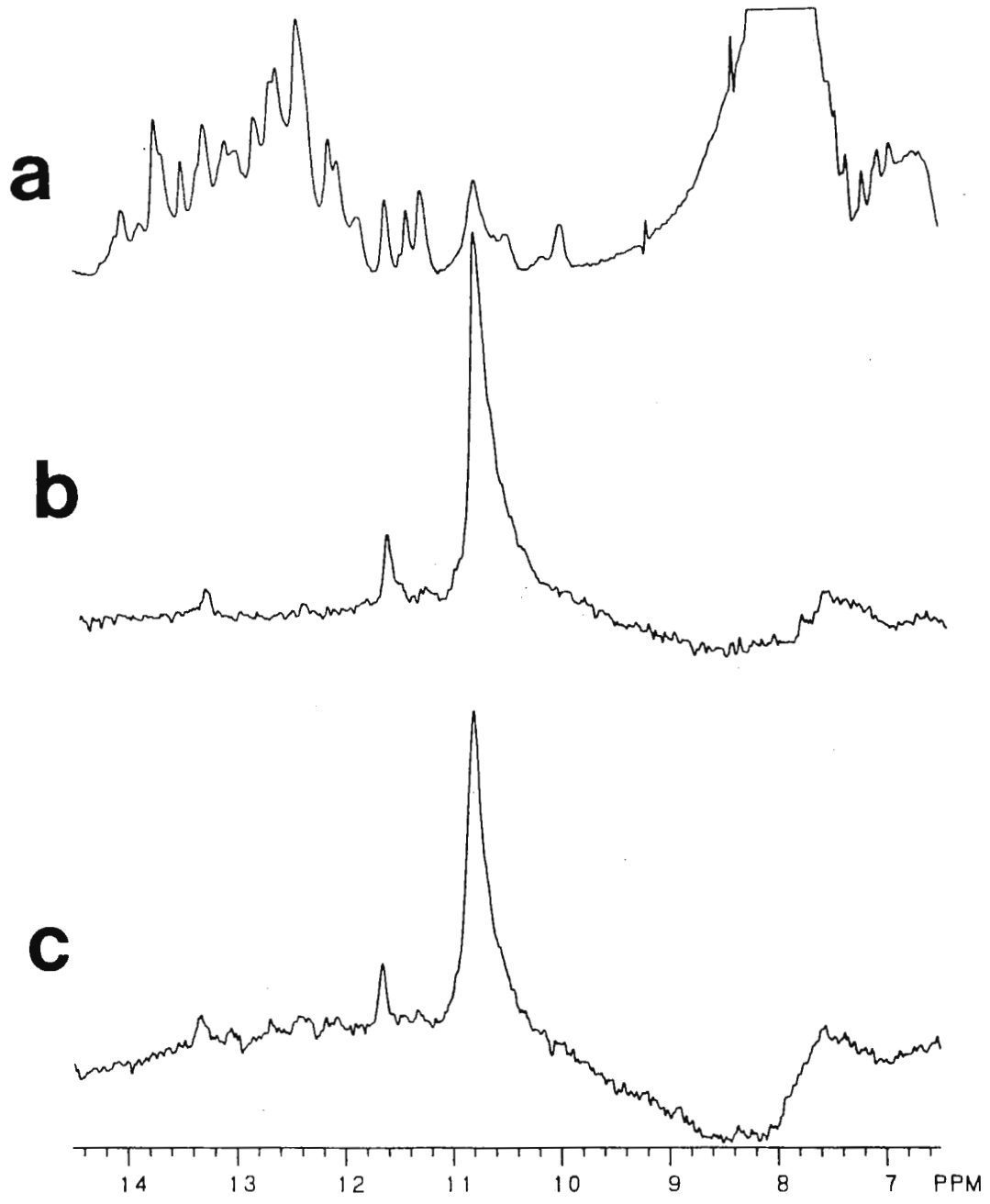


Figure 1. (a): B. subtilis 5S RNA (0.75 mM) in 95%/5% $H_2O/D_2O$: modified Redfield excitation with alternating delayed acquisition.
(b): NOE difference spectrum, with alternating addition/subtraction of on- and off-resonance FID's (see text).
(c): NOE difference spectrum (8000 scans off- minus 8000 scans on-resonance) for pre-irradiation of GU proton at 10.7 ppm for 0.6 sec. Alternating-delayed acquisition was used.

311-29


# QUEEN MARY COLLEGE

UNIVERSITY OF LONDON

DEPARTMENT OF CHEMISTRY
Professor R.Bonnett, BSc., PhD., DSc. (Head of Department)
Professor D C.Bradley, DSc., FRS
Professor K.W.Sykes, MA ,BSc., DPhil.

MILE END ROAD
LONDON E1 4NS
Tel. 01-980 4811
Telex 893750


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

9th July, 1984

$^{13}C$ Spectra of some 2nd Order Paramagnetics

Dear Barry,

Nearly twenty years ago when Derek Shaw was a lad and was working here, we published the first[1] of a number of papers on the $^{1}H$ n.m.r. of complexes ofRe(III), Re(IV) and Os(IV) with phosphine and arsine ligands.[2] The complexes are paramagnetic but give narrow line $^{1}H$ spectra which show large chemical shifts because of the anisotropy of the paramagnetic susceptibility. They also show interesting "$T_1$-decoupling" effects: some $^{1}H$-$^{1}H$ and $^{1}H$-$^{31}P$ couplings were absent although they are present in diamagnetic model complexes of Ir(III) and Rh(III). Incidentally those were the days before lanthanide shift reagents.

Now it is several spectrometers later and the Varian A.60 has long ago given way to new instruments the latest of which is the Bruker WH400. As a project exercise for Tony Brinklow, a third year undergraduate, we dusted off the old samples over a year ago and ran some $^{13}C$ spectra. We expected chemical shift ranges closer to the $^{1}H$ ranges ($\sim$ 12 ppm) rather than to the very large values ($\sim$ 790 ppm) reported[3] by Neville Boden for $^{31}P$, and this is what we found ($\sim$ 15 ppm). The $^{13}C$ lines for $ReCl_3(PR_2Ph)_3$ [R = Et, n-Pr] were narrow except for the $\alpha$- and $\beta$-carbons in the alkyl groups and show no evidence of $^{31}P$ couplings, only of $^{1}H$ couplings. Using $^{13}C$ ($^{1}H$) specific decouplings Brinklow was able to assign the $^{13}C$ spectra from the published $^{1}H$ assignments. Maybe the next student will measure the various $T_1$ s. During our evaluations of several medium field spectrometers (Bruker, Jeol and Varian) Geoff Hawkes and I obtained some 2-D shift correlated spectra.

Many thanks to you and many other friends for splendid hospitality in the U.S. after the 25th ENC.

Best wishes from Geoff Hawkes

Yours sincerely,

Ed

Professor E.W. Randall


1. D. Shaw and E.W. Randall, Chem. Commun., 1965, 82.
2. E.W. Randall and D. Shaw, J. Chem. Soc. A., 1969, 2867 and references therein.
3. see N. Boden in "Determination of Organic Structures by Physical Methods," edited by J.J. Zuckman and F.C. Nachod, Chapter 2, Volume 4, 1971 (Academic Press).

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NORTHWESTERN UNIVERSITY COLLEGE OF ARTS AND SCIENCES

Department of Chemistry

Evanston, Illinois 60201
2145 Sheridan Road

July 10, 1984

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

Dear Barry:

As your readers are well aware, NMR can do almost anything. We have now found that it can even supply dates (the chronological type). To our knowledge, NMR has not been put to this use before, although our sibling science ESR has. There is no good technique to date very ancient (beyond $^{14}C$ limits) organic materials, other than geological context. In collaboration with Jim Frye of the Colorado State University Regional NMR Center, George Poinar of Berkeley, and Curt Beck of Vassar, we have been looking at the CP/MAS $^{13}C$ spectra of amber. Because amber is millions of years old, $^{14}C$ dating methods are inapplicable.

In examining amber from several sites in the Dominican Republic, we have found trends in the alkene resonances that could be attributed to different relative ages (see the Figure, which contains only the alkenic region). The resonances at δ110 and 150 come from the two ends of exo-methylene groups ($C{=}CH_2$). These groups appear to be lost gradually during burial and fossilization. A recent resin of similar botanical source (H in the Figure) has well developed exo-methylene resonances (labeled 1 and 6). A Cretaceous amber from Lebanon (L in the Figure) is much older than the Tertiary Dominican samples and shows no exo-methylene resonances. The Dominican mining sites appear to grade from youngest to oldest in the order C, B, P, V, A, T, and Q by this criterion. This order agrees with the expectations of other properties such as hardness.

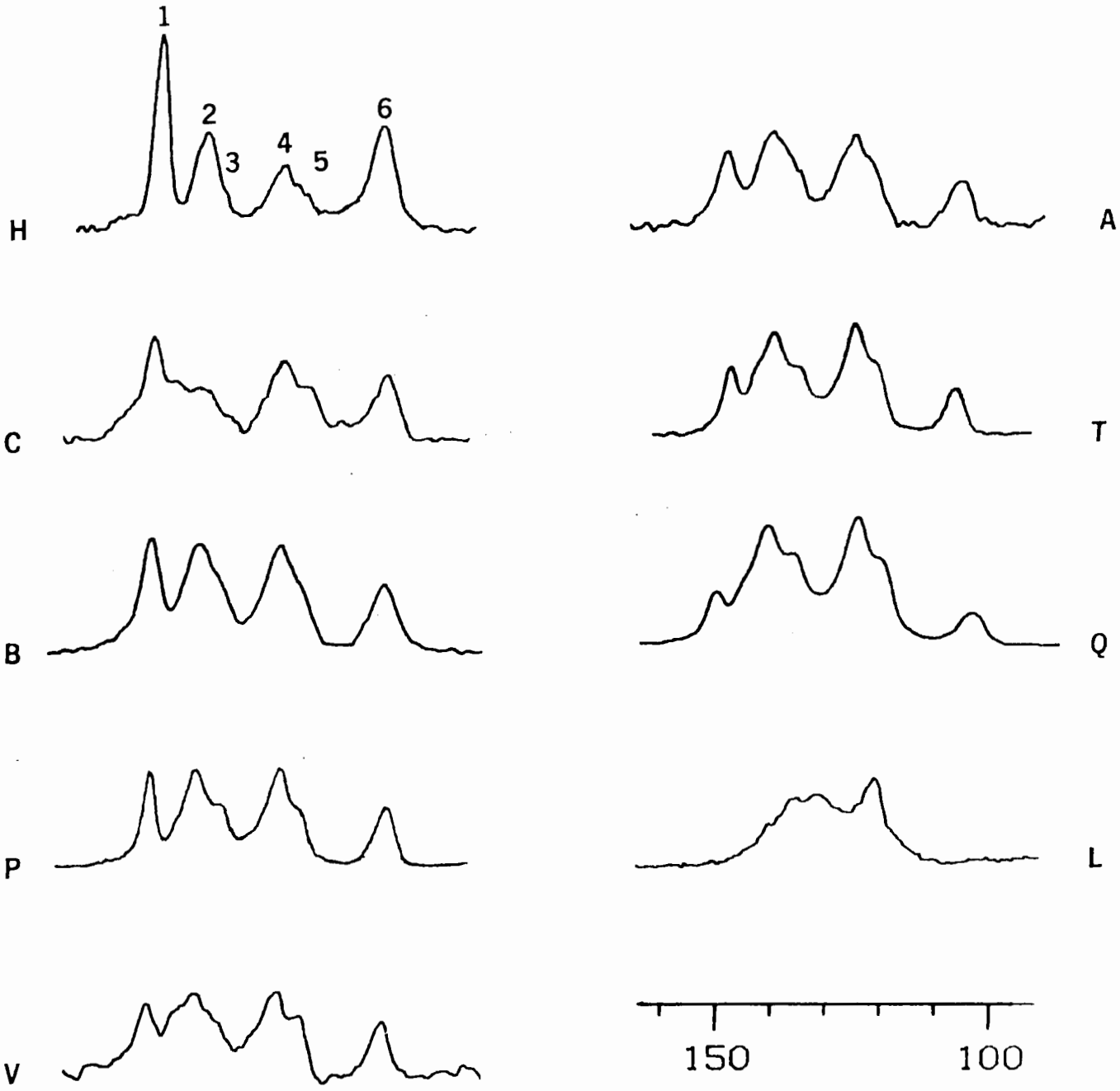
With proper controls and standards, we hope to develop this approach into an absolute dating technique. Causes other than age, such as paleo-botanical origin and differing conditions of burial, also must be examined.

Sincerely,

Joseph B. Lambert

Title: Dates by NMR

JBL:cs


1
2
3
4
5
6
H
A
C
T
B
Q
P
L
V
150
100

UNIVERSITY OF SOUTH CAROLINA

COLUMBIA, S. C. 29208

SOUTH CAROLINA MAGNETIC
RESONANCE LABORATORY

(803) 777-7341

11 July 1984

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

Dear Dr. Shapiro,

As the nmr field continues to mature, experimental techniques are developed which tax the capabilities of existing hardware. Representative is the experiment proposed by Shaka and Freeman.(1) This experiment, selective excitation of protons by polarization transfer from adjacent carbon nuclei, cannot be executed by our Facility's Bruker WH-400; no provision is made for experiments which require nuclei of low gyromagnetic ratio to be pulsed when the proton spectrum is to be observed. This lack of flexibility is easily circumvented by the simple hardware modification we describe here.

The standard configuration of the WH-400 includes a double-pole/single throw switch on the front panel "synthesizer input" unit. This switch controls frequency synthesis on both the receive mixer (MLB-1) and the transmit mixer (MLB-2) boards. Replacement of the double pole switch with separate switches (see "Modification" in Figure 1) allows the receive mixer to remain in the proton observe setting while the transmit mixer is switched to its low frequency setting.

This new mode of operation provides for low frequency pulses through the transmit channel, proton pulses through the decoupler channel, and proton signal detection. The mixer boards can easily be reset to either of the two original modes of operation: proton pulses with proton detection or low

frequency and/or proton pulses with low frequency detection.

As yet, no experimental results are available for operation in this hardware mode, however, interested individuals have strongly encouraged immediate publication. We request the interested individual to please credit this contribution to the rapidly expiring subscription of Professor Paul D. Ellis.

Yours Sincerely,

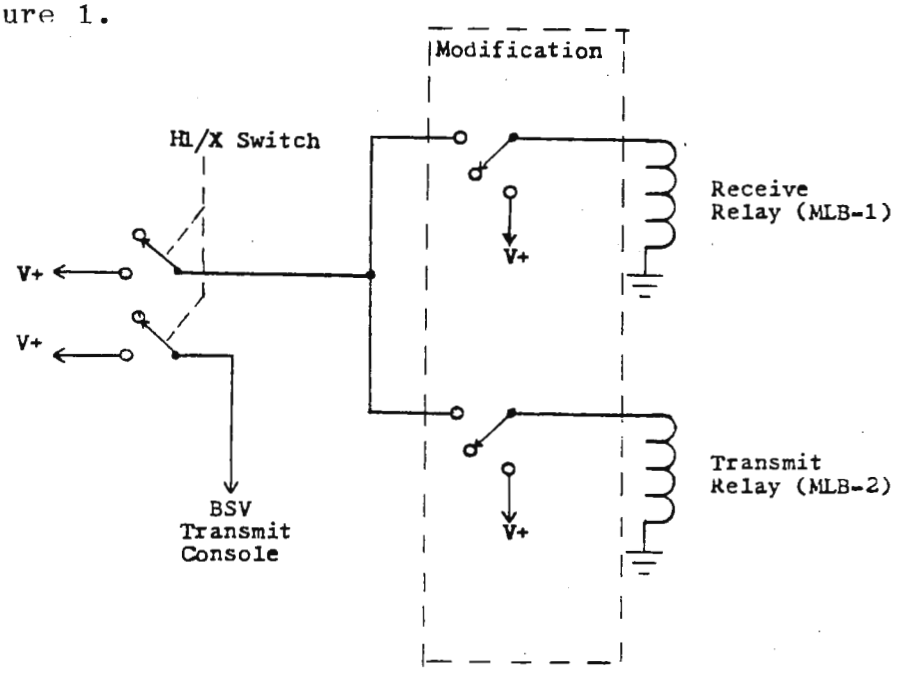
Ted C. Claiborne

Paul D. Ellis
Facility Director

---

1. A.J.Shaka and R.Freeman, J. Magn. Reson., 50, 502-507 (1982).

Figure 1.



UNIVERSITÉ DES SCIENCES ET TECHNIQUES DU LANGUEDOC

311-35

GROUPE DE DYNAMIQUE DES PHASES CONDENSEES

Laboratoire Associé au C.N.R.S. N° 233

Montpellier, le July 11, 1984

Professor B.L. SHAPIRO
Department of Chemistry
Texas A and M University
College Station, Texas 77843
USA

NMR Studies of Conducting Polymers(2)

Dear Dr Shapiro :

Since several years we have been currently investigating the magnetic properties of doped polyacetylene (1) and we have been focusing our work on alkalin-doped polyacetylene. We present here results obtained on Li-doped $(CH)_x$ by high resolution MAS-NMR on a Brüker CXP200 spectrometer.

The doping is achieved by putting a piece of cis-polyacetylene in a solution of Lithium-benzophenone in THF for 40h under vacuum.

The well-known fast degradation of the doped samples in air and the difficulties inherent to the observation of MAS-NMR on conducting samples led us first to investigate the doped and subsequently degraded sample. This approach of the problem allowed us to prove the existence of residual THF molecules in the Li-doped system.

The NMR experiment combined Magic Angle Spinning, Cross Polarization and Proton Decoupling. The spectrum obtained is shown in Fig.1. We visibly see the relatively narrow resonance lines of THF at 26.7 ppm and 68.6 ppm (from TMS). By dynamic pumping for 2 d, an important fraction of the THF is removed from the sample, as shown in Fig.2., but traces of THF still remain in it. This is the first experimental evidence of the presence of THF in Li-doped $(CH)_x$. We will go into further investigations to determine more exactly the number of THF molecules per Lithium ion and try to answer to the question of the degree of solvation of $Li^+$ by these solvent molecules.

Sincerely yours,

P. BERNIER M. AUDENAERT F. RACHDI

(1) See preceding letter : BERNIER P., NMR studies of "Conducting Polymers", N° 301 (October 1983).

Place Eugène Bataillon 34060 MONTPELLIER CEDEX - Tél. (67) 41.30.19 - Télex : USTMONT 490944 F

Fig. 1.

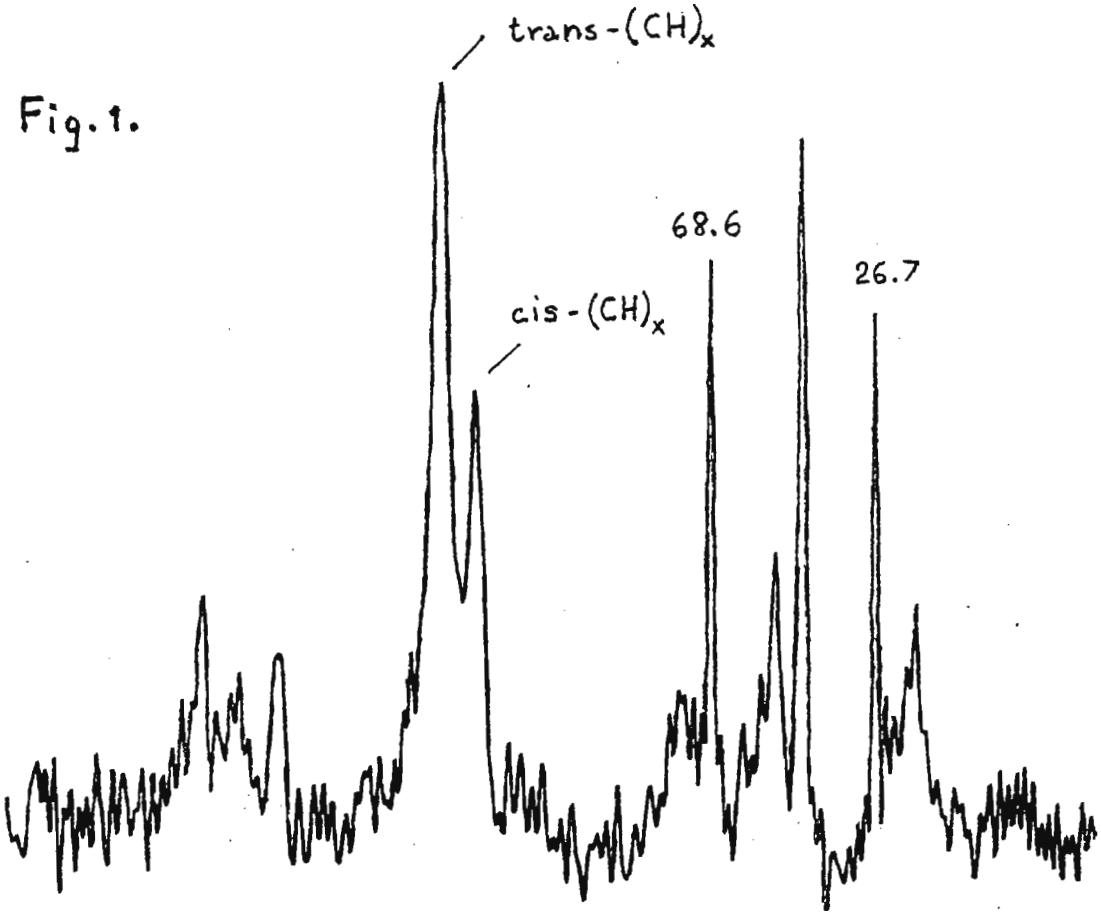
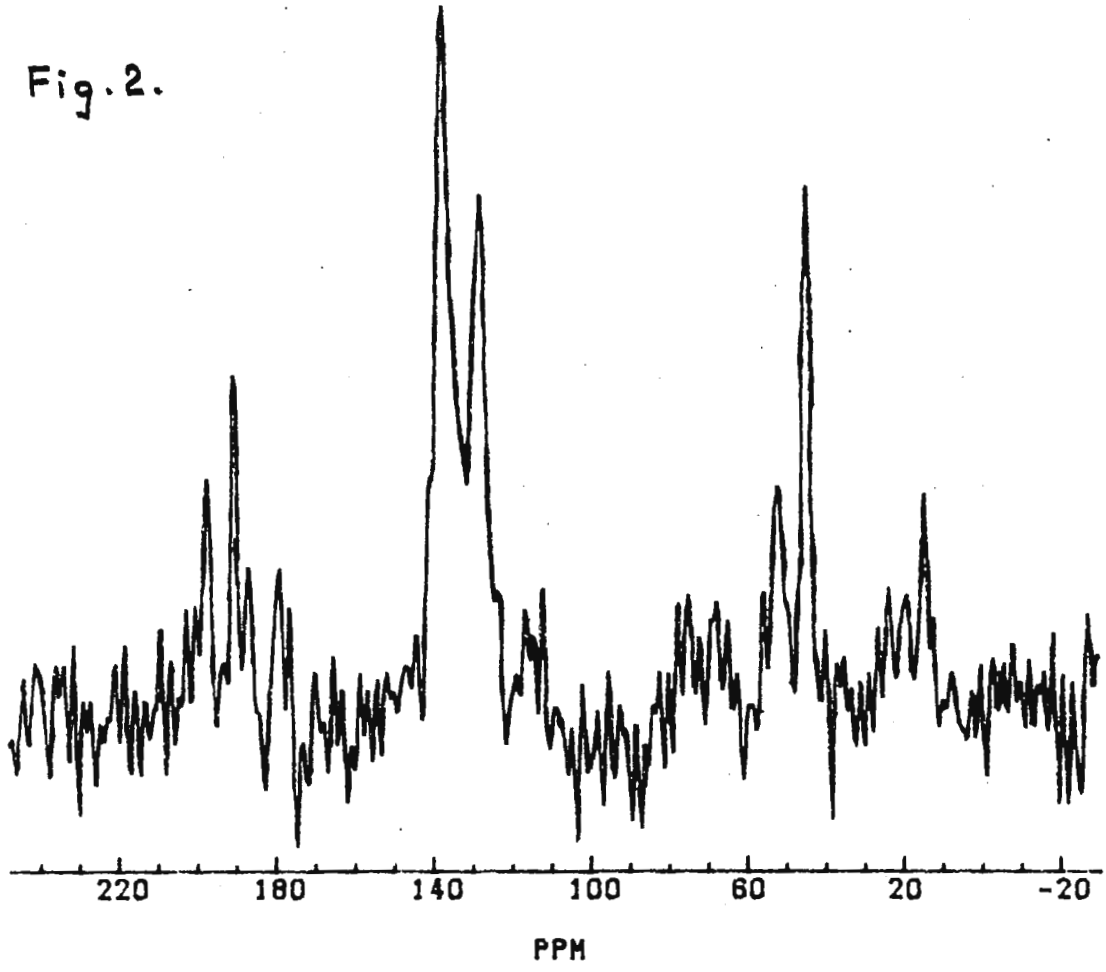



Fig. 2.



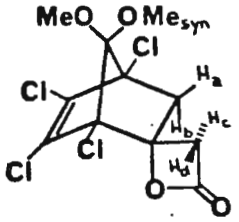
July 12, 1984

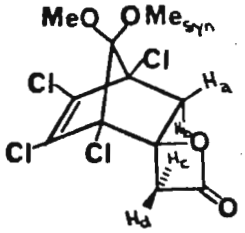
Professor Bernard L. Shapiro
Department of Chemistry
Texas A and M University
College Station, TX 77843

Dear Professor Shapiro:

Subject: Structure Elucidation via n.O.e. Difference Spectroscopy

The Diels-Alder reaction of diketene with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene produces the product shown below as either its exo- or endo-configuration.

ENDO 


EXO 


The simplicity of the proton NMR spectrum (Figure A) made this compound an ideal candidate for the n.O.e. difference experiment on our JEOL GX-400 NMR spectrometer.

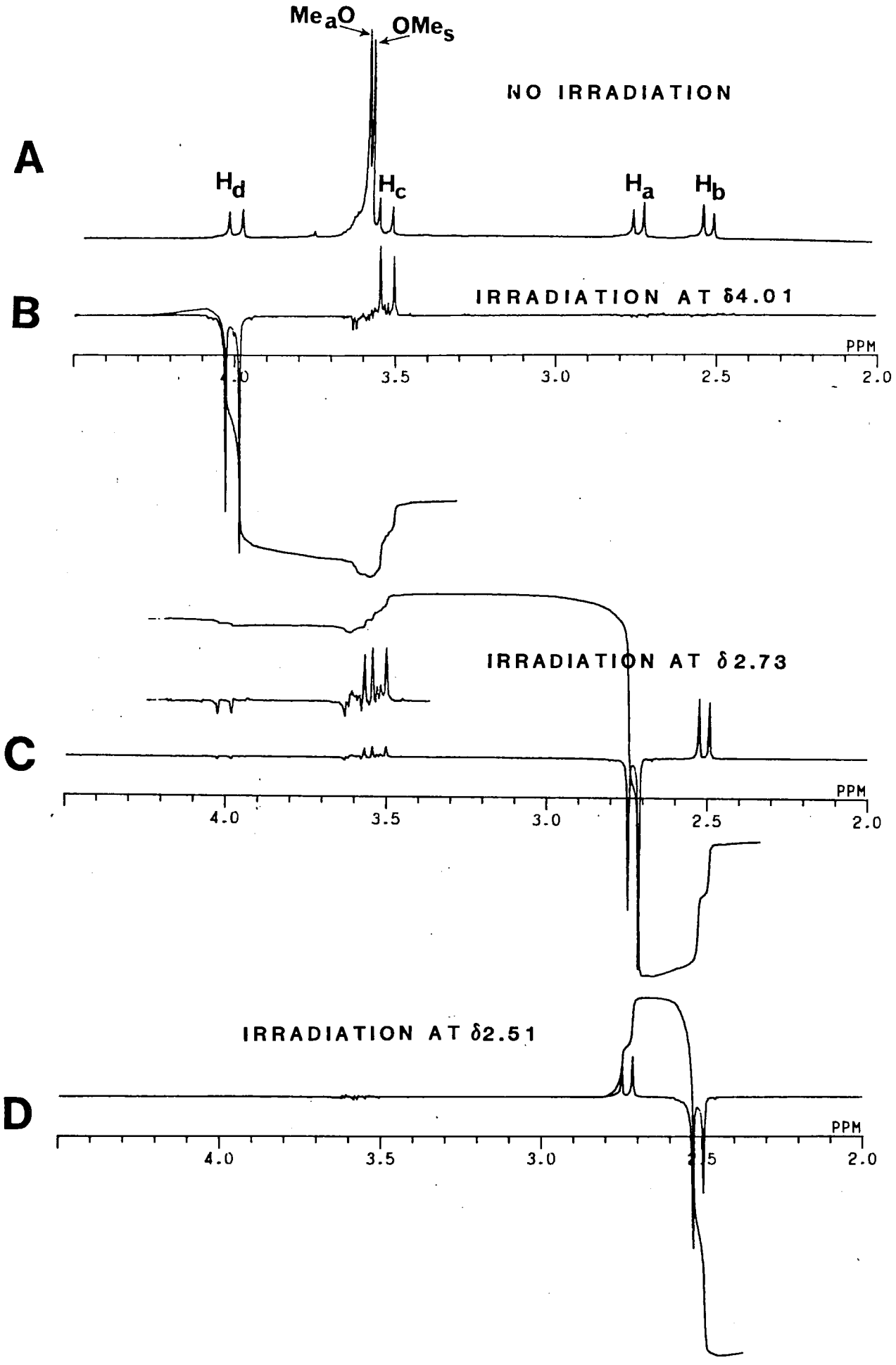
For the purpose of differentiating these two possible structures, molecular models suggested that there should be an observable enhancement between $CH_3$ (syn) and $H_a$ for both configurations, between $H_a$ and $H_c$ for the endo adduct, and between $H_b$ and $H_c$ for the exo adduct. Irradiation of the doublet resonance at $\delta 2.73$ ($H_a$) showed an enhancement of the resonance for $CH_3$ (syn) (0.6%), $H_c$ (5%), and $H_b$ (29%) (Figure C). Irradiation of the doublet resonance at $\delta 2.51$ ($H_b$) showed an enhancement of the resonance for $H_a$ only (Figure D). Irradiation of the doublet resonance at $\delta 4.01$ ($H_d$) showed enhancement of the resonance for $H_c$ (28%) only (Figure B).

This data, as well as the results from irradiation of the other proton resonances in the molecule, gave results consistent with the endo configuration thus saving the extra expense of a crystal structure determination.

Yours very truly,

Douglas W. Lowman
Senior Research Chemist
Research Laboratories
P. O. Box 1972

Robert J. Clemens
Research Chemist
Research Laboratories
P. O. Box 1972


MeaO
OMes
NO IRRADIATION
A
Hd
Hc
Ha
Hb
B
IRRADIATION AT δ4.01
PPM
4.0
3.5
3.0
2.5
2.0
IRRADIATION AT δ2.73
C
PPM
4.0
3.5
3.0
2.5
2.0
IRRADIATION AT δ2.51
D
PPM
4.0
3.5
3.0
2.5
2.0

*Prof. Dr. D. Leibfritz*
*Universität Bremen*
*Fachbereich Chemie/Biologie*

*NW 2 Leobenerstraße*
*2800 Bremen 33*
*Telefon (0421)218-2818/17/41*

Prof. B.L. Shapiro
Dept. Chemistry
Texas A & M University
College Station, TX 77843

20-7-1984

Title: The ideal NMR vegetable

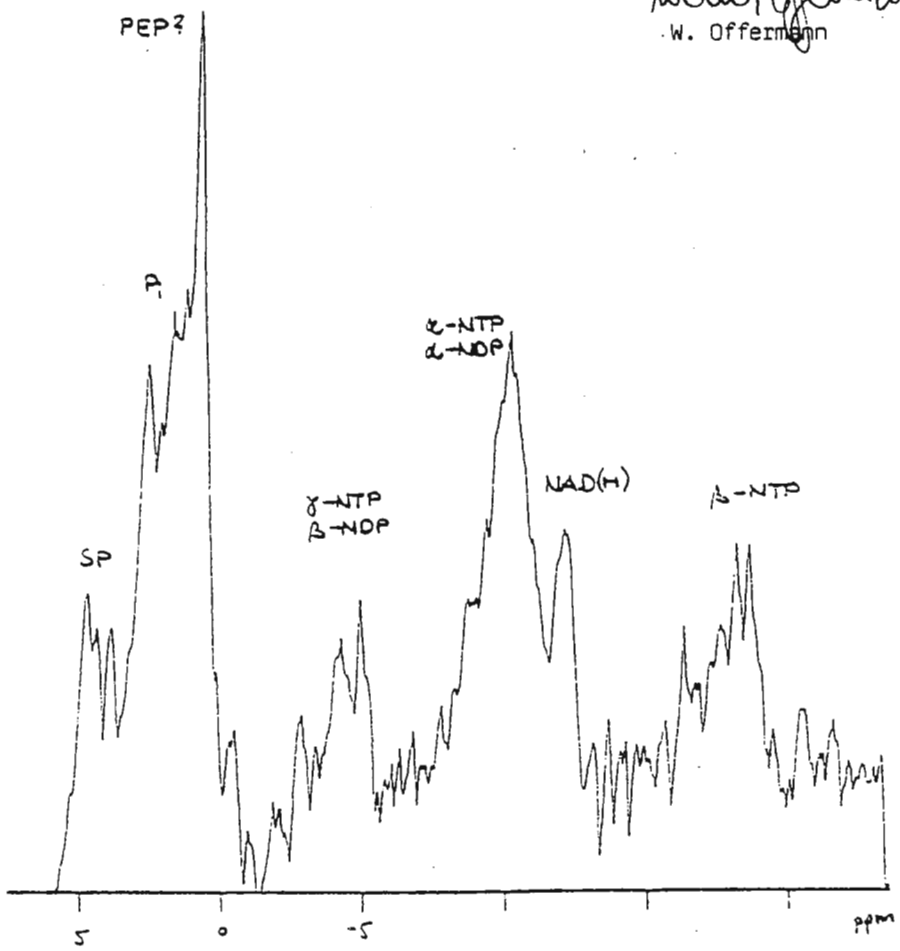
Dear Dr. Shapiro:

Since some time our interest turned to applications of P-31-NMR of biological material, but we don't want to show another spectrum of Langendorff heart, liver, muscle, cell culture etc. from our collection.

On the other hand, there is still a demand for an ideal narrow bore magnet vegetable. We have found a candidate: the asparagus. It may not be of much interest, but it nicely fits in almost evry spectrometer. If the asparagus is ideally grown, a skilful operator may hook the spinner directly to the object and even save the sample tube. The spectrum (below) of the tip from a white asparagus shows several high energy phosphates in the expected manner.

Yours sincerely

W. Offermann  D. Leibfritz



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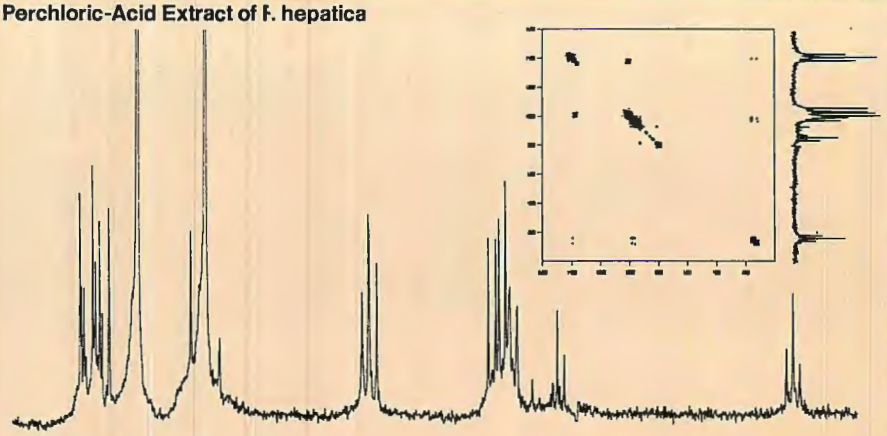
# XL performance for demanding biological NMR studies

Recently, NMR has become an important tool for biochemists interested in studying metabolism *in vivo*. The applications shown on this page illustrate the broad range of capabilities required in an NMR spectrometer used in biological research. These capabilities demand superb sensitivity, flexibility in pulse programming, and software that permits taking advantage of available experiments and techniques.

**Perchloric-Acid Extract of F. hepatica**

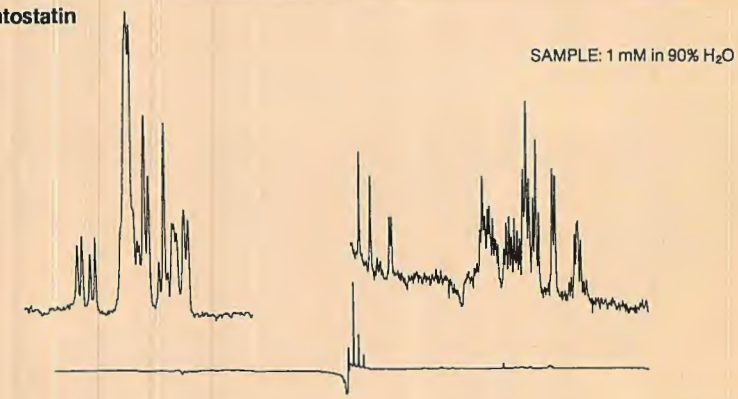


*The high-sensitivity probes of the XL-200 allow spectra to be obtained from biologically relevant compounds at low concentration. The $^{31}P$ spectrum above is of a perchloric-acid extract of F. hepatica (bovine liver flukes) and was obtained in 4 hours (1500 transients) at 81 MHz, using a 10-mm probe. The spectrum has been resolution-enhanced to facilitate the identification of the $^{31}P$-containing compounds present. The average concentrations of metabolites present in the sample are submillimolar.*

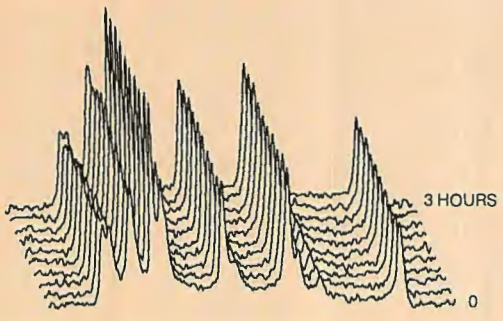
*Two-dimensional NMR is a powerful method for analyzing complex mixtures. The contour plot shown above the spectrum is the result of a $^{31}P$ homonuclear shift correlation experiment carried out on a portion of the fluke extract using a 5-mm $^{1}H$ broadband switchable probe at 81 MHz. The total experiment time was approximately 12 hours. The experiment led to the discovery of a nucleotide pyrophosphate compound whose presence is indicated by the cross peaks between the P-α-nucleotide peaks and the peak at 800 Hz.*

*Biological NMR often requires the observation of protons in $H_2O$, particularly for observation of exchangeable protons. The strong signal from the solvent can be suppressed effectively by pulse sequences such as time-shared Redfield 2-1-4 or, as here, the Jump-and-Return pulse sequence. This XL-400 spectrum is the result of only 16 accumulations using a 1-millimolar solution. The aromatic expansion (rephased for upright presentation) shows the single-proton sensitivity that can be obtained in a half-minute period.*

**$^{1}H$ Somatostatin**

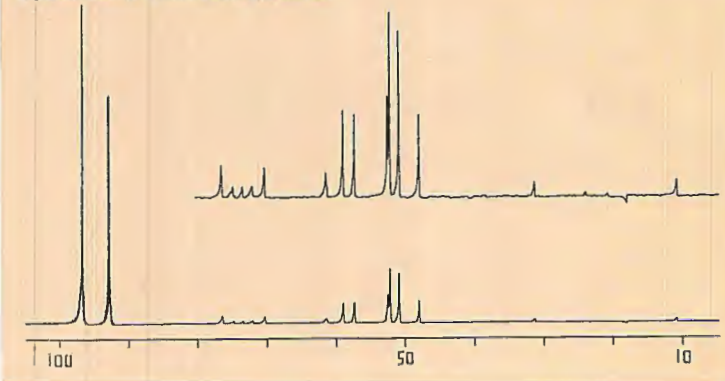



**Perfusion of Tissue**




*Use of a modified 10-mm tube permits the NMR study of intact tissue while perfusing with temperature-controlled nutrient. No hardware modification of the spectrometer is necessary. The stacked plot shows the time course of ATP resonances during tissue perfusion with a nutrient medium and illustrates how tissue preparations can be maintained in a viable state during experiments. Insufficient or poor perfusion causes rapid degradation of the ATP and resultant cell or organism death. The ability to retain viability over many hours permits extensive study of metabolism in metabolic, nutrative, and cell research.*

**Spectrum of Perfusion Medium**




*NMR is a valuable tool for following metabolism in isotope labeling experiments. This spectrum is of the perfusion medium taken at the end of an experiment in which the bovine liver flukes (above) were perfused with (1-$^{13}C$) glucose. A large number of labeled species are formed as the (1-$^{13}C$) glucose is metabolized. Subsequent analysis of the sample using spectral editing pulse sequences and heteronuclear correlation experiments are essential for assignment of these resonances.*

Prof. Dr. GERHARD HÄGELE
Institut für Anorganische Chemie
und Strukturchemie I
der Universität Düsseldorf

Dipl. Chem. W. Kückelhaus

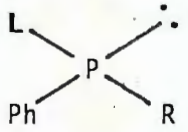
4000 Düsseldorf, den 27. 7. 1984
Universitätsstr. 1/26.42.U1.32
Telefon 0211 - 311-2288/2287
Telex 8 587 348 uni d

Professor
Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843-3255
USA

Title : Force Field Calculations as a Useful Help for NMR-Studies

Dear Professor Shapiro,

we have recently investigated the molecular structures of some l-menthyl-phenylsubstituted phosphines:




L : l-$C_{10}H_{19}$
Ph: $C_6H_5$
R : H, $CH_3$, i-$C_3H_7$, t-$C_4H_9$

Here we want to describe our results for the two epimers $R_{(P)}$- and $S_{(P)}$-LPhPCH$_3$. In a first step we determined the molecular structures of both diastereomers corresponding to the minimum level of steric energy. For that purpose we made use of N.L. ALLINGER's ·ogram MM2[1-2] (Molecular Mechanics Program; Version 2). The optimized molecular geometries of $R_{(P)}$- and $S_{(P)}$-LPhPCH$_3$ are shown in Fig.1. In accordance with the results of earlier works[3] we found a significant conformation for the terminal isopropylgroup of the menthylsubstituent. In both epimers of LPhPCH$_3$ the i-$C_3H_7$-group is orientated near to the aromatic system. Therefore we discussed the influence of the ring current effect on a quantitativ basis. We employed the JOHNSON-BOVEY-Model[4] in connection with the tables, being compiled by EMSLEY, FEENEY and SUTCLIFFE[5], and computed the contributions $\Delta\delta H$ for the protons $H_8$, $H_{9a-c}$, $H_{10a-c}$ and $H_{17a-c}$. With the calculated values we could explain the magnetic unequivalence of the methylprotons $H_{9a-c}$ and $H_{10a-c}$. The upfield shift of $H_{9a-c}$ is traced to the high shielding caused by

the aromatic ring current. Moreover we calculated the differences $\Delta\delta H_i(R_{(P)}) - \Delta\delta H_i(S_{(P)})$. The results, given in Tab. 1, demonstrate that $H_8$ is a sensible indicator to differentiate between the high- and lowfield form of LPhPCH$_3$. The predicted values were found in good agreement to the observed one[6]. So we were able to assign the $^1$H-resonance signals of $R_{(P)}$- and $S_{(P)}$-LPhPCH$_3$.
I hope you don't mind that Prof. Hägele's signature is missing. He is on holiday until the 8$^{th}$ of august.

Sincerely yours

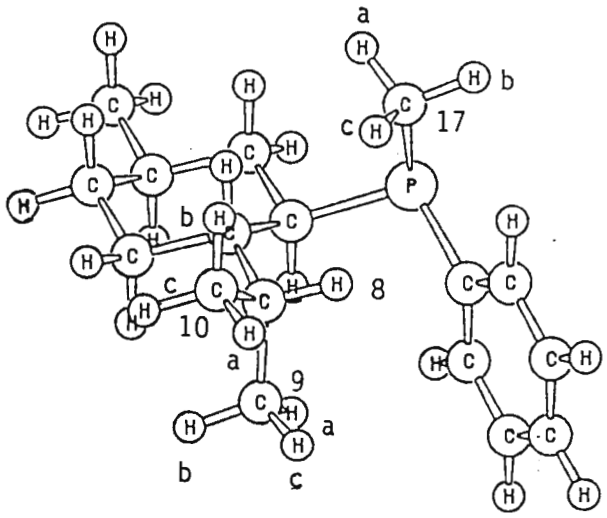
(Professor G. Hägele) (W. Kückelhaus)


1) N.L. Allinger and Y.H. Yuh, Program MM2 (Molecular Mechanics, CDC-Version 2), QCPE-Nr. 395
2) W. Kückelhaus, Diplomarbeit, University of Düsseldorf, 1984
3) W.S. Sheldrick, G. Hägele and W. Kückelhaus, J. Mol. Struct. 74, 331 (1981)
4) C.E. Johnson jr. and F.A. Bovey, J. Chem. Phys. 29, 1012 (1958)
5) J.W. Emsley, J. Feeney and L.H. Sutcliffe, "High resolution NMR-Spectroscopie", Vol. 1, Pergamon Press, Oxford, 595 (1965)
6) J. Seega, Diplomarbeit, University of Düsseldorf, 1984


| $H_i$ | $\Delta\delta H_i(R_{(P)}) - \Delta\delta H_i(S_{(P)})$ in ppm : calc. | obs. |
|---|---|---|
| $H_8$ | -0.35 | -0.28 |
| $H_9$ | 0.02 | 0.04 |
| $H_{10}$ | -0.04 | -0.04 |
| $H_{17}$ | 0.18 | 0.11 |

Tab 1.: Calculated and observed differences between the contributions $\Delta\delta H_i$ of $R_{(P)}$- and $S_{(P)}$- LPhPCH$_3$
( For methylprotons $H_{i(a-c)}$ averaged values are given )

a) $R_{(P)}$-**L**PhPCH$_3$ :



b) $S_{(P)}$-**L**PhPCH$_3$ :

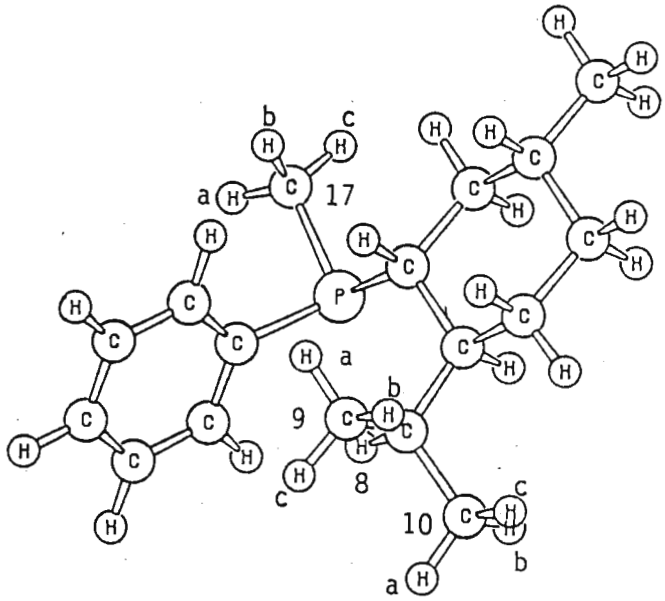


Fig. 1.: Molecular structures of $R_{(P)}$- and $S_{(P)}$-**L**PhPCH$_3$

**University of Cincinnati**

Cincinnati, Ohio 45221
(513) 475-2263

DEPARTMENT OF CHEMISTRY

**Solid State Si-29 NMR of Cross-Linked Siloxane Networks**

July 12, 1984

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843-3255

Dear Barry:

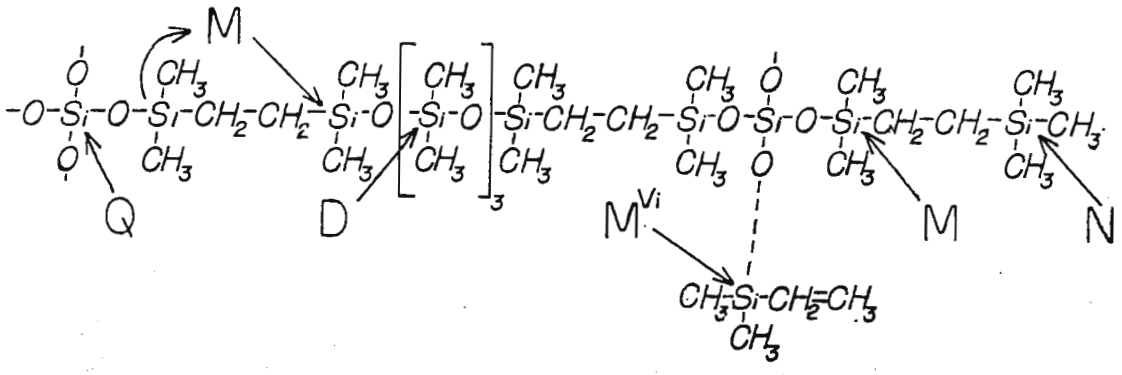
Noting the overabundance of references to your gentle reminders, we will refrain from making even the slightest mention of your second green sheet.

The CP/MAS technique in solid state NMR has been widely used in structure elucidation of various polymers and networks. With polarization transfer from $^{1}H$ to $^{29}Si$, we are studying the various Si chemical units, and hence the structure of cross-linked polydimethylsiloxane (PDMS) networks. These networks are rubber-like materials at room temperature. Since there is substantial molecular motion of these networks at room temperature, further sample spinning at the magic angle averages the remaining anisotropy, resulting in liquid-like spectra with a resolution of 0.4 ppm at FWHH.

The two spectra shown are obtained from vinyl end-linked networks with molecular weight of about 520 between cross-links. The structure of this network is shown in the diagram at the top. In Fig. A, the spectrum of a network prepared with exact stoichiometric proportion is shown. Fig. B is obtained from a network with excess polymer in the cross-linking reaction. In Fig. B, there are two additional peaks than there are in Fig. A. These are due to dangling ends from excess polymer. They have been identified as end Si ($M^{VI}$) at -4.4 ppm and D group Si associated with the dangling end, which is the left shoulder in the D region. Furthermore, triplets are observed in the Q region, indicating that the cross-linking process results in a multiplicity of structures, such as loop formations. The networks are far from perfect, contrary to previous assumptions.

Overall, $^{29}Si$ NMR using CP/MAS gives information on the fine details of PDMS network structure. The wide chemical shift dispersion, over 130 ppm, helps to resolve the various $^{29}Si$ chemical units and facilitates the interpretation of the spectra.

Kebede Beshah James E. Mark Jerome L. Ackerman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Q
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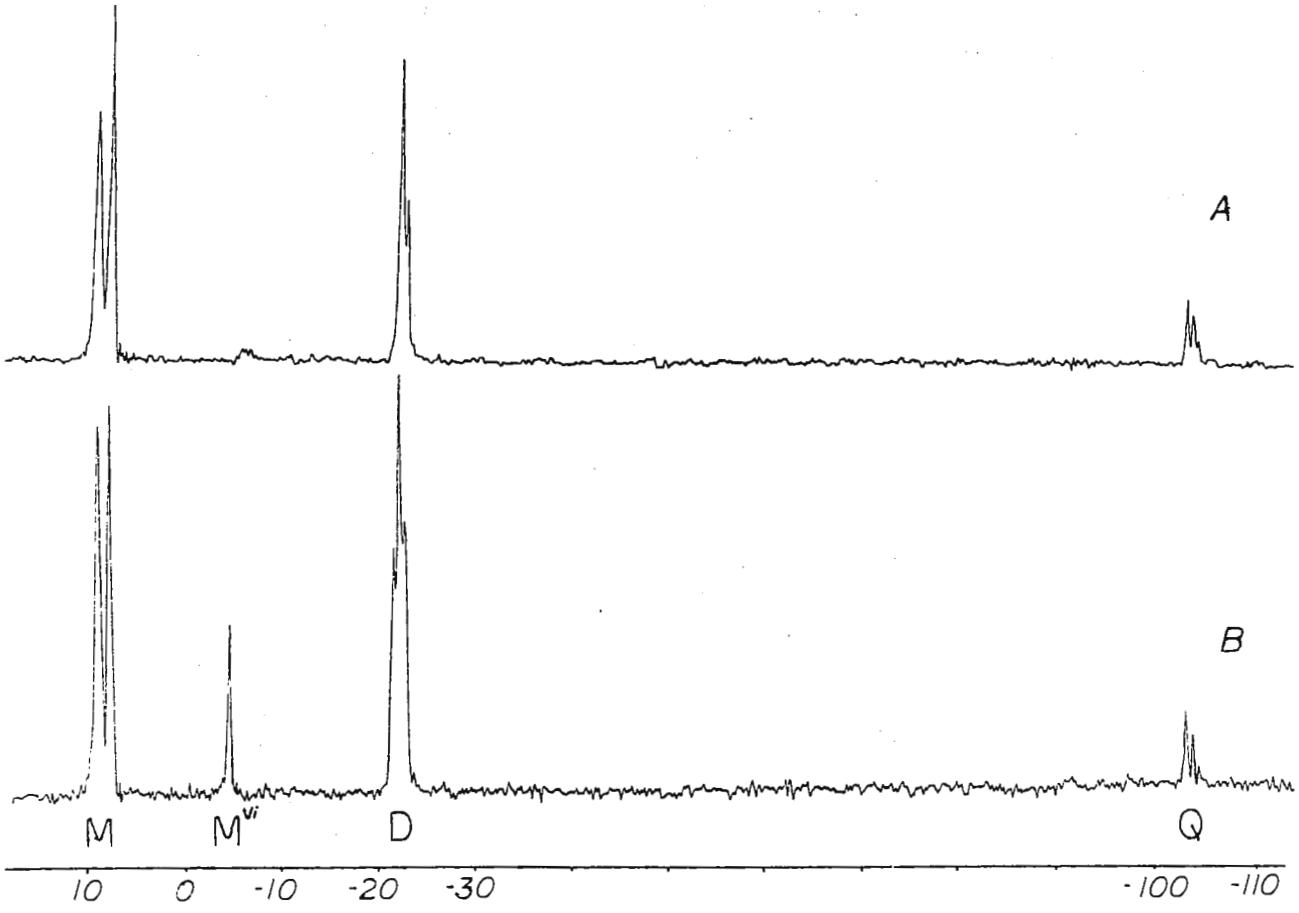
M
N
CH3-Si-CH=CH2
CH3


A
B
M
M^Vi
D
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-20
-30
-100
-110

**Weyerhaeuser Company**

Tacoma, Washington 98477
(206) 924-2345

July 19, 1984

Prof. Bernard L. Shapiro
Dept. of Chemistry
Texas A&M University
College Station TX 77843-3255

RE: Chemically Amplified NMR for Cellulose Carbonyls

Dear Prof. Shapiro:

Most of the last seven months has been spent getting to know our first supercon system, a Nicolet (GE) S-100. I'm pleased to say that the versatility, sensitivity, throughput and high spinning rates make this CP/MAS spectrometer a real boon to the forest products industry. Besides studying the usual mix of woods, lignins and synthetic polymers, we have been using NMR to measure rare functional groups in processed celluloses. Our main interest currently is the oxidative effect of chemical bleaching as gauged by carbonyl and carboxyl group contents.

Even in heavily bleached pulps, the carbonyl and carboxyl groups constitute only about 10 carbons out of 1,000 anhydroglucose (AHG) units, or 10 out of about 6,000 carbons. Dynamic range limitations keep these peaks at the noise level when the largest AHG peak is at full scale. We have devised a simple way around this problem for carbonyl groups and will start soon on a similar approach for carboxyls.

The basis of the measurement is CP/MAS NMR analysis after selective labeling of carbonyls with $^{13}$C-enriched cyanide and alkaline hydrolysis to the stable carboxylate product (a heterogeneous Kiliani-Fischer synthesis):

$$\text{Cell-CHO} + \text{Na*CN} \xrightarrow[23^{\circ}, 48\ \text{hr}]{H_2O,\ \text{pH}\ 11.5} \text{Cell-CH(OH)-*CN} \xrightarrow[80^{\circ}, 4\ \text{hr}]{} \text{Cell-CH(OH)-*COO}^{-}\text{Na}^{+}$$

Using $^{13}CN^{-}$ of 99% isotopic purity amplifies the carbonyl group 90-fold relative to natural abundance. Cross-polarization with a 2-msec contact time yields quantitative results which are reasonable based on current bleaching knowledge and, on the single well-characterized sample examined so far, agree with another, more tediuos procedure.

The spectra attached are of a commercial microcrystalline hydrocellulose before (lower) and after labeling. The morphology information (crystalline/noncrystalline, most noticeable by the doublets for C4 and C6 at 80-90 and 60-65 ppm, respectively) is preserved through the very gentle workup. Some results are shown in the table. We have yet to resolve any detail in the *COO$^{-}$ peak; although the labels on aldehyde and ketone groups should be resolved by about 5 ppm, we are not sure that we've created any of the latter.

Respectfully,

Larry Amos

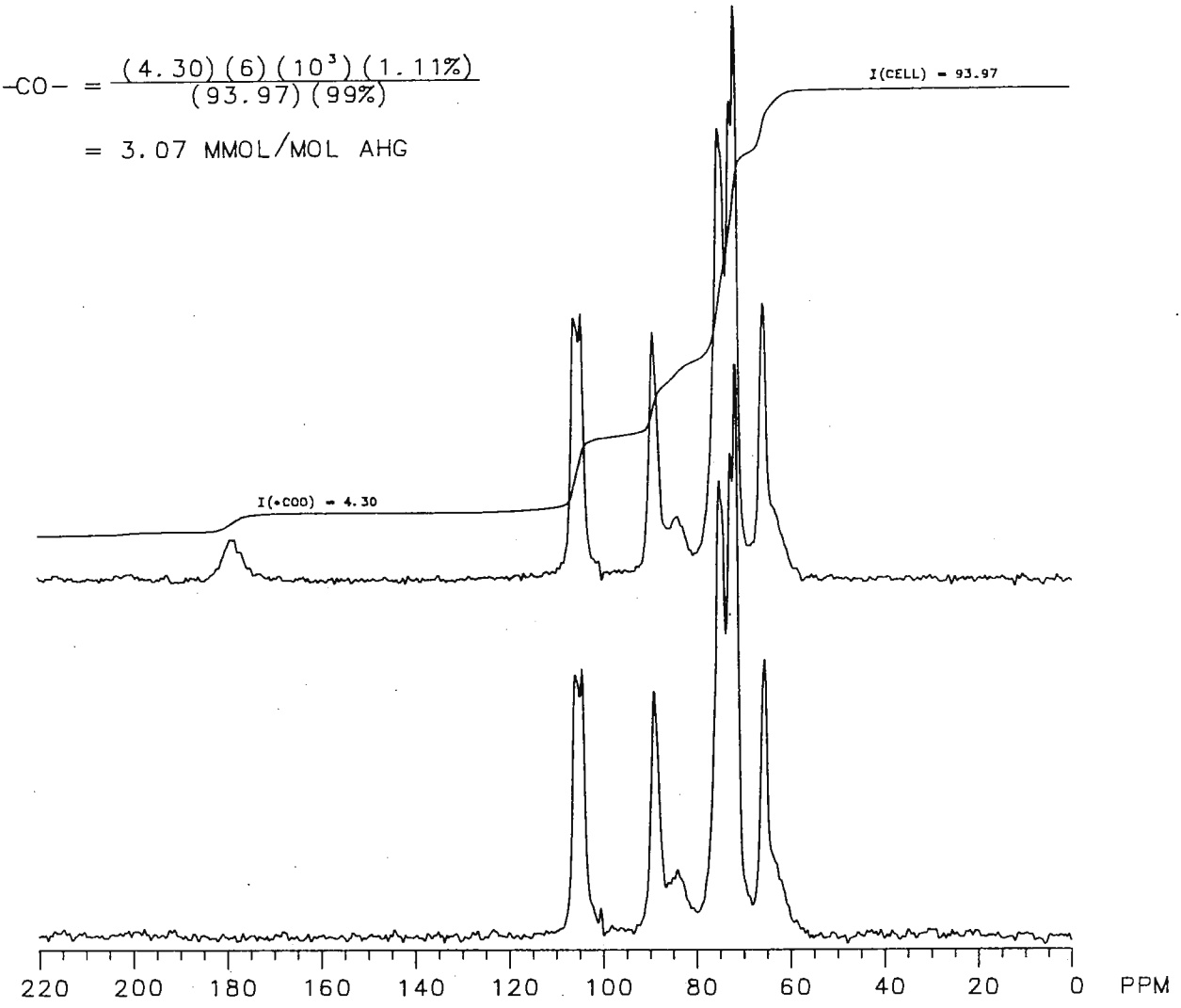
Larry W. Amos

LWA:dc22/82/c12

Attachment

$$-CO- = \frac{(4.30)(6)(10^3)(1.11\%)}{(93.97)(99\%)}$$

$$= 3.07 \text{ MMOL/MOL AHG}$$




| Sample Description | Accessible -CO-, mmol/mol AHG |
|---|---|
| Cotton hydrocellulose[a] | 1.0 |
| Kraft pulps: | |
| CEDED bleach | 0.56 |
| CEDED + HOCl | 8.4 |
| CEDED + ozone | 2.6 |
| Ozone | 2.2 |

[a]Accessible carbonyl by borotritide, 1.1 mmol/mol AHG. Sample and analysis provided by V. M. Gentile and L. R. Schroeder, Institute of Paper Chemistry

311-49

UNIVERSITÉ RENÉ DESCARTES (PARIS V)

UER DES SCIENCES PHARMACEUTIQUES ET BIOLOGIQUES

DÉPARTEMENT DE CHIMIE ORGANIQUE
ERA 613 DU CNRS
U 266 de l'INSERM
PROFESSEUR B. P. ROQUES

Paris, July 19th, 1984.

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

Dear Professor Shapiro,

**Conformational studies of renin inhibitors.**

Pepstatin is a potent inhibitor of several acid proteases inclusing renin (1). It is a pentapeptide containing the unusual amino acid statine [3-(S)-hydroxy-4-(S)-amino-6-methylheptanoic-acid] (2). Its sequence is :

**Iva-Val-Val-Sta-Ala-Sta-OH**

In order to understand relationships between structure and inhibition activity of pepstatin we start its conformational study by proton NMR spectroscopy on a Bruker 270 MHz. The first step in this investigation is the assignment of all resonances in $^1H$ NMR spectrum. For this purpose one could use both one and two dimensional techniques, although were are limited for the two dimensional ones by the DRI 30.

On Figure 1 is represented the assigned cosy spectrum of pepstatin dissolved in DMSO-$d_6$ (5 mM) and on Figure 2 a high resolution one dimensional spectrum for coupling constant analysis.

The Hα and Hβ protons of Isovaline are severely overlapping, they were assigned by double quantum experiments with delays modulating for 8 Hz and 2 Hz coupling constants, as one expect for two coupled protons with similar chemical shifts to lie on the double quantum diagonal.

Although all resonances belonging to the different type of aminoacids were assigned, we are unable at this stage to differenciate the two valines and the two statines residues in the sequence.

Yours Sincerely.

Bernard P. ROQUES

Muriel DELEPIERRE

**Acknowledgments**

We gratefully acknowledge Dr D. NISATO and CLIN MIDY laboratory for generous gift of pepstatin.

1. T. Aoyagi, S. Kuhimoto, H. Morishima, T. Takeuchi and H. Umezawa. J. Antibiot. Tokyo 24, 687 (1971).
2. D.H. Rich, Y. Terada and M. Kawai. Int. J. Peptide Protein Res. 22, 325-332 (1983).

4, AVENUE DE L'OBSERVATOIRE 75270 PARIS CEDEX 06 TÉL 329 12 08

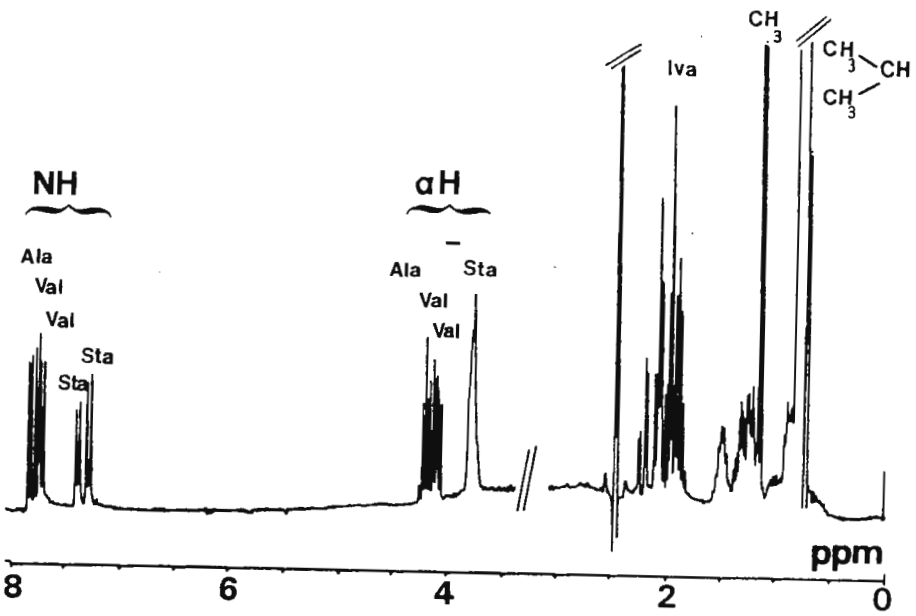



Figure:2. 270 MHz $^{1}H$ NMR spectrum of Pepstatin in DMSO-$d_6$

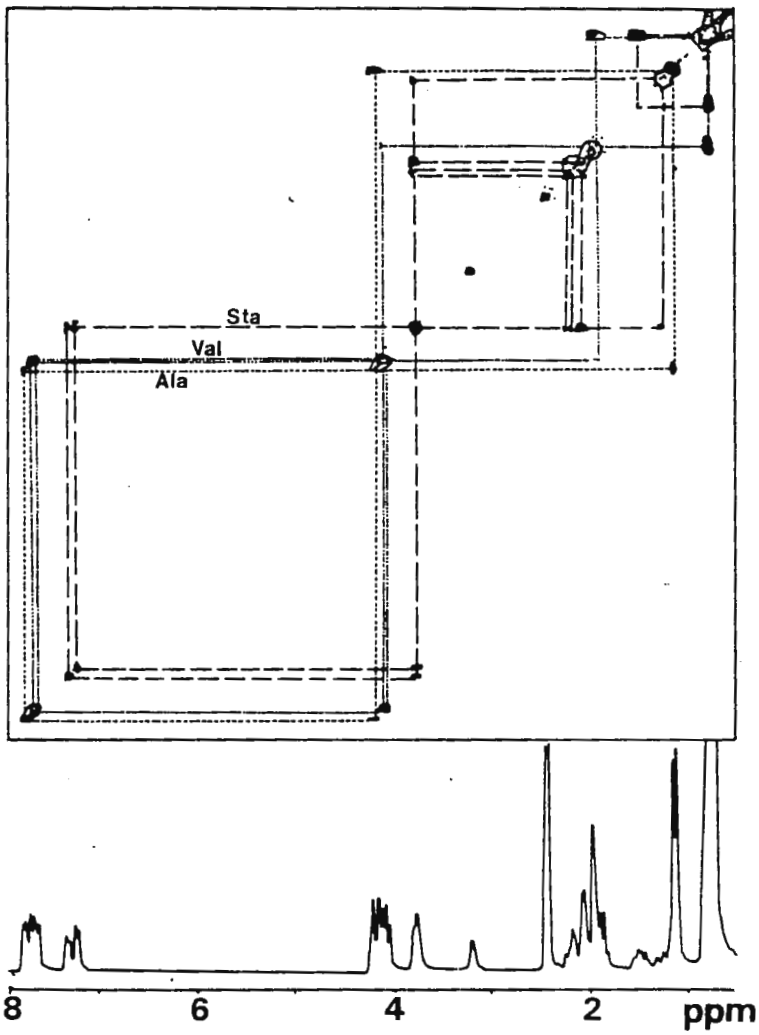



Figure:1. Proton correlated spectrum of Pepstatin (270 MHz matrix 512.512 , after symetrisation 64 scans).

311-51

GORLAEUS LABORATORIES
STATE UNIVERSITY LEIDEN
DEPARTMENT OF CHEMISTRY

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

| Your reference | Your letter | Our reference | Date |
|---|---|---|---|
| -- | -- | GWC-dd | July 19, 1984 |

76, Wassenaarseweg
Phone 31/71 - 148333

From

Ext. 4256 /

Subject $^{31}P$ NMR studies on hormone-sensitive glucose transport in rat adipocytes

Dear professor Shapiro,

In our studies on hormone-sensitive glucose transport in rat adipocytes we observed a correlation between ATP-levels and the rate of sugar uptake. To test a possible correlation between transport and phosphorylation we are using $^{31}P$ NMR and biochemical techniques.

Addition of ATP to the mitochondrial and the plasma membrane fractions separately produces identical $^{31}P$ NMR spectra (see fig. A). Addition of ADP to the two fractions however, results in different spectra: ADP is converted by the mitochondrial fraction mainly into ATP and AMP (fig. B), while in the plasma membrane fraction $P_i$ and AMP are formed (fig. C).

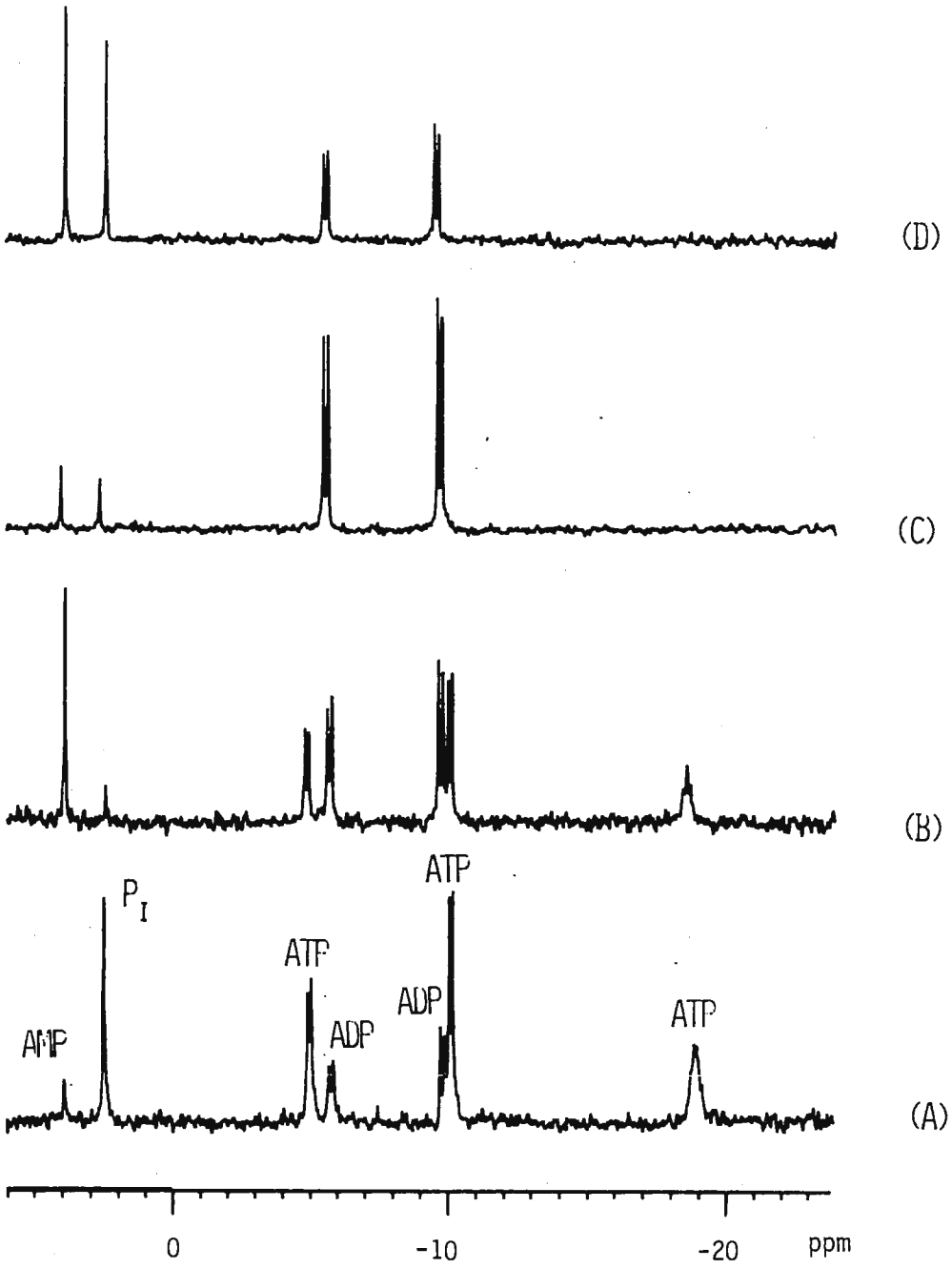
When the fractions are combined and ADP is added, no ATP formation is seen (fig. D). Apparently the ATP formed by the mitochondrial membranes is consumed immediately by the plasma membranes. Further work is in progress to identify the various enzymatic activities in both fractions.

Sincerely yours,

T. Wieringa
Academic Hospital
Laboratory for Endocrinology
State University Leiden

G.W. Canters
Gorlaeus Laboratories
State University Leiden

Please credit this contribution to Johan Lugtenburg's subscription.




$^{31}P$ NMR spectra after about 1 hour of incubation of: mitochondrial fraction with 10 mM ATP (A); mitochondrial fraction with 10 mM ADP (B); plasma membrane fraction with 10 mM ADP (C); and mitochondrial and plasma membrane fraction together with 10 mM ADP (D).

311-53

Columbia University in the City of New York | *New York, N.Y. 10027*

DEPARTMENT OF CHEMISTRY Havemeyer Hall

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

19 July 1984

Dear Barry:

Because of the current interest in the use of phase sensitive displays of 2-D spectra, we decided to try to implement the improvement in the conventional heteronuclear 2-D chemical shift correlation experiment which has been suggested by Ernst. (JACS 1983, 105, 6944)

The basic sequence should be improved by the insertion of simultaneous refocusing pulses at the midpoint of the $\tau$ and $\tau'$ intervals, (using the notation of Ernst). At present, in our hands, this has proved to be far from true!

The accompanying spectra show a comparison of the results of the basic sequence (top) with that of the refocused sequence (bottom). The experimental parameters and data processing were identical apart from the change in pulse sequence. The sample was longifolene.

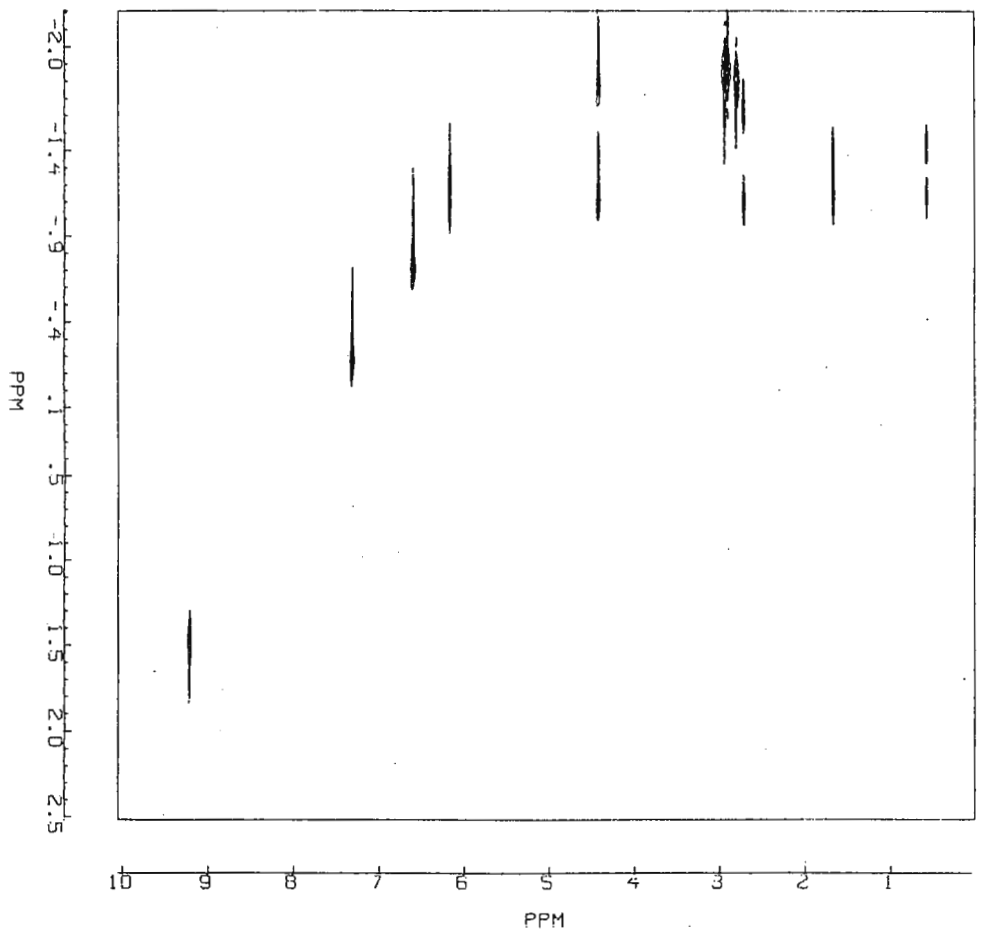
Notice what happens to the $CH_2$ groups! There are also changes in the relative intensities of the signals. Since the same contour levels are plotted in both spectra, this data suggests that there is, in fact, a sensitivity loss with the addition of these refocusing pulses, contrary to our expectations. In our next contribution, we hope to have an explanation of these (and other) intriguing effects.

I also enclose a short "for sale" notice, since we have a spare magnet and some associated electronics that we want to get rid of.

Best Wishes

Chris

C. J. Turner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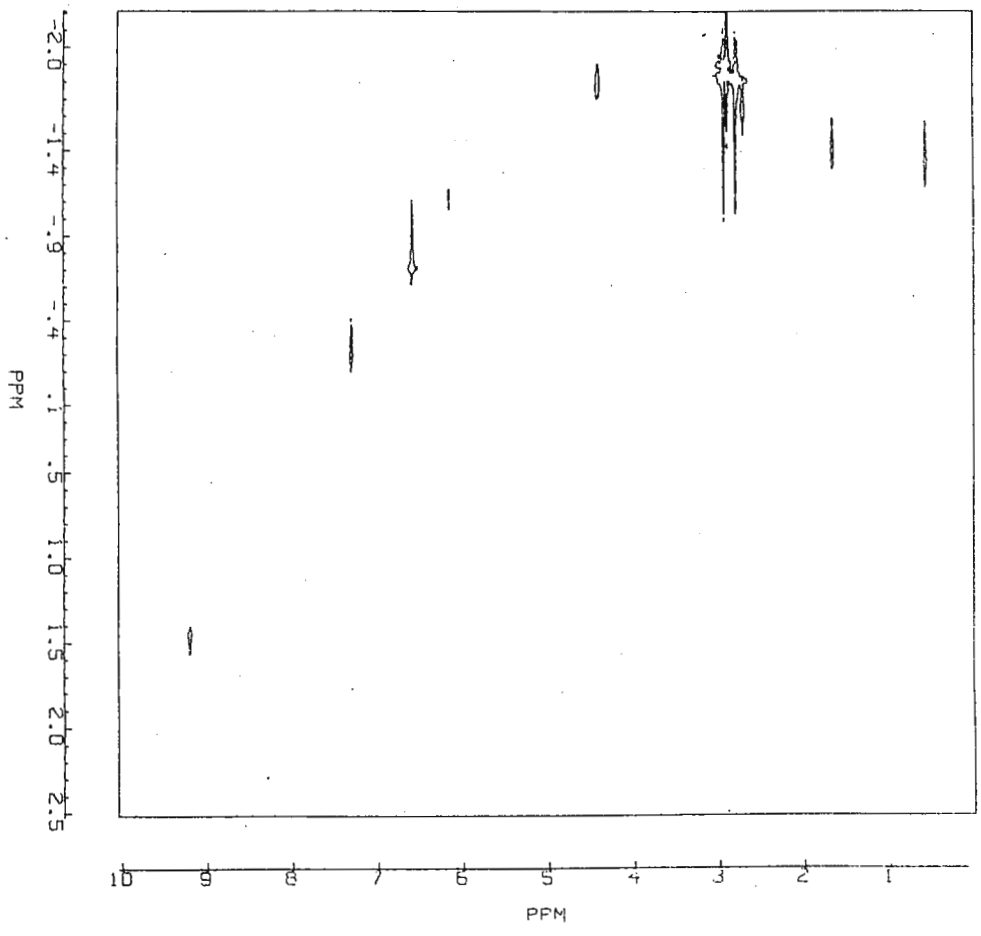
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PPM

Laboratoire de Chimie Organique Physique - Institut de Chimie - Université de Liège - Sart-Tilman par 4000 Liège 1 - Belgique

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

July 20, 1984

"While the cat is away, computers run"

Dear Barry,

I don't have to tell you that kinetics can be a chore. My co-worker, Dr. Yvette Houbrechts, has talked the ASPECT 3000 computer attached to our Bruker AM 300 into taking over while she enjoys her weekends, by recording spectra at regular, pre-set times.

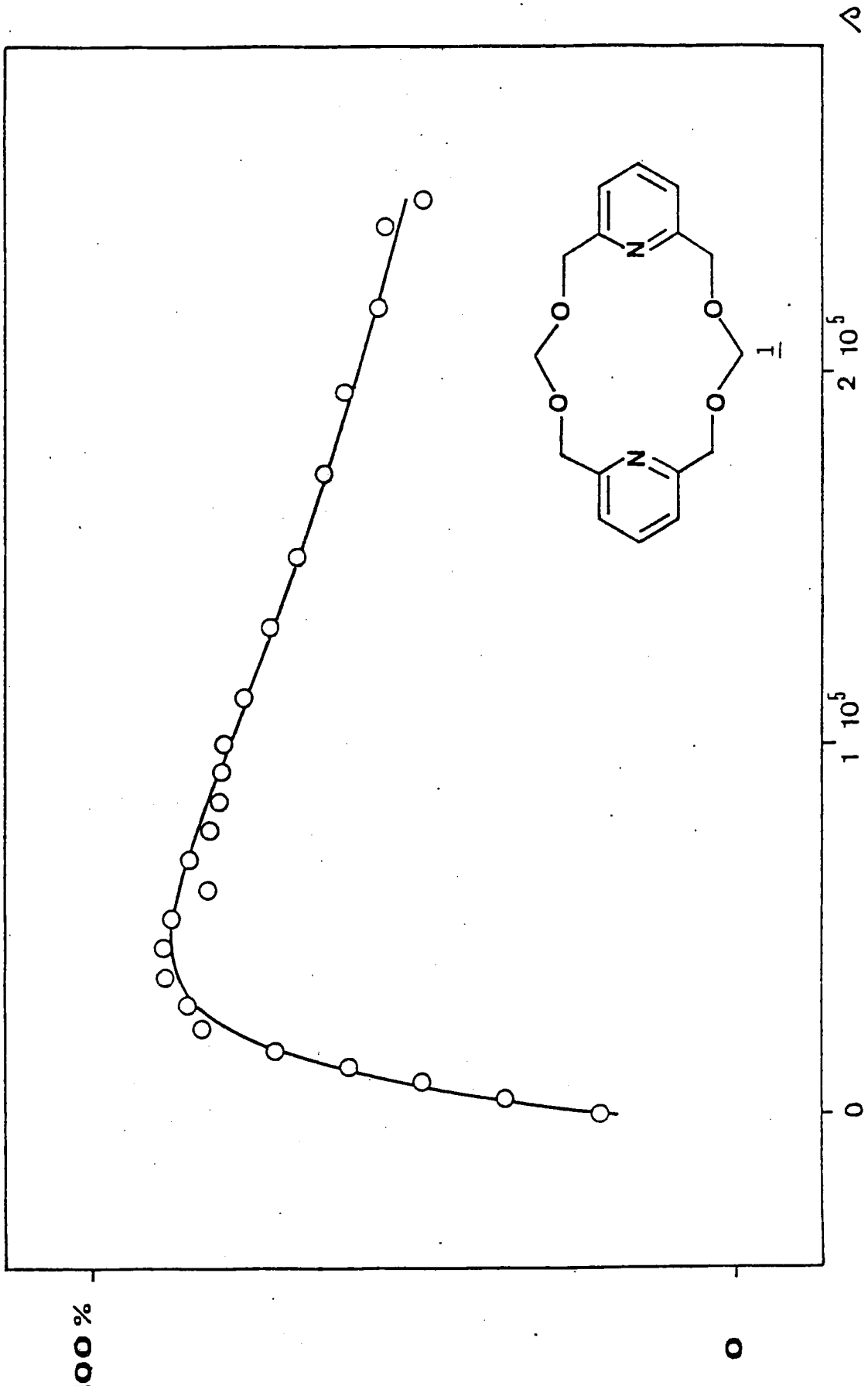
The bispyridyl crown ether 1 reacts with borane-tetrahydrofuran to form a complex 2 having two $BH_3$ units attached to the two pyridine nitrogens. Upon dissolution in nitromethane, 2 displays a conformation in which methylene protons have become diastereotopic. The supramolecular assembly 2 proceeds to slowly lose a $BH_3$ molecule according to first-order kinetics ($k_1 = 3.9\ 10^{-5}\ s^{-1}$ at probe temperature in $CD_3NO_2$), which leads to a new, monoborane complex 3. The conformation of 3 is also chiral; and 3 is not an hypervalent molecule, as we had originally hoped. Loss of the remaining borane by 3 also occurs by first-order kinetics, with $k_2 = 2.9\ 10^{-6}\ s^{-1}$ under the same conditions. The attached figure is a plot of the build-up and demolition of the intermediate species 3, recorded automatically during one of the long May weekends Europeans indulge in.

With best regards,

Cordially yours,

Houbrechts Pierre Laszlo Arthur Mathy

Yvette Houbrechts Pierre Laszlo Arthur Mathy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UNIVERSITY OF DENVER
An Independent University
University Park, Denver, Colorado 80208
Department of Chemistry / 303 · ~~753-2436~~ 871-2980

July 23, 1984

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, TX 77843-3255

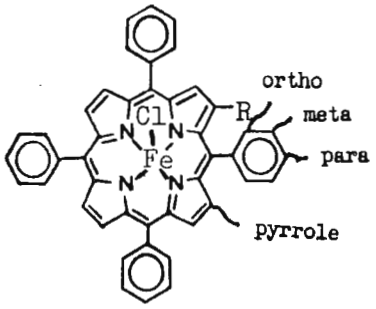
Re: Our a-200, Spin Delocalization in Iron Porphyrins

Dear Barry:

We are starting to get data from our Chemagnetics a-200. Since installation is not complete, we will wait until our next letter to report on overall performance. However, it is already obvious that the use of two displays - one for spectra and the second for the parameters - is very convenient.

We are interested in examining the extent of spin-delocalization in a variety of metal complexes and relating the spin-delocalization to the electron-electron spin-spin splittings that we observe in related spin-labeled complexes. We have looked extensively at a series of spin-labeled copper porphyrins by EPR and are starting to examine the iron(III) analogs. We have also begun to look at the $^1H$ NMR spectra of the high spin iron porphyrins. The following isotropic shifts in ppm were obtained at room temperature in $CDCl_3$ solution with the free porphyrins used as the diamagnetic reference.

| | pyrrole | ortho | meta | para | $H_A$ |
|---|---|---|---|---|---|
| I | -70.2 | +1.7 | -4.5 | +1.4 | |
| II | -71.5<br>-73.0<br>-81.0 | +2. | -4.5<br>-5.7 | +1.4 | -14.7 |
| III | -70.0<br>-72.0<br>-73.0<br>-80.0 | +2.5 | -4.5<br>-5.7 | +1.3 | -32.3 |




R

H (I)

$-C(H_A)=C(H_B)-COOEt$ (II) trans isomer

$-C(H_A)=C(H_B)-COOEt$ (III) cis isomer

The isotropic shifts for the phenyl protons in II and III are similar to those of unsubstituted I which indicates that these substituents (R) have little impact on the molecular geometry, magnetic anisotropy, and spin delocalization. The shifts for the pyrrole protons in II and III are split by the substitution on one of the rings. The resonance for one pyrrole proton is about 8 ppm downfield of the other pyrrole resonances. It is likely that the unique proton is the one on the substituted ring. The larger downfield shift for that proton indicates a larger spin density in the substituted pyrrole ring than on the other rings. The splittings of the pyrrole resonances are similar for the two isomers. However, the shifts for $H_A$ are very different for the isomers. The value observed for the cis isomer is similar to that which has been reported for the $CH_2$ of the ethyl groups on the pyrrole rings in Fe(OEP)Cl (-35 and -39 ppm for the two diastereotopic signals) (1). The isotropic shift for $H_A$ in the trans isomer is substantially less negative than for the cis isomer. The geometrical constraints of the molecule require that the dipolar contributions to the shifts for $H_A$ (1) cannot be very different for the cis and trans isomers. The difference must be largely due to changes in the contact term which suggests that there is less net spin delocalization at this position for the trans isomer than for the cis isomer. The visible spectra for the free porphyrin and for the related copper complexes indicate greater interaction between the substituent and the porphyrin ring for the trans isomers than for the cis isomers (2). In related spin-labeled copper complexes there was greater spin-spin interaction through the trans linkage than through the cis linkage. Perhaps the smaller negative value of the isotropic shift for $H_A$ in the trans isomer than in the cis isomer reflects a positive contribution to the net shift which is not present in the cis isomer or in FeOEPCl. Clearly we need to assign the resonances for other protons of the substituent to determine whether this pattern persists further along the chain. We have not yet assigned the resonances for $H_B$. Apparently they are shifted much less than $H_A$.

Sincerely,

Gareth R. Eaton
Professor

Sandra S. Eaton
Visiting Professor

(1) G. N. LaMar, G. R. Eaton, R. H. Holm, and F. A. Walker, J. Am. Chem. Soc. 95, 63 (1973).
(2) K. M. More, S. S. Eaton, and G. R. Eaton, Inorg. Chem. 20, 2641 (1981).

Brandeis University

Graduate Department of Biochemistry
Waltham Massachusetts 02254

August 1, 1984

NMR Computer System Based on 8086 and 8087 Multibus System

A. Redfield

Dear Barry:

This is a further description of our home-brew high resolution 500 MHZ system, primarily of its new computer system. In general the spectrometer has worked well; we have had some trouble with spinning, finally solved with judicious placement of pieces of paper tape on the probe, and with rf breakdown in the probe dewar (the one around the sample itself), solved by breaking its vacuum to air. Our first paper on $^{15}$N-proton 2D NMR, based on the paper of Bax, Griffey, and Hawkins, will appear shortly (S. Roy et al, Biochemistry).

I spent more than six months of evenings programing our new computer to emulate and improve on our old Nova 1220 and it has now been working for several weeks. It was supplied by Distributed Computer Systems of Waltham, MA, and is a straightforward and reliable industrial multibus system based on 8086 and 8087 chips, currently 5 MHZ. It has a 256kB TI DRAM, a Winchester disc, and a 1 MB 8" floppy. I have programmed it to drive a Houston DMP40 plotter, and also built a 16 bit in/16bit out I/O board for Nova emulation. Cost <$15,000 for hardware. Much of the software would run on IBM PC or clones thereof, though more slowly, since these can be fitted with 8087's, I believe.

The standard FT and related transorm takes 16 sec for 8K complex points (16K points). This includes a two-fold zerofill from 4K input complex points, premultiplication by a stored massaging function, and post-phase and amplitude correction by a stored complex function.[1] About 80% of this time is the FT itself. This time will be cut by 5/8 when 8 MHZ 8087's are available, if ever. The software could do twice as big an FT with only trivial modification, and could be increased without limit using disc swapping.

We now store entire 2D runs as FID's on the hard disc and process them later. A typical $^{15}$N 2D run on tRNA uses 256 input complex points and 64 values of $\tau_1$; each of the latter involves 64 FID's of which 32 are taken with the $^{15}$N pulses in phase, or 180° out, and the other 32 are taken with pulses $\pm$90° out of phase. In an overnight run we obtain about 30 cycles of such data. These are FT'd with two-fold zerofill as described above, and the inner 3/4 of the real part of all the proton spectra are then stored in a disc file in semitransposed form[2], giving a 128 x 384 x 32 bit data set. The semitransposed data are then read from disc in sequential groups, unshuffled, and the second transformations are performed with twofold zerofill, giving 128 x 384 real output points which are stored on disc. This real phase 2DFT requires 8 minutes. Runs of up to 1024 x 768 output points will be feasible on our system and will require roughly 10 times as long to process. However

we can speed up processing perhaps four-fold by (a) doing the first dimension during the last cycle of the run as I described previously2 , storing both the FID's and the semitransposed half transformed data on disc. (b) at some point compressing the data to 16 bit, probably after the first FT. This will permit making a floppy image of a 1024 x 768 run on two floppy discs. Even greater speed could be obtained if we had a decent operating system with interrupts so that time spent seeking sectors would not be wasted, and an array processor. In that case a 1024 x 768 output run could be processed in as little as five minutes, I believe. Note that this is what would usually be called a 2K x 2K 2DFT.

The FT program is speeded by grouping together butterflies that use the same cosine and sine values, and by performing the (32 bit integer) additions and subtractions of one butterfly on the 8086 while the 8087 does the multiplications for the following butterfly. Floating point arithmetic is not really very good for NMR FT because noise is always present at predictable constant levels. The 8087 furthermore spends about half its time being loaded and unloaded. A less sophisticated 32 bit signed integer-multiply version would be better. A data set of up to 128 Kbyte can be FT'd since I use the data segment for real, and the extra segment for imaginary numbers.

The software uses CP/M small model, and C language; and assembler for FT, phase correction thereof, high speed analog display, and for major data moving and shuffling, based on paragraph pointers. We continue to use the input processor built by Sara Kunz[3] (similar in principle to, but much simpler than, that on current Varian XL's) which has been invaluable to achieve this performance.

In no way would I urge that people program their own systems in a big way, or use this particular processor. Our instrument has a relatively primitive timing system (not largely computer controlled), no fancy graphics, and no peak printout routines. I hope to get these things by transferring data to our new XL 300, if I can figure out how. Our system is user-unfriendly; we (the computer and I) decide what you can do; and it is probably the only remaining FTNMR in the world with no keyboard entry (well, almost; we do use CP/M for hard-to-floppy file transfers, etc.). Instead, the computer polls numerous switches. This scares off many organic chemists (a mixed blessing), though it's really just as easy as looking up all those commands.

1. A.G.R., NMR Principles and Progr. 13, p. 137 (Diehl, Fluck, and Kosfeld, eds., Springer Verlag 1976).

2. A.G.R., J. Magn. Res. 52, 310 (1983).

3. S. D. Kunz and A.G.R., Rev. Sci. Instrum. 54, 503 (1983).

Al Redfield

Lilly

**Lilly Research Laboratories**
A Division of Eli Lilly and Company

307 East McCarty Street
Indianapolis, Indiana 46285
(317) 261-2000

August 3, 1984

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

Dear Barry:

EXPERIENCE WITH THE IBM 9000

We have had an IBM 9000 in our laboratory for the better part of a year now. We have written many programs, most in Pascal, and we would be pleased to discuss with other CS-9000 owners our experiences with the system, or the possibility of swapping programs.

Some of the programs we have written are:

1. ARM This is an old program, originally written over ten years ago on a DEC-10, which uses substituent shifts to estimate the proton and carbon chemical shifts in benzenoid aromatics. We have translated and transported this program to other computers over the years. At some point we also added methods of estimating proton chemical shifts at aliphatic carbons, changing the program name from AROM to ARM to celebrate the occurrence. The program was moved to the CS-9000 in the original FORTRAN form, but we also have a Pascal version written for the ASPECT computer. The program suffers from the facts that it uses substituent parameters, and that we have not been diligent in keeping these parameters up to date.

2. AX This is a Pascal program, started on the ASPECT but moved to the CS-9000 on its arrival, which calculates the density matrix for two-spin loosely-coupled systems. The program includes routines to pulse (with 90° phase shifts) the system, compute the effects of time evolution (sans relaxation!), and report the intensities of signals induced. It does not compute FIDS or do any graphics. The

program has lots of commentary which tries to explain what is happening, and I wrote a more detailed discussion on a separate memo, which my colleagues say they can't make heads or tails of. I wrote these programs and memos primarily in an attempt to explain the elements of DM theory to myself, and I'd like to acknowledge John Grutzner's very important contributions to this self-education project.

3. REFSPEC This is another Pascal program which was originally developed to alleviate the task of creating correlation diagrams. We also use it to enter and store reference spectra on disk. The program can recall reference spectra from disk, create stick plots or stack two plots above each other, draw dashed lines to correlated peaks, etc. The program does not (yet) handle "real spectra," but keeps only tabulated data. REFSPEC is under constant development, but we do try to stop occasionally and document what we've got. It uses Pascal units for inputting real numbers and graphing which might be generally useful for other applications. Much of the code in these units are based on demonstration programs from Jim Cooper's publications (and "to be publications"), and we are pleased to acknowledge a lot of help and advice from Jim.

We look forward to hearing what others have been doing with laboratory mini-computers.

Best regards.

LILLY RESEARCH LABORATORIES

Mary Ann

Mary A. Bogan
Physical Chemist
Physical Chemistry Research

Doug

Douglas E. Dorman, Ph.D.
Research Scientist
Physical Chemistry Research

jcw

311-63

**Varian** / 611 Hansen Way / P.O. Box 10800 / Palo Alto / California 94303 / U.S.A.
Tel. (415) 493-4000
Telex 348476

varian

August 3, 1984

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

Dear Barry,

Subject: Positions Available

As you know, our NMR business has been growing rapidly. As a result, we are currently seeking several additional people to work in our NMR Research & Development group. We currently have positions open in the RF, probe, and software development groups. Anyone interested in joining our new product development group in any of these areas should send his or her resume to either of us.

Howard Hill. Rene Richarz

Howard Hill, Manager Research & Technology
Rene Richarz, Manager Software Development

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SOLID-STATE OR MULTINUCLEAR SPECTROMETER COMPONENTS FOR SALE
1.Nicolet-Nalorac 3.5 Tesla 4" bore supercon magnet, bought in 1978-good condition $16,000 2.Room temperature shim set for above.$1000 3.E/RTS power supply for above $800 4.Nicolet multinuclear probe for above magnet 18-40 Mhz Model 150235-150280 $1000 5. Nicolet variable temperature computer controlled unit$1000 6. RF Commm. Model 805 10 watt wideband power amp. $300 7. ENI Model 310L 10 watt wideband power amp. $300 8. Telco Cyclone 500 2-30 Mhz 100watt linear power amp. $100 9. TEMPO Model 2002 150 Mhz 1Kw linear power amp. $500 10. Drake Model L-4b 3-30 Mhz 1 Kw linear power amp. $300 11. Henry 100 watt 150 Mhz linear power amp.$150 12. RHG IF amp. 10 Mhz $100 13. RHG IF amp 60 Mhz $100.

If interested contact Dr. Christopher Turner, box 555, Havemeyer Hall, Dept. of Chem,Columbia University,New York,N.Y. 10027 or phone 212-280-4601

ANALYTICAL FACULTY OPENING AT PURDUE

We would like to bring to your attention that the analytical division of chemistry at Purdue is currently seeking candidates for a position at the assistant or associate professor level, effective August 1985.

Minimum requirements include a Ph.D. in chemistry and exceptional promise in research and teaching at the undergraduate and graduate levels. Applicants for associate professor must have demonstrated distinguished research and teaching abilities.

One of the research areas of interest is nuclear magnetic resonance. The continued strength of the department in this area is indicated by the recent establishment of the Purdue University Biochemical Magnetic Resonance laboratory. This laboratory contains two superconducting-solenoid NMR spectrometers: a Nicolet NT-360 narrow-bore spectrometer with probes for $^{1}H$, $^{31}P$, $^{13}C$, and $^{15}N$, and a Nicolet NT-150 wide-bore spectrometer with probes for $^{1}H$, $^{31}P$, and $^{13}C$. Each spectrometer has its own computer, disk, graphics display, and digital plotter. In addition the department recently acquired a 200 MHz Varian superconducting NMR and a 470 MHz Nicolet instrument.

Curriculum vitae, including undergraduate and graduate transcripts for applicants at the Assistant Professor level, a summary of planned research and three letters of recommendation should be sent by October 15, 1984 to: Professor H.L. Pardue, Head; Department of Chemistry; Purdue University; West Lafayette, Indiana 47907. Purdue is an Equal Opportunity/Affirmative Action Employer.

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*Department of Chemistry*

YORK UNIVERSITY

FACULTY OF SCIENCE

4700 KEELE STREET, DOWNSVIEW, ONTARIO M3J 1P3

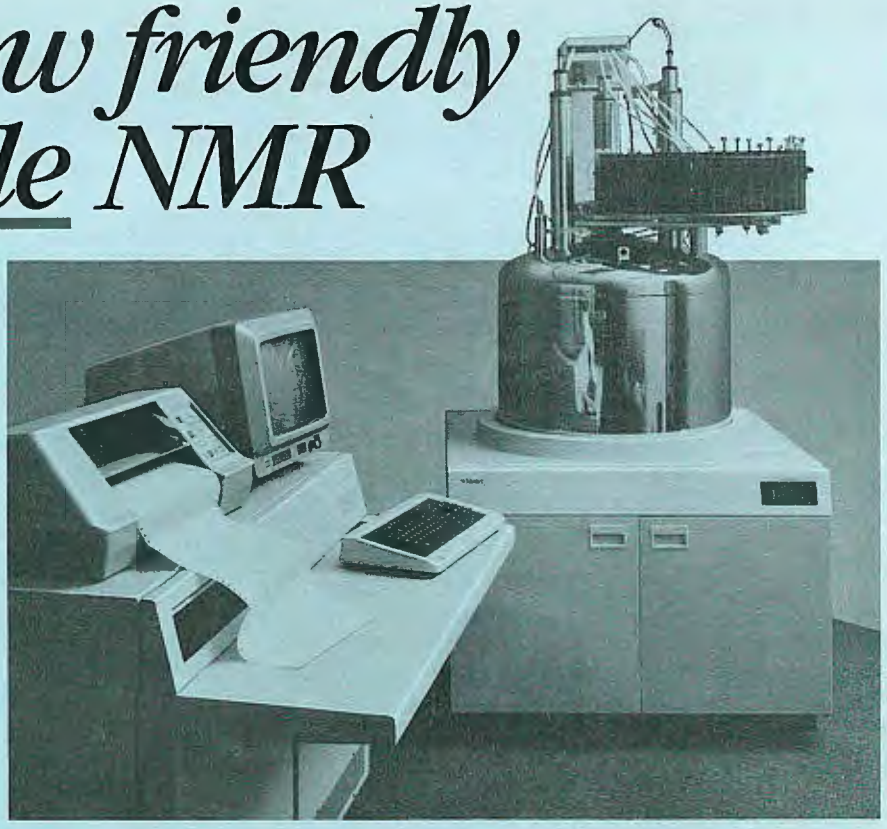
NMR TECHNOLOGIST POSITION OPEN

We currently have available a vacancy for a person with a background commensurate with operating and maintaining a high field FTNMR facility. The applicant would be expected to perform routine maintainance and be able to trouble shoot in the event of operational problems. Both Bruker (300 MHz) and Varian 80 MHz instruments are involved and both companies have good service centres in the Toronto area.

Familiarity with other modern spectroscopic equipment (e.g. FTIR, ESR, GC-MS), and computer interfacing would be a distinct advantage.

The position would particularly suit a Canadian citizen wishing to re-establish in Canada, otherwise ability to obtain landed immigrant status is required. Starting salary is approximately $25 K Canadian funds. Applications should be made to the Chairman of the Chemistry Department, Professor C.R. McArthur, at the letterhead address.

# *Find out how friendly and versatile NMR can be.*



The QE-300 spectrometer was specifically developed for high efficiency, high-throughput carbon and hydrogen NMR. It provides a complete range of routine and high resolution capabilities with a 300 MHz (7 Telsa) superconducting magnet, synthesizer based frequency control, quadrature phase detection, high-speed pulse programming, and a dual $^{13}C/^{1}H$ switchable probe. To make operation dramatically simple, the QE-300 also features auto-locking, auto-shimming, and auto-spectral phasing plus an incredible menu driven software package called CHARM.

And now, to make the QE-300 even more versatile, we've added a number of accessories to make your work faster and more efficient than ever before.

## Around-the-clock data acquisition and processing

First, there's the QE-300 Automatic Sample Changer for unattended, sequential analysis of up to 100 samples. It lets you collect spectra continuously—overnight and even over weekends. So, instead of facing a stack of samples when you walk into your lab in the morning, you have a stack of results, completely phased and annotated to your specifications.

## Multiple megabyte speed and power

Winchester and other optional hard disk accessories for the QE-300 dramatically expand your data handling capacity. And to speed up Fourier Transforms and spectral phasing, you can add a high-powered array processor as well.

## Remote data stations for multi-user productivity

Increased data requires more data processing capability. To meet that need, you can add a remote, interactive data station to the QE-300. It communicates directly with the QE-300 as well as other Nicolet 1280-based NMR spectrometers and enables you to process NMR data off-line while the main spectrometer is being used to acquire spectra.

## VT capability for temperature dependent studies

A new microprocessor controlled Variable Temperature accessory for the QE-300 allows acquisition of experimental data at differing sample temperatures. The controller ranges from +160C to −100C with ±0.1C precision.

## Enhanced $^{13}C$ sensitivity

An optional dual 10mm $^{13}C$/5mm $^{1}H$ switchable probe increases $^{13}C$ sensitivity to more than three times that of the standard $^{13}C/^{1}H$ probe.

## Broadband console electronics and X nucleus probes

Broadband console electronics and X nucleus probes for the QE-300 are offered for observing nuclei other than $^{13}C$ and $^{1}H$, including a dual 5mm $^{31}P/^{1}H$ switchable probe for analyzing phosphorous in biological, medical, and related applications.

Call or write today for complete information on the QE-300. We'll help you select the accessories to meet your NMR needs.

The QE-300 with CHARM. Friendly, *versatile* NMR for the laboratory that has alot of work to do.

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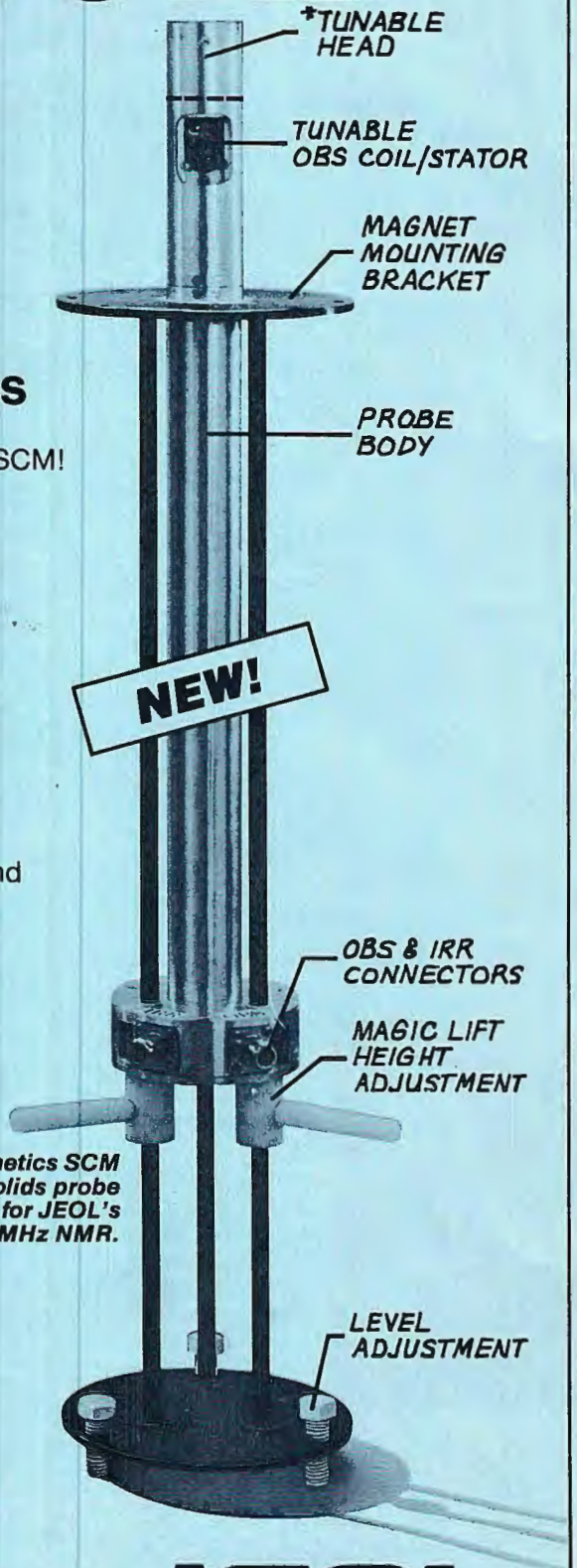


*Chemagnetics SCM Solids probe for JEOL's 270 MHz NMR.*

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