

TEXAS A&M UNIVERSITY

NMR

NEWSLETTER

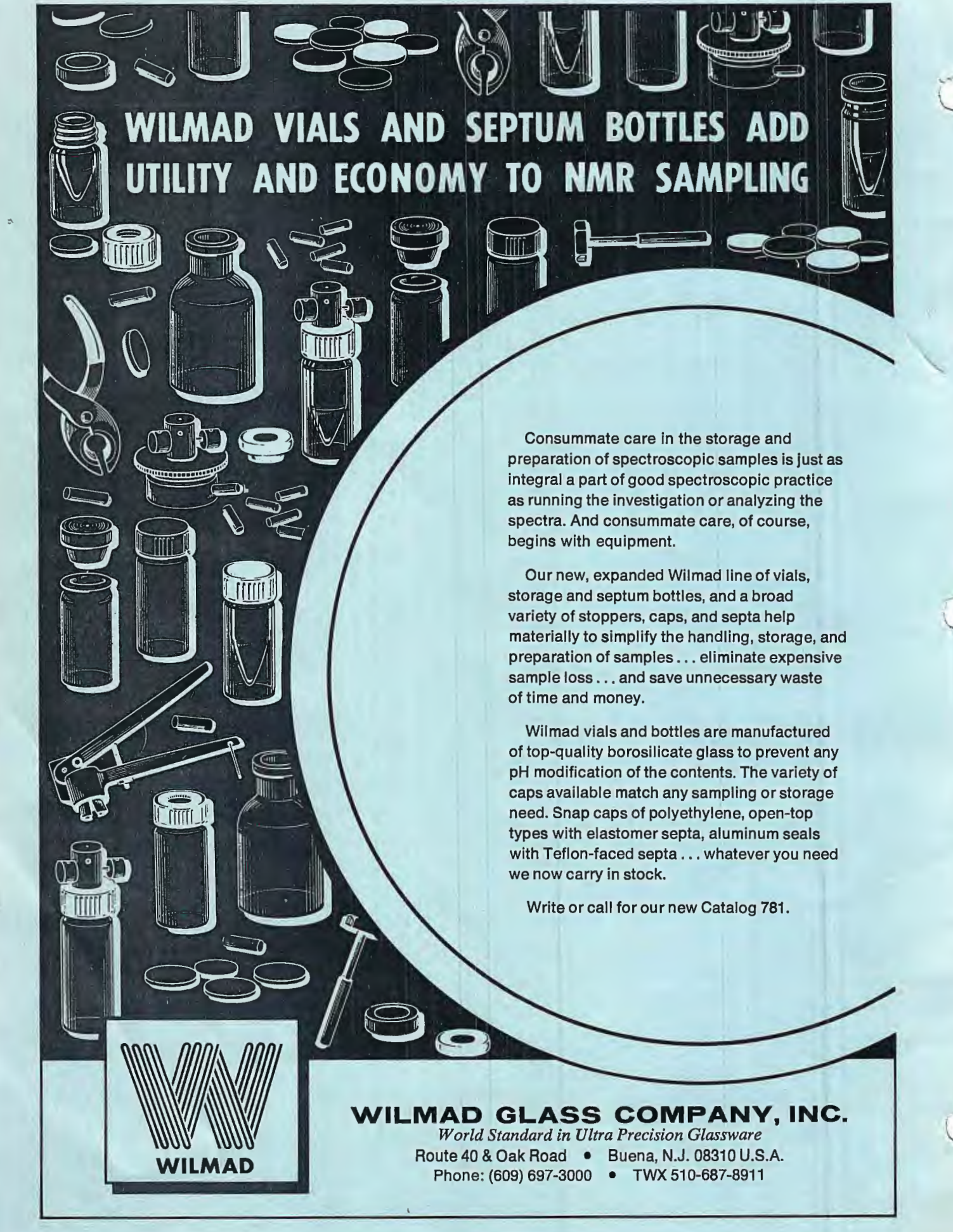
No. 280

January, 1982

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

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DEADLINE DATES: No. 281 1 February 1982
 No. 282 1 March 1982

All Newsletter Correspondence, Etc., Should be Addressed To:

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

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Paul Rösch

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6900 HEIDELBERG 1, 9.11.1981
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Prof. Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843 USA

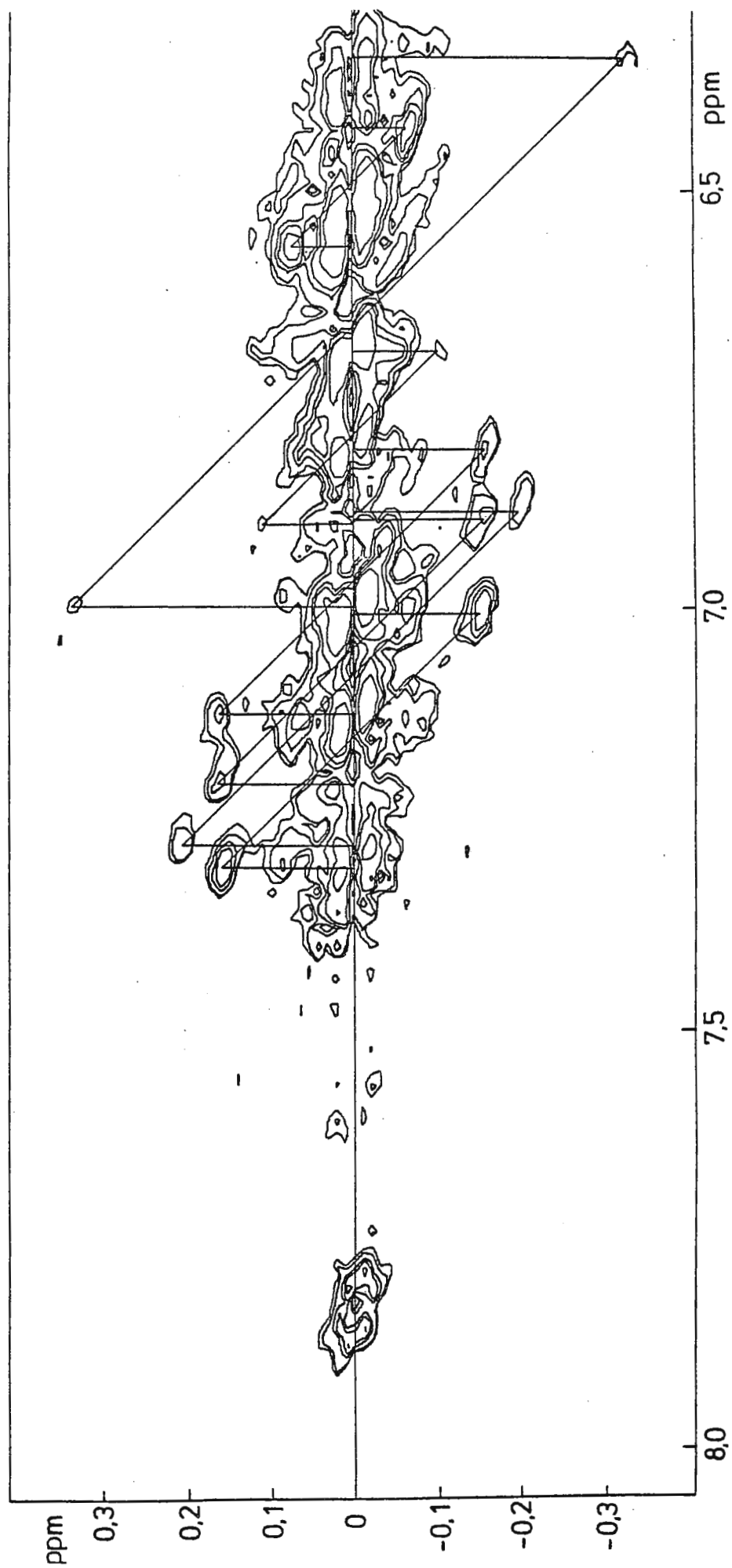
Dear Prof. Shapiro,

the discussion about the usefulness of 2D-NMR methods in biochemistry - real biochemistry, it is - still continues. Most work has been done so far on BPTI, which is easily accessible to 2D methods because of its low molecular weight, its excellent solubility, and the fact that it is available in virtually unlimited amounts. In our lab we work with the protein adenylate kinase from pig muscle, an ATP:AMP phosphotransferase of MW 22000, which is rather stable in 1 mM solutions. One of the tactical goals of our work was the first order assignment of the 7 tyrosyl residues of the enzyme, and therefore we tried a SECSY experiment. The 1mM solution was kept in our 360 MHz spectrometer for four days, and the resulting spectrum is shown in the figure as a contour plot. Seven connected resonances show up quite clearly. This may be taken as a tentative assignment of resonances to the seven tyrosyl residues in adenylate kinase. (A few of them were also assigned by double resonance experiments earlier). We hope that our results encourage more people to try the game.

Silke von Stiernberg
Rainer Marquetant
Hans Robert Kalbitzer
Paul Rösch

Best wishes

Silke von Stiernberg
R. Marquetant
Paul Rösch
H. R. Kalbitzer



CENTRO DE INVESTIGACION DEL IPN

APARTADO POSTAL 14-740

MEXICO 14, D. F.

DEPARTAMENTO DE QUIMICA

November 30, 1981.

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

Dear Professor Shapiro:

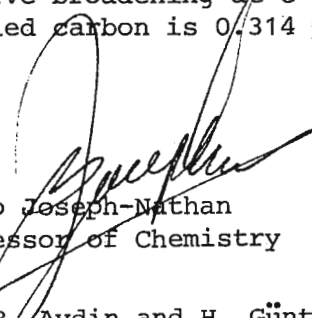
Deuterium isotope effects on ^{13}C nmr signals

Recently published work of Professor Günther^{1,2} regarding deuterium induced shifts on ^{13}C nmr signals, certainly opens new avenues for the understanding of organic molecules and inspires us to report our own observations on the subject.

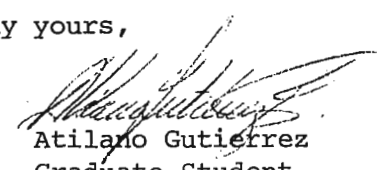
During a systematic study of the ^{13}C nmr spectra of natural occurring cedranolides and some of their derivatives, it became necessary to introduce deuterium atoms at specific positions in order to secure some assignments. The spectra of one of such cases, namely neocedranol are shown in the accompanying figure. The lower trace corresponds to a sample with natural abundant distribution of isotopes, while the upper one is due to a specimen labeled at C-4.

Detailed comparison of these spectra measured at 25.2 MHz, by acquiring 32 K data tables before Fourier Transform, reveals that in addition to the carbon at which the deuterium is placed, isotope effects at two other signals are evident. These are those due to the oxygen bearing carbon (C-5) and to C-8a. On the remaining signals, as far as our measurements can tell, there are no observable isotope induced shifts, although C-8a is separated from the D atom by the same number of bonds as C-3, C-6 and C-9. These preliminary results suggest that stereochemical and related factors have to be studied for deuterium induced effects. Furthermore, it is clear that measurements at frequencies quite higher than 25.2 MHz are necessary for the estimation of induced shifts, since we only observe broadening at C-5 and C-8a. The isotope induced shift at the directly labeled carbon is 0.314 ppm and $^1\text{J}_{\text{C-D}} = 19.2 \text{ Hz}$.

Sincerely yours,



Pedro Joseph-Nathan
Professor of Chemistry



Atilano Gutierrez
Graduate Student

(1) R. Aydin and H. Günther, J. Amer. Chem. Soc., 103, 1301 (1981).

(2) H. Günther and J. Wesener, TAMU NMR Newslet., 276, 34 (1981).

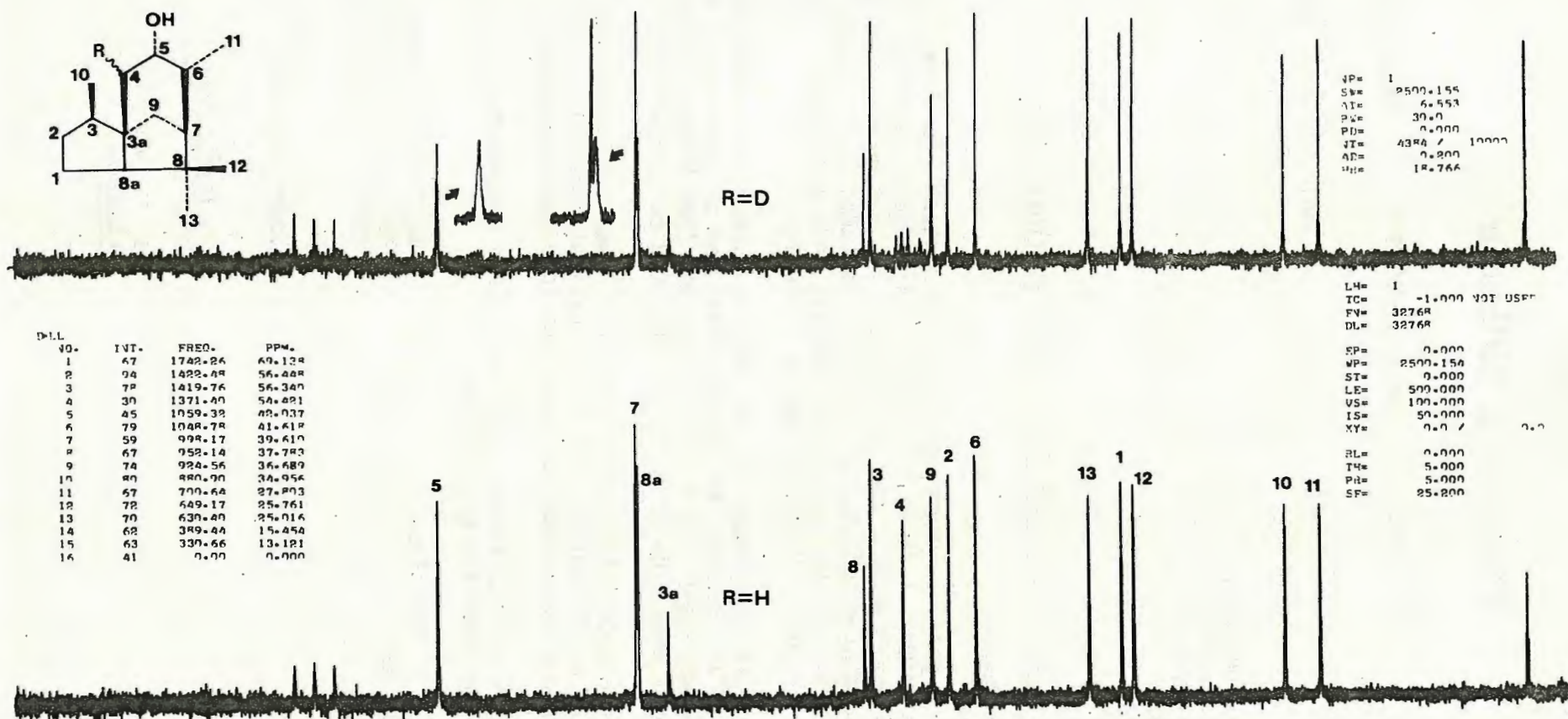


Figure.- Carbon-13 nmr spectra of neocedranol (bottom) and of a deuterated analogue at C-4.



University of Melbourne

DEPARTMENT OF ORGANIC CHEMISTRY

Parkville, Victoria 3052

16th December, 1981

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

4th National NMR Conference - Australia 1983

Dear Professor Shapiro,

Over the past few years, NMR users in Australia have organized National NMR conferences aimed at disseminating the latest techniques and applications of NMR amongst our colleagues. The success of these has been due in large part to the major instrument manufacturers, who have provided funds enabling us to invite overseas speakers. In the past these speakers have included G. E. Maciel, I. C. P. Smith, H. O. W. Hill, P. Laszlo and G. C. Levy.

Although the programme for the 4th Conference, to be held in February 1983 is still in its infancy, we thought that some advance notice to our colleagues overseas may be welcomed. In the event that any TAMU Newsletter readers may be in the South East Asia area at that time we would be pleased to see them.

The Conference will be held at Lorne, a seaside resort approximately 80 miles South West of Melbourne. The extra curricular activities may include tennis, surfing and bushwalking in excellent late summer weather.

Persons requiring further information are welcome to contact any one of the Organizing Committee given below.

Dr R. T. C. Brownlee
Dr I. D. Rae
Dr S. R. Johns

La Trobe University.
Monash University.
CSIRO (Fishermans Bend).

Yours sincerely,

D. P. Kelly,
Chairman.

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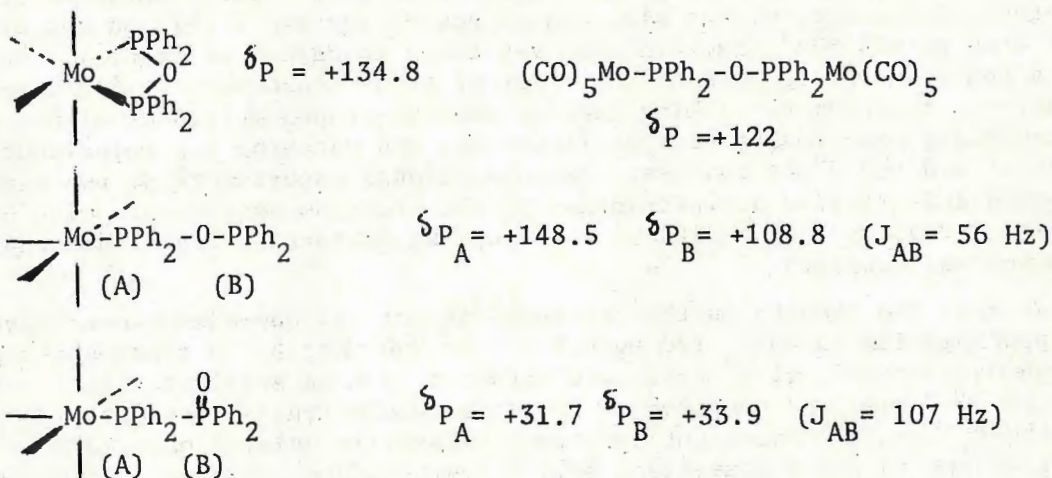
Department of Chemistry
College of Engineering and Physical Sciences
Parsons Hall (603) 862-1550

December 11, 1981

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

Dear Barry:

Thanks for your recent gentle reminder. We have been working on a variety of ligands containing phosphorus-oxygen-phosphorus bonds (POP) and their tautomers. We have successfully isolated several such complexes using transition metal carbonyls. Some contain tautomers not normally favored in the uncoordinated state. Examples of molybdenum complexes of these types along with their P-31 data are:



You may want to title this "Variations on a MolyPOP".
Please credit this to Ms. Kathleen S. Gallagher.

Sincerely yours,

Edward H. Wong
Assistant Professor



BLUE HEN NMR COMPLEX

CHEMISTRY DEPARTMENT
UNIVERSITY OF DELAWARE
NEWARK, DELAWARE 19711
(302) 738-1150

December 8, 1981

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

2D NMR OF PEPTIDES: ANALYSIS OF A COUPLED SYSTEM WITH SEVERE OVERLAPS

Dear Barry:

We have been exploring the use of two-dimensional NMR in conformational studies of peptides. A particularly pretty example of its power is illustrated in spectra of cyclo(D-phenylalanyl-L-prolyl-glycyl-D-alanyl-proline), a rigid cyclic pentapeptide that takes up a conformation, both in solution¹ and in crystals^{2,3}, stabilized by two intramolecular hydrogen bonds. The ¹H NMR spectrum of this peptide has a region of severe overlaps: the resonances of the α-protons of the Phe, of the Ala, and of one of the Pro's fall on top of each other even at 600 MHz⁴ (ca. 4.8 ppm, see arrow in part A of figure). We had made a tentative assignment of the order of these resonances in the one-dimensional spectrum by walking through the overlapped multiplet with a series of decoupling experiments at 1 Hz intervals, and watching for coincident collapses of N-H and H^β resonances. Two-dimensional experiments of two types were performed and afforded a confirmation of the previous assignments with clarity and with certainty. In addition, the coupling pattern of each individual H^α resonance was obtained.

We show the results in the attached figure: A. one-dimensional spectrum of this pentapeptide in CDCl₃ (20 mg/0.5 ml) at 250 MHz; B. 2D cross-sections through each individual H^α resonance obtained from an absolute value, resolution enhanced 2D-J resolved spectrum of the same sample (relaxation delay-90-t₁/2-180-t₁/2-t₂; 32 scans per spectrum; relaxation delay 4 sec; 2200 Hz sweep width, 4K pts in the δ dimension; 68.4 Hz sweep width, 128 pts in the J dimension; quadrature detection; total acquisition time 3.45 hrs); and C. absolute value, resolution enhanced spin echo correlated spectrum of this sample showing coupling connectivities (relaxation delay-90-t₁/2-90-t₁/2-t₂; 16 scans per spectrum; relaxation delay 6 sec; 2000 Hz sweep width, 512 pts in both dimensions; quadrature detection; total acquisition time 8.81 hrs).

We feel that the 2D approach has definite promise for sorting out complex spectra of peptides, and despite the long experiment times will become a much used technique in these systems.

Sincerely,

Martha Bruch

Martha Bruch

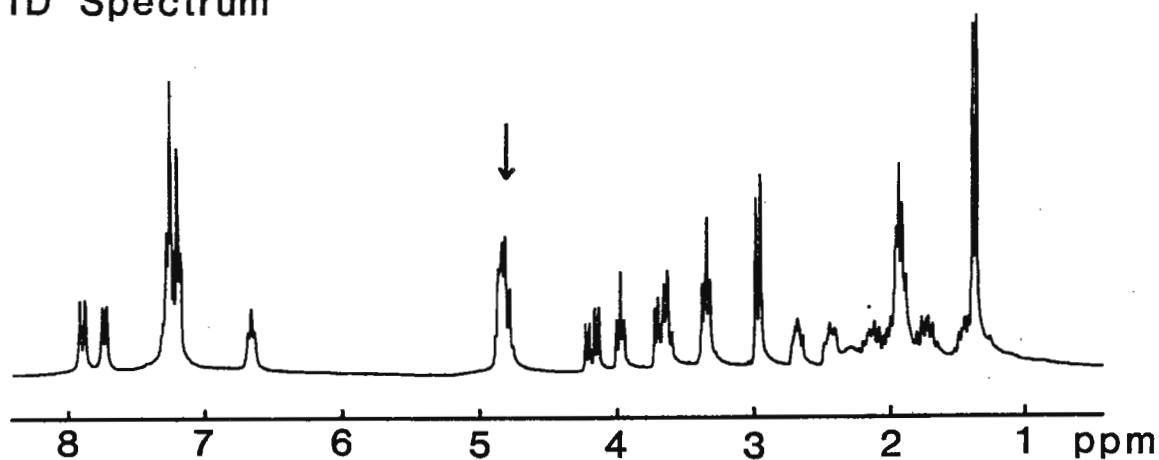
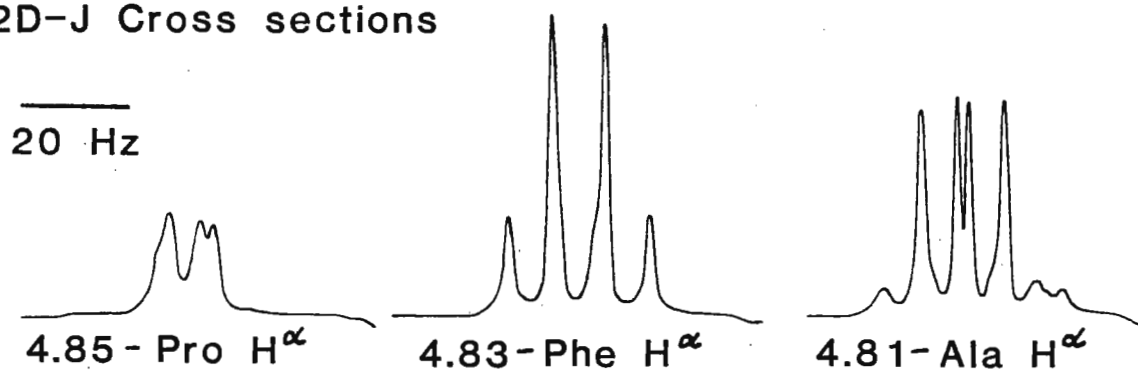
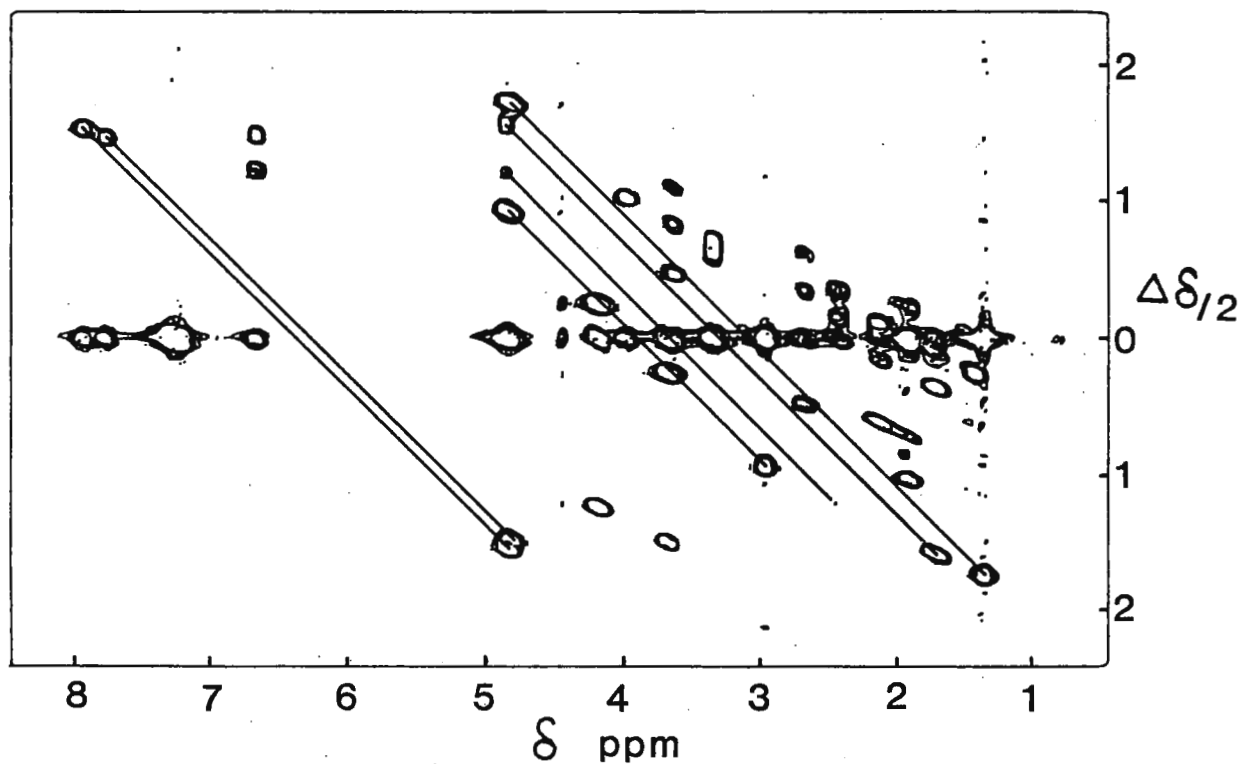
Lila M. Gierasch

Lila M. Gierasch

Joseph H. Noggle

Joseph H. Noggle

1. L. G. Pease, in Proc. Sixth Amer. Peptide Symp., E. Gross and J. Meienhofer, Eds., Pierce, Rockford, IL (1979), pp. 197-200.
2. I. L. Karle, in Perspectives in Peptide Chemistry, A. Eberle, R. Geiger, and T. Wieland, Eds., S. Karger, A. F., Basel (1981), p. 261
3. L. G. Pease, M. H. Frey, and S. J. Opella, J. Am. Chem. Soc. (1981), **103**, 467.
4. A. C. Bach, II, A. A. Bothner-By, and L. M. Gierasch, J. Am. Chem. Soc., In press.

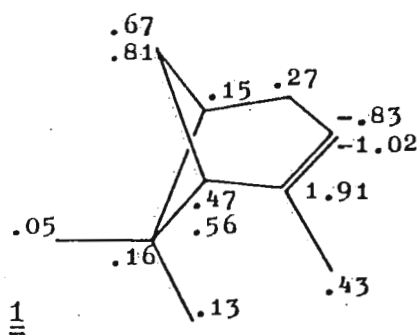
cyclo-(D-Phe-Pro-Gly-D-Ala-Pro) in CDCl_3 **A** 1D Spectrum**B** 2D-J Cross sections**C** Spin Echo Correlated Spectrum

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

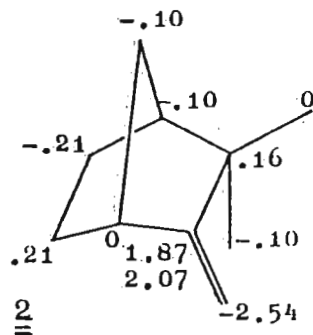
Chiral Recognition of Terpene Hydrocarbons by ^{13}C NMR

Dear Professor Shapiro,

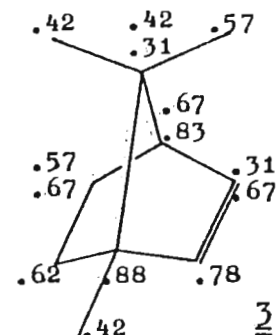
The first Silver/Lanthanide Induced Shift (SLIS¹⁾) in ^{13}C NMR have apparently been mentioned for 4-vinylcyclohexene by Wenzel and Sievers²⁾. Smith³⁾ applied their approach to some alkene hydrocarbons. In addition, use of an *optically active* reagent led us to detect Silver/Lanthanide Induced Chiral Shifts (SLICS⁴⁾) in the ^{13}C NMR spectra of α -pinene and camphene⁵⁾. We report⁶⁾ ^{13}C SLIS values (in ppm) of α -pinene (1), camphene (2), and bornene (3) in CDCl_3 at 30°C , induced by $\text{Ag}(\text{fod})$ (4) and (+)-Yb(hfbc)₃ (5), (+)-Eu(hfbc)₃ (6), or (+)-Pr(hfbc)₃ (7). A negative sign means an induced shift to higher field. The upper one of two numbers refers to the (-)-enantiomer of the hydrocarbon.



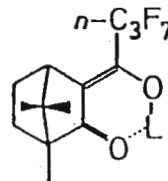
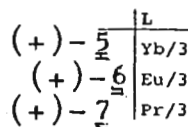
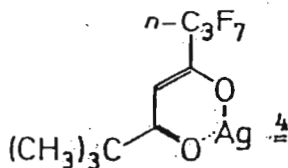
$$\underline{1}/\underline{4} = .1, \underline{1}/\underline{6} = .41$$



$$\underline{2}/\underline{4} = .11, \underline{2}/\underline{7} = .1$$




$$\underline{3}/\underline{4} = .11, \underline{3}/\underline{5} = .16$$



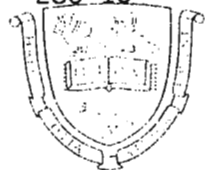
In most cases, the Yb reagent 5 produces the largest SLIS effects. Clearly, the distance between the nucleus on resonance and the reagent is not the whole story. Especially from the different SLIS of (+)- and (-)-enantiomers a substantial contribution of the anions, (hfbc)⁻ and (fod)⁻, must be inferred.

Sincerely yours,


(W. Offermann)


(A. Mannschreck)

-
- 1) We are not the first to describe this phenomenon but claim absolute priority for the ingenious invention of this expressive abbreviation.
 - 2) T.J.Wenzel and R.E.Sievers, Anal.Chem. 53, 393 (1981).
 - 3) W.B.Smith, TAMUNN 274, 8 (1981); W.B.Smith, Org.Magn. Resonance 17, 124 (1981).
 - 4) Invented in this laboratory, too.
 - 5) W.Offermann and A.Mannschreck, Tetrahedron Lett. 22, 3227 (1981).
 - 6) W.Offermann and A.Mannschreck, manuscript in preparation.



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

TEL: 051 - 709 - 6022

The University of Liverpool

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

11th December, 1981.

Dear Barry,

More on Porphyrin Ring Currents.

Your reminder prompts me to relate some of our recent work on the development and application of the porphyrin ring current model.

Following the realisation that a well parametrised model may be sufficiently accurate to be able to provide the geometries of attached ligands on metallocporphyrins, Geoff Bedford and I¹ have been exploiting this application with some TPP derivatives. E.g. the metal to nitrogen bond lengths in Zn, Mg, Co TPP (pyridine) complexes were determined from the N.M.R. shifts and compare well with the data of the crystalline complexes. Steric interactions between the ligand and the porphyrin in complexes of ZnTPP with 2-picoline and quinoline produce a dramatic increase in the Zn-N bond length (compared to the unstrained complexes with pyridine and isoquinoline), but comparatively minor angle distortions. Also we have shown that the specificity of the ZnTPP complexation shifts is linearly related to the basicity of the ligand for a variety of ligands.

Whilst I was in Davis this summer, Kevin Smith and I constructed and parametrised a ring current model for the chlorin ring of chlorophyll derivatives.² The exocyclic ring E has no appreciable effect on the macrocyclic ring current, but the C₉ keto function and the reduction of ring D reduce the ring current by ca. 6 and 10% respectively. In this model an improved close range approximation which gave both first-order and second-order continuity at all points in space, except through the current loop itself, was developed.³

Also back in Liverpool, Jim Plant has successfully separated and characterised by ¹H and ¹³C all the four possible atropisomers of meso tetra (2-methoxynaphthyl) porphyrin.⁴ The shifts of the naphthyl protons in these molecules provide a further stringent test of the ring current model, and it can be shown that part at least of the atropo shifts are due to the ring currents of the meso naphthyl substituents.

We are also currently investigating some further applications of ZnTPP as an NMR shift reagent, particularly for multifunctional ligands, and I hope to report on these subsequently.

Yours sincerely,



Dr. R.J. Abraham.

1. R.J. Abraham, G.R. Bedford and B. Wright, Org. Mag. Res. (in press).
2. R.J. Abraham, K.M. Smith, D.A. Goff and J.J. Lai, submitted.
3. Program DIPCALC2.
4. R.J. Abraham, G.R. Bedford and J. Plant, manuscript in preparation.



PURDUE UNIVERSITY

SCHOOL OF SCIENCE
at INDIANAPOLISPHYSICS DEPARTMENT
1201 East 38th Street
Indianapolis, Indiana 46205
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December 16, 1981

Professor B. L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843Errors in T_1 measurements due to partial overlap of resonances

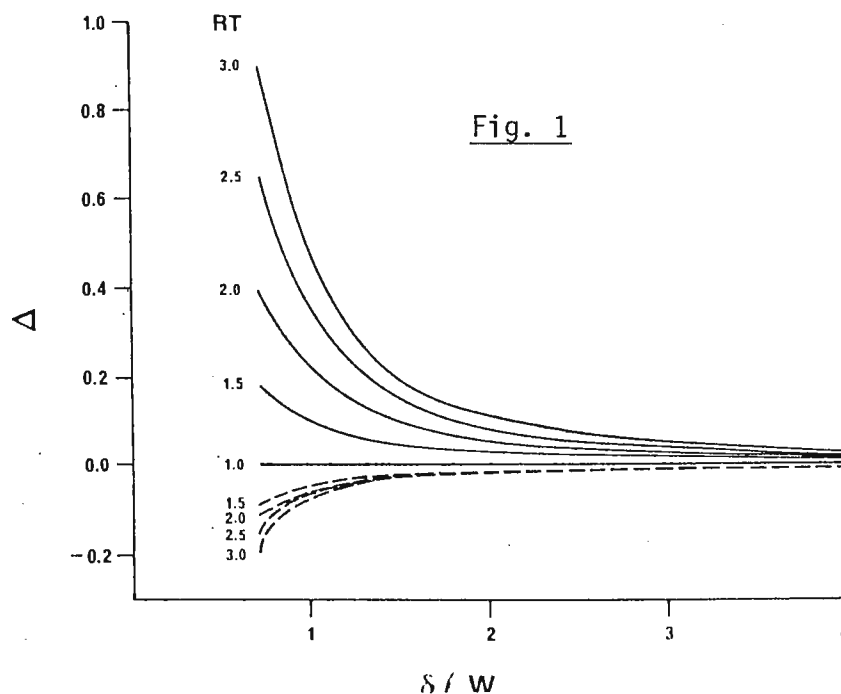
Dear Barry:

Errors in spin-lattice relaxation time measurement may originate from various experimental and analytical sources. A systematic error which did not receive much (or any) attention in the past, and which nonetheless may significantly affect the accuracy of measured relaxation times, results from partial overlap of resonances. Fig. 1 demonstrates the dependence of $\Delta = (T_1^{\text{exp}} - T_1^{\text{true}})/T_1^{\text{true}}$, for two resonances with equal amplitudes and linewidths (W), on their spectral separation (δ), for several relaxation time ratios $RT = T_1^{\text{true}}(2)/T_1^{\text{true}}(1)$. The solid and the dashed lines correspond to the deviations in $T_1^{\text{true}}(1) = 1$ sec and $T_1^{\text{true}}(2) = RT \cdot T_1^{\text{true}}(1)$, respectively. In general, the error in the shorter T_1 is always positive ($\Delta > 0$) and larger than that in the longer T_1 (which has $\Delta < 0$). For example, for $RT = 3$ and $\delta/W < 1$, $\Delta > 40\%$ for the shorter T_1 . Things get worse when the partially overlapping lines have different amplitudes and/or linewidths. More details are given in a manuscript recently submitted for publication.

Please credit this contribution to Dr. B. D. Nageswara Rao's account.

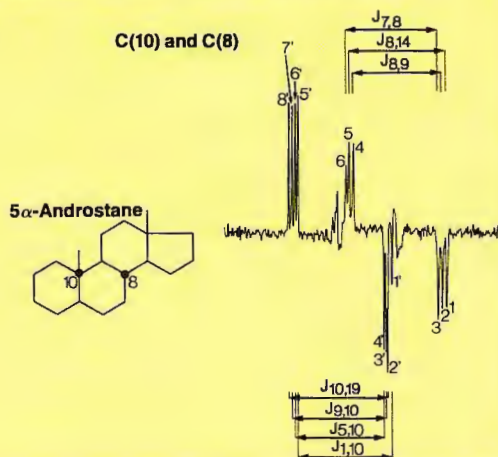
Yours sincerely,

J. Granot
Joseph Granot



We produced these spectra—

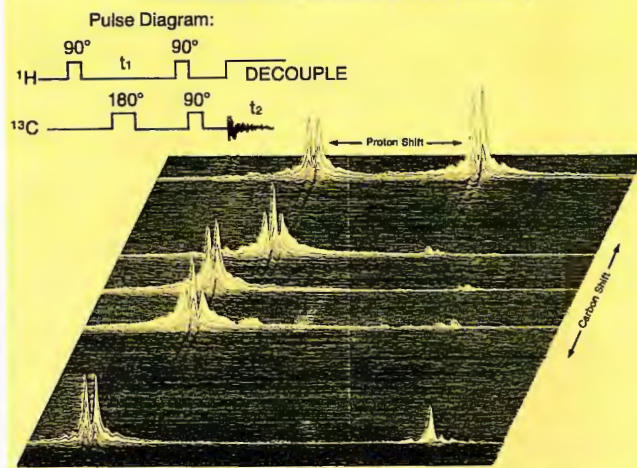
¹³C-Satellite Excitation Using "INADEQUATE"*



Expansion of the partial INADEQUATE spectrum of 5 α -androstane, showing overlapping ¹³C satellites of carbon 8 and 10. Note the efficiency of center-band cancellation resulting from the hardware stability and the software flexibility of the XL-200 pulse programmer. Assignments shown are the result of the "COSMIC" automatic analysis program on the XL-200.

*A. Bax, R. Freeman and S.P. Kempell, JACS, 102, 4849 (1980).

Heteronuclear Correlated 2-D Coumarin



Heteronuclear Correlated 2-D NMR on coumarin. Presence of a resonance indicates presence of a C-H bond. The sub-splittings along the proton direction are the homonuclear ¹H-¹H splittings, even though the experiment is ¹³C observe. The phase cycling employed in the pulse sequence allows quadrature operation in both frequency domains.

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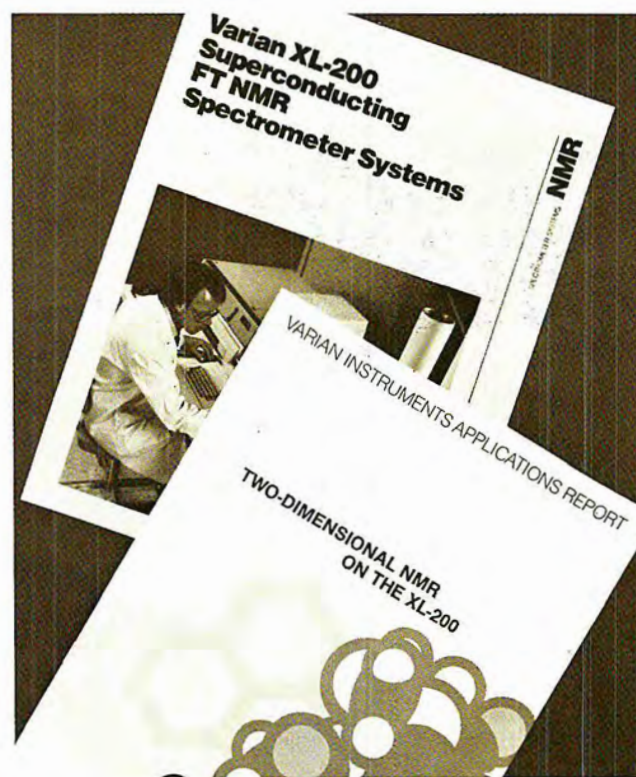
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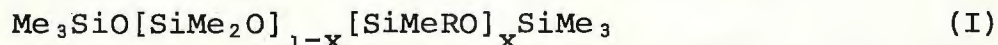
December 17, 1981

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

Subject: The Speciation of Mercapto Functional Siloxane
 Building Units at Low Levels by Inept NMR

Dear Professor Shapiro:

The ability of polydimethylsiloxane (PDMS) to adhere to a given surface may be markedly improved by the incorporation of small amounts of functional siloxane units into the polymer chain (I), in which R is a suitable functional group and $X \ll 0.01$:



For a recently submitted sample, we were asked to determine whether R was either of two possible functional groups:



or



It should be noted here that two complicating factors were present:

- i) the ratio of $[\text{SiMe}_2\text{O}]/[\text{SiMeRO}]$ was more than 500 to 1.
- ii) the average degree of polymerization was only about 110 to 120 units; so that, statistically, only a small fraction of the PDMS molecules possessed a sulfur atom.

Our solution to this problem illustrates the power and utility of INEPT¹ as a method for speciation at low levels.

By setting up our Varian XL-200 instrument to do a ¹³C INEPT NMR experiment, we were able to obtain spectrum A after an overnight acquisition. For one experiment, J = 125 Hz and MULT = 5 (which causes methylene carbon resonances to be positively phased, while methyl and methine carbon resonances are negatively phased). Note that there are two closely positioned, positively phased signals at ca. 27 ppm and a third signal (signals?) at ca. 11 ppm. The lack of observed inverted signals (other than for Si-Me) indicates that II is the mercapto structure that is present.

To verify this, a ¹H decoupled, ¹³C spectrum of IV was taken and our assignments are as indicated in spectrum B:



Again, two closely spaced signals occur at ca. 27 ppm and a third (corresponding to Si-CH₂) occurs at ca. 11 ppm. This observation is consistent with III as the correct functional group.

The above example illustrates that the use of INEPT in NMR provides the means to solve an analytical chemistry problem that, at best, is difficult to answer by other analytical techniques.

Sincerely yours,

Thomas M. Carr

Thomas M. Carr
Analytical Dept.

N.C. Angelotti

Nicholas C. Angelotti
Analytical Dept.

¹G. A. Morris and R. Freeman, J.A.C.S. 102, 428 (1980)

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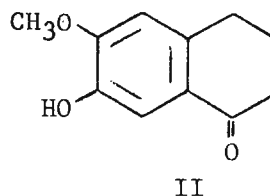
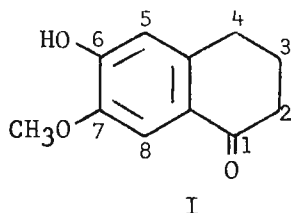
December 21, 1981

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

Dear Barry:

NOE Studies of Some α -Tetralones

In order to distinguish between isomers I and II we have resorted to one of the "old" NMR techniques, the Nuclear Overhauser effect (NOE). When the methoxy protons are irradiated there is an enhancement in the integrated area of the H-8 proton. From this we determined that the compound in question was I rather than II.



This prompted us to measure the NOE of the proton ortho to the methoxy group (Table I) of a series of compounds (5,6- and 6,7-disubstituted α -tetralones). The percent enhancement is based on the increased integral for each compound relative to an internal standard. The data in Table I show that the NOE of the proton ortho to the methoxy group is relatively large (ca 30%) when the methoxy group is irradiated. These data indicate that the NOE is independent of the size of the group adjacent to the methoxy group. In addition, the NOE is not diminished if there is a proton adjacent to the one of interest. In 6-benzyloxy-7-methoxy- α -tetralone we found that irradiating the benzyl-CH₂ resulted in a 24% enhancement of the H-5 proton.

In measuring the NOE on our XL-100 spectrometer it was necessary (although undesirable) to leave the decoupler on during the acquisition. For I it was observed that there was a larger increase in the peak height (43%) than in the integral (32%) of the H-8 proton. The larger increase in the peak height is presumably due to the loss of unresolved long-range coupling between the -OCH₃ group and the H-8 proton. The width at half-height of the H-8 proton was 1.0 Hz when the decoupler was centered on the -OCH₃ group. If the decoupler was offset the width of the H-8 proton was 1.2 Hz.

Yours sincerely,

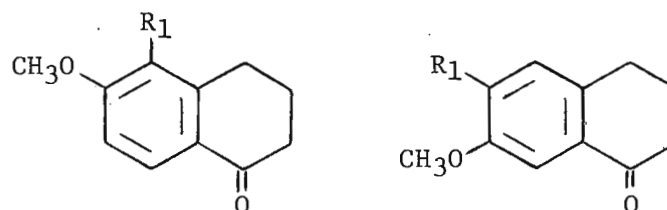
Merrill Nuss, David Arendsen, John DeBernardis

MS:DA:JD:dmh



December 21, 1981

Table I



R_1		
-OH	27%	32%
-OCH ₃	34%	32%
-OCH ₂ φ	32%	†

†In this compound the H-8 proton and the aromatic protons of the benzyl group were not resolved. As expected there was a large NOE enhancement in the aromatic region when the -OCH₃ group was irradiated.

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Professor B.L. SHAPIRO
 Dpt of Chemistry
 Texas A & M University
 COLLEGE STATION

N/réf. JJB/SL

V/réf.

TEXAS 77843

U.S.A.

PIERRE-BÉNITE, LE December 15th, 1981

Dear Professor Shapiro,

³¹
P-NMR study of the desulfuration of P_4S_7 by triphenylphosphine

Recently we have been studying the NMR of sulfur abstraction from various phosphorus sulfides by triphenylphosphine. We would like to illustrate it using the example of phosphorus heptasulfide.

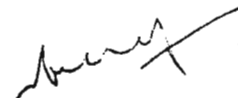
When CS_2 solutions of P_4S_7 (0.23 g/l) were shaken at r.t. with Φ_3P (molar ratio $\rho = \Phi_3P/P_4S_7 = 0.5$ to 1.5) and examined a few minutes after dissolution, the following species were observed (fig. 1) : residual P_4S_7 (unresolved A_2X_2 , δ 84.6-111), Φ_3PS (δ 42.04), two equivalent triplets (δ 80.4-130.2, J 45 Hz) due to P_4S_5 and an AM_2X system (δ_A 55.57 [1P], δ_M 178.46 [2P], δ_X 198.5 [1P], J_{AX} 112, J_{AM} 11, J_{MX} 46 Hz) assigned to P_4S_6 .

The reaction appears to follow the sequence $P_4S_7 \rightarrow P_4S_6 \rightarrow P_4S_5$ as shown by the amount of P_4S_5 increasing with the ρ ratio.

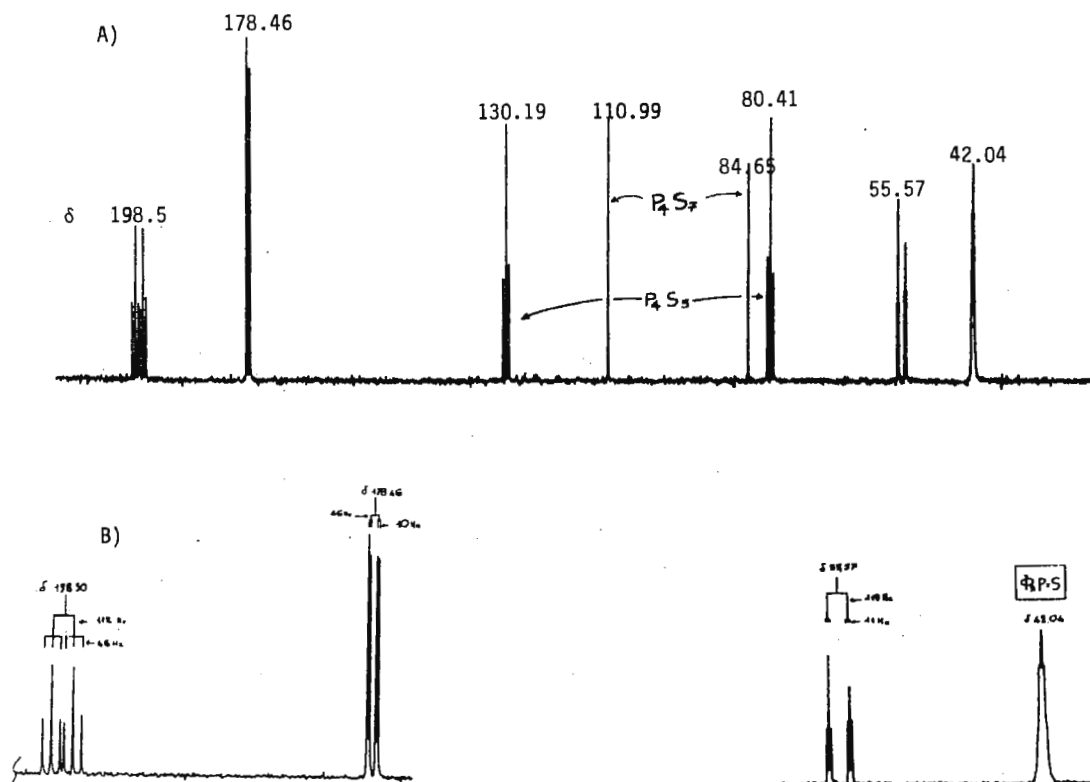
Substituting trichlorobenzene (mixture of isomers) for CS_2 allowed us to carry out the reaction at 150° with higher concentrations of P_4S_7 (~ 3.2 g/l) ; again P_4S_6 and P_4S_5 were produced with two additional signals at δ 198 (α P_4S_4 resulting from the abstraction of the S atom bridging P_3 and P_4 - fig. 1) and δ 220 (non assigned species).



J.J. BARIEUX
 (PCUK)



M.C. DEMARCQ
 (INSA-LYON)

Figure 1 : ^{31}P NMR (80.76 MHz)A) conditions : PW1 5 μ PD 10 $\%$ freq. 20 KHz OBS. 30.07 KHz
21 500 scansB) expansion of the P_4S_6 zoneTentative assignment of $\delta(\text{ppm})$

Y	Z		P_1, P_2	P_3	P_4
S	S	P_4S_7	111	84.6	84.6
S	l.p.	P_4S_6	178.46	55.57	198.5
l.p.	l.p.	$\beta\text{-P}_4\text{S}_5$	130.2?	80.4?	80.4?

(l.p. = lone pair)

Department of Chemistry

Evanston, Illinois 60201

December 28, 1981

Professor Bernard L. Shapiro
TAMU NMR Newsletter
Department of Chemistry
Texas A&M University
College Station, Texas 77883

Dear Barry:

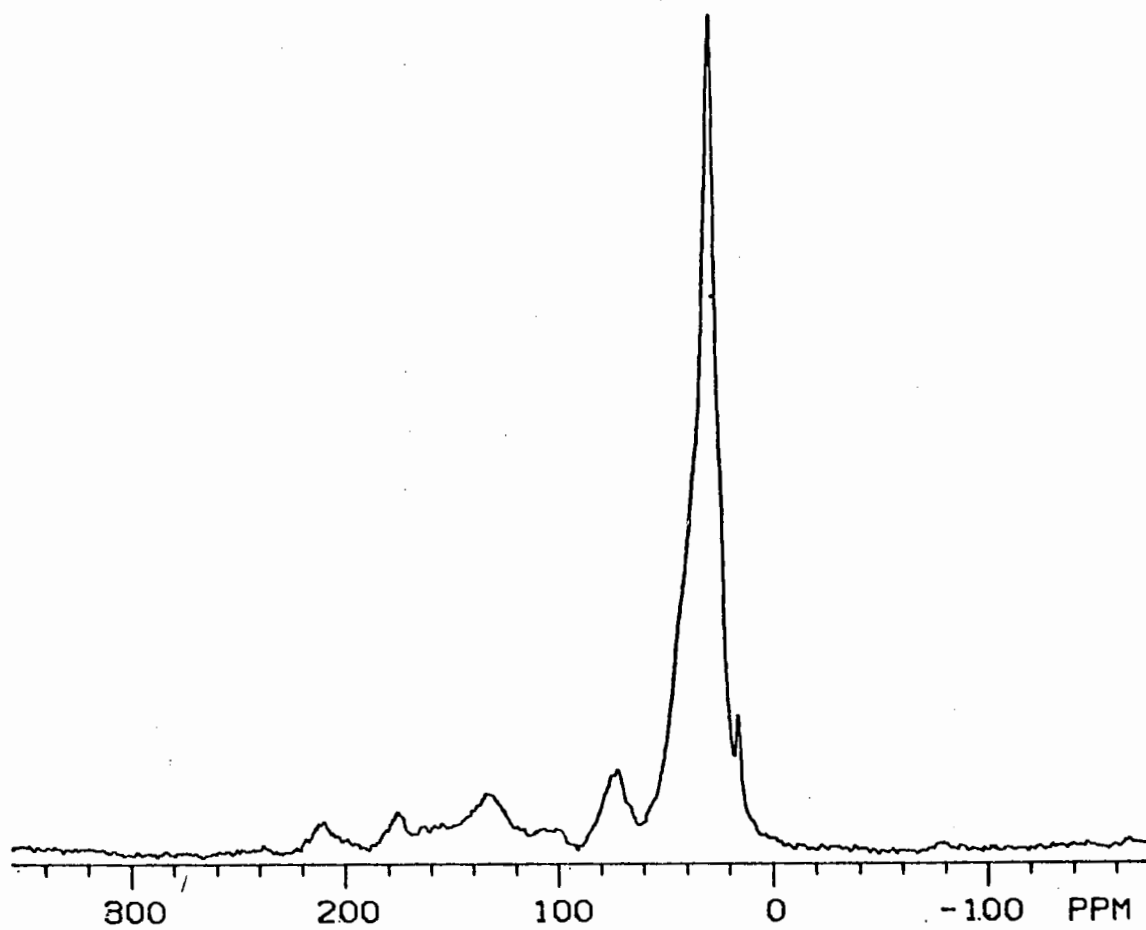
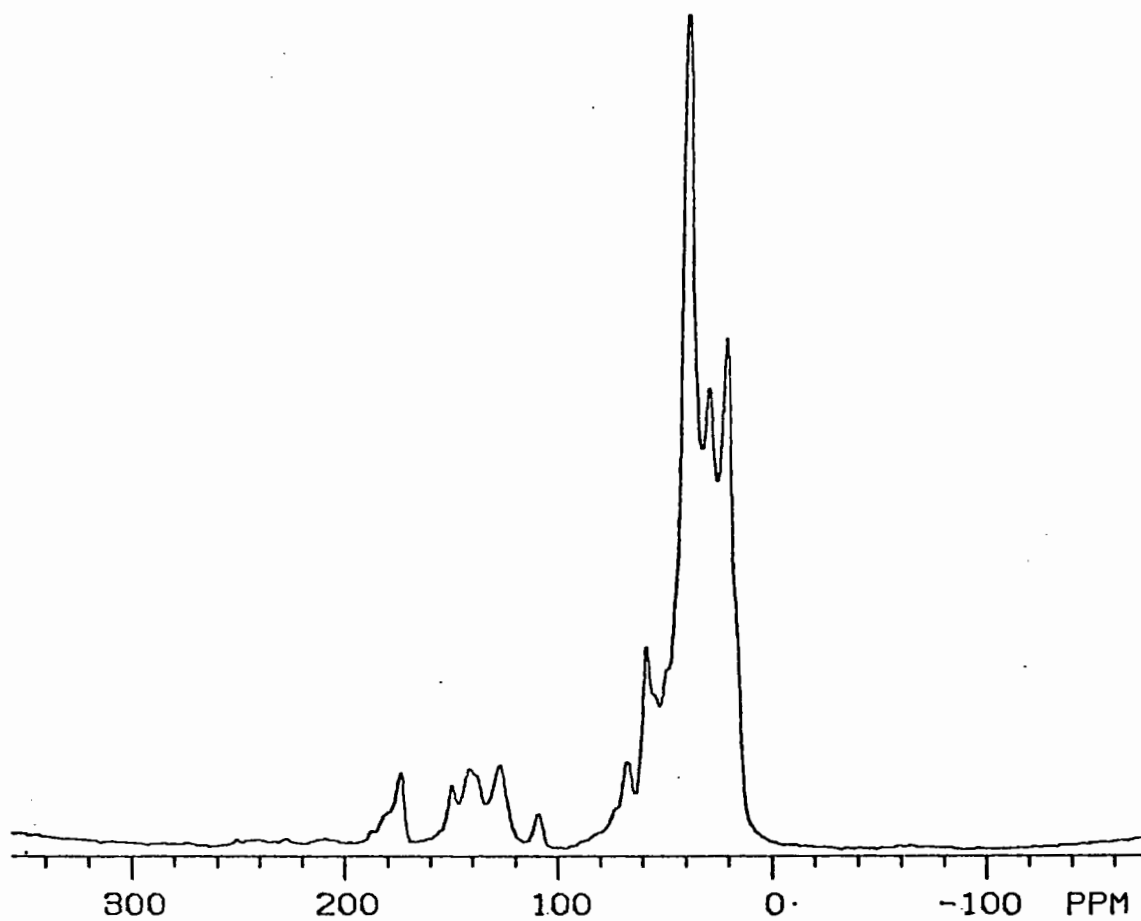
We have been working in archaeological chemistry for some time now and publishing in journals your audience may never have heard of, much less have read.¹ At last, we are working on an archaeological problem suitable for NMR. Amber is a material widely used since ancient times for decorative purposes. As a nearly intractable organic rock, it has proved difficult to analyze structurally. We are currently examining a wide variety of archaeological ambers by CP/MAS ¹³C methods. The ambers were provided by Curt Beck of Vassar and the spectra were taken at the Colorado State University Regional NMR Facility by James Frye. The attached pair of spectra show a good deal of structure. We can easily discern the aliphatic, the alkenic/aromatic, and the carbonyl regions. The Baltic amber (upper) and the Burmese amber (lower) differ considerably. We are writing a detailed analysis by functional group, with integrations, to be published soon.

Sincerely,



Joseph B. Lambert

1. Archaeometry, 21, 115 (1979); 20, 107 (1978); 18, 169 (1976); Am. J. Phys. Anthropol., 48, 199 (1978); Arch. Chem. II, 189 (1978).





U.S. Department of Energy
Laramie Energy Technology Center
P.O. Box 3395, University Station
Laramie, Wyoming 82071

December 31, 1981

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

Dear Barry,

For several years the Department of Defense in cooperation with the Department of Energy has had research programs aimed at characterizing and evaluating jet fuels obtained from various fossil sources. Both Carbon-13 and ^1H NMR have been used extensively to characterize liquid hydrocarbon fractions from various crude oil sources. However, to use ^{13}C NMR effectively as an analytical technique, the long spin-lattice relaxation times and variable NOE enhancement factor for carbon atoms in molecules generally comprising jet fuels must be substantially reduced or eliminated. It is well known that spin-lattice relaxation times and NOE can be reduced by using relaxation reagents. These reagents have been used in various systems for over ten years since the paper by G. N. La Mar¹. The theoretical principles are well understood^{2,3}. Unfortunately the comprehensive papers dealing with relaxation reagents have been on systems such as formic acid², dioxane¹, vinyl acetate² (which are not present in jet fuel) or have measured the effects of the reagents on the intensities of the carbon resonances⁴. Most appropriate to fossil fuel studies would be the change in the spin-lattice relaxation time of aromatic and alkane hydrocarbons with increased molar concentration of the relaxation reagents. A brief literature search did not provide any pertinent articles.

Figure 1 shows the change in the spin-lattice relaxation times with increased concentration of chromium acetylacetonate (CrAcAc) for n-hexane, 2,6-dimethylnaphthalene and benzene⁵.

The advantage of the data shown in figure 1 is that the pulse delay time can easily be determined ($5 \times T_1^E$) for a given molar concentration of CrAcAc in which the solubility is dependent upon the hydrocarbon system (From a linear plot of the rate, R_1^E , versus molar concentration of CrAcAc a more exacting T_1^E can be determined if necessary²). Also shown

Letter to Dr. Shapiro

December 31, 1981

is that increasing the concentration of CrAcAc above .05M does not significantly alter the experimental time to achieve analytical results. Differences in T_1 for a given molar concentration of CrAcAc noted for alkanes and aromatics is attributed to the degree of interaction with CrAcAc.

Sincerely,



Daniel A. Netzel

David M. Barnhart
Eastern Montana College

1. G. N. La Mar, J. Am. Chem. Soc. 93, 1040 (1971).
2. R. Freeman, K. G. R. Pachler and G. N. LaMar, J. Chem. Phys. 55, 4586 (1971).
3. H. S. Gutawsky and D. F. S. Natusch, J. Chem. Phys. 57, 1203 (1972).
4. J. N. Shoolery, Prog. in NMR Spectroscopy, 11, 79 (1977).
5. JEOL Technical Bulletin NBS-11, 1977, 10.

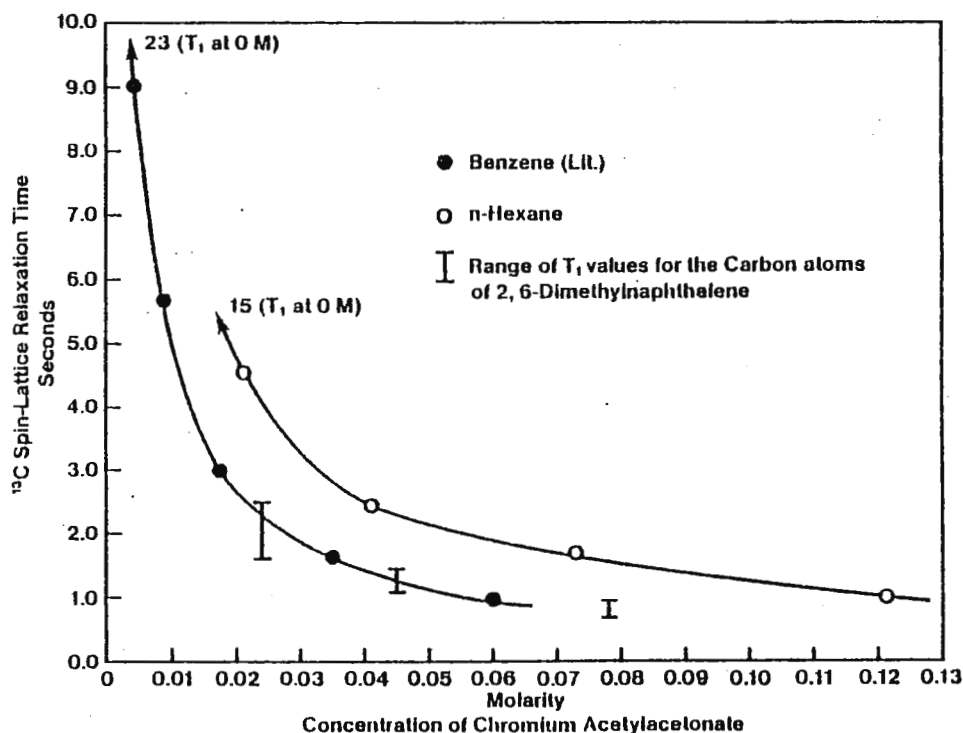


FIGURE 1. - Spin-Lattice Relaxation Times for Hydrocarbons as a Function of the Concentration of Chromium Acetylacetonate



THE PROCTER & GAMBLE COMPANY

MIAMI VALLEY LABORATORIES

November 17, 1981

P. O. BOX 39175
CINCINNATI, OHIO 45247MAGIC-ANGLE SPINNING NMR OF HALF-INTEGRAL QUADRUPOLEAR NUCLEI AT HIGH FIELD

Dear Barry:

Renewed interest in the MAS-NMR of half-integral quadrupolar nuclei (TAMU 275 9, August, 1981) prompts us to report on some unpublished magic-angle spinning experiments of ^{23}Na , ^{27}Al , ^{11}B , ^{81}Br , and ^7Li that we carried out using the ^{13}C and ^{31}P MAS probes on our Bruker CXP-300 (7.0 Tesla).

Our main conclusion was that although in certain selected compounds the central $1/2 \rightarrow -1/2$ transition of these half-integral spin nuclei could be narrowed sufficiently to obtain chemical shift information, for many compounds of interest the second-order quadrupole effect prevents truly high-resolution spectra from being obtained. In addition, these second-order effects will result in peaks being shifted from the "true" resonance position (chemical shift) of the nucleus. Recently-published work (Chem. Phys. Letters 83, 229, 1981) suggests that such spectra can be successfully analyzed for samples with only one chemical shift and one nuclear quadrupole coupling constant.

The accompanying Table illustrates these points. Thus, ^{27}Al nuclei with small nuclear quadrupole coupling constants, such as $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (see Figure 1), show relatively narrow linewidths under magic-angle spinning, but this is not true for clays such as calcium montmorillonite and hectorite, and for aluminum chlorohydrates.

The relatively small nuclear quadrupole coupling constants of ^7Li make it easier to achieve narrowing by magic-angle spinning; however, the small chemical shift range of this nucleus lessens the utility of the method.

We have also observed substantial narrowing of the ^{11}B resonance in BPO_4 (see Figure 2) and of the ^{81}Br resonance in NaBr and decyltrimethylammonium bromide (C_{10}TAB). However, these are compounds where the quadrupole coupling constant is likely to be small or zero, and thus do not address the general utility of magic-angle spinning for these nuclei.

Although the ^{23}Na resonance of NaBr is well-narrowed by magic-angle spinning, this is less so for sodium zeolite-A, amorphous sodium silicates, and clays such as partially-exchanged Ca-montmorillonite and hectorite. For $\text{Na}_4\text{P}_2\text{O}_7$, second-order quadrupolar effects are even more troublesome (Figure 3).

One incidental aspect was our search for a sample containing a sensitive nucleus whose linewidth would be strongly dependent upon the spinning angle adjustment. One might use such a sample mixed with another sample of interest whose signal was very weak in order to optimize the angle adjustment. Unfortunately, none of the samples we studied exhibited a sufficiently dramatic narrowing effect.

Sincerely yours,

James Yesinowski
(513) 977-2551

st/JPYpub

Table

<u>Sample</u>	<u>Nucleus</u>	<u>Non-Spinning Linewidth</u>	<u>Linewidth with Magic-Angle Spinning**</u>
*NaBr	^{23}Na	----	250 Hz
*NaBr	^{81}Br	2100 Hz	200 Hz (2.9)
C ₁₀ TAB	^{81}Br	1700 Hz	200 Hz (>3)
*AlCl ₃ ·6H ₂ O	^{27}Al	(see Figure 1)	400 Hz (7.5)
*BPO ₄	^{11}B	2700 Hz	220 Hz (>3)
Li ₂ CO ₃	^7Li	8400 Hz	1100 Hz (3.4)
*LiSO ₄ ·H ₂ O	^7Li	----	780 Hz (3.1)
Sodium zeolite-A (hydrated)	^{23}Na	980 Hz	830 Hz
Sodium zeolite-A (hydrated)	^{27}Al	1640 Hz	440 Hz (3)
Aluminum chloro- hydrate	^{27}Al	8300 Hz	~4000 Hz (~7)
Calcium montmoril- lonite	^{27}Al	12000 Hz	3000 Hz (4.1)
Calcium montmoril- lonite	^{23}Na	12000 Hz	2800 Hz (~3)
Sodium silicate (amorphous, 2.4 ratio, 19% H ₂ O)	^{23}Na	7300 Hz	2700 Hz (>3)
Na ₄ P ₂ O ₇	^{23}Na	(see Figure 3)	

* compounds that would be suitable MAS-NMR chemical-shift references for the five nuclei under discussion

** spinning frequency in kHz in parentheses

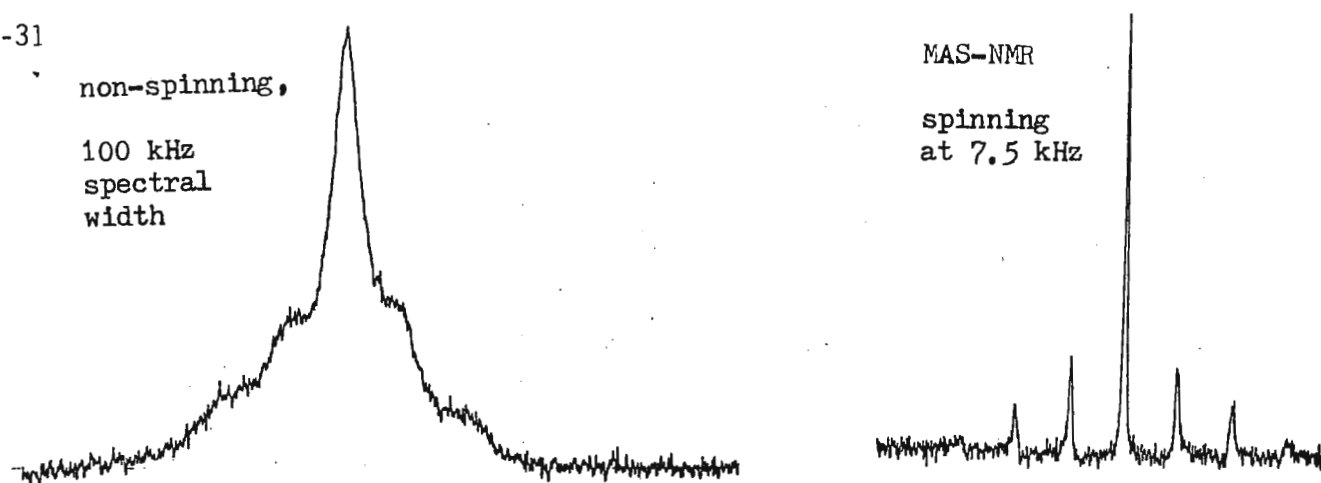


FIGURE 1: ^{27}Al NMR of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (same scale)

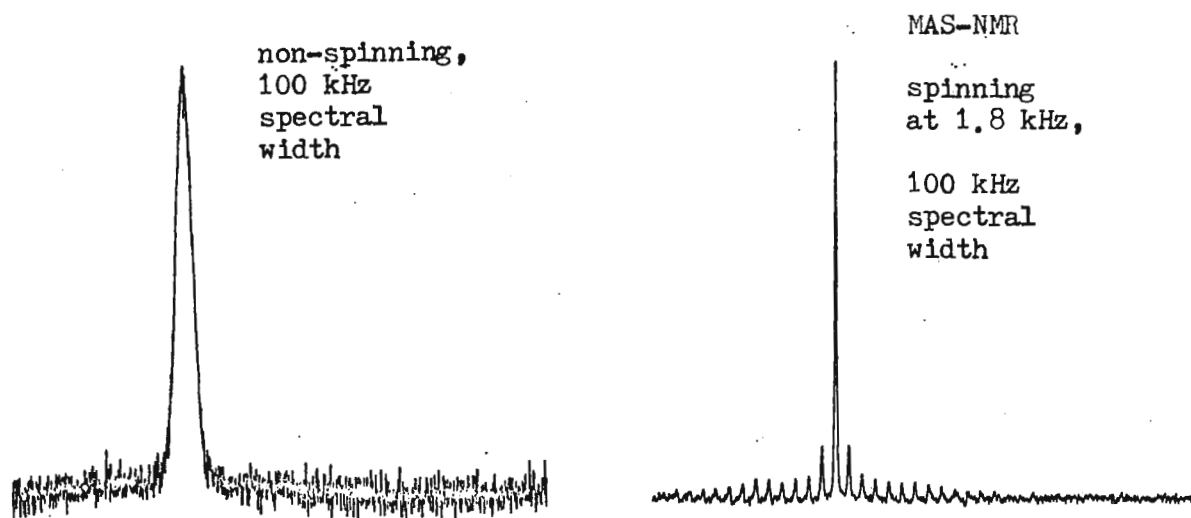


FIGURE 2: ^{11}B NMR of BPO_4 (same scale)

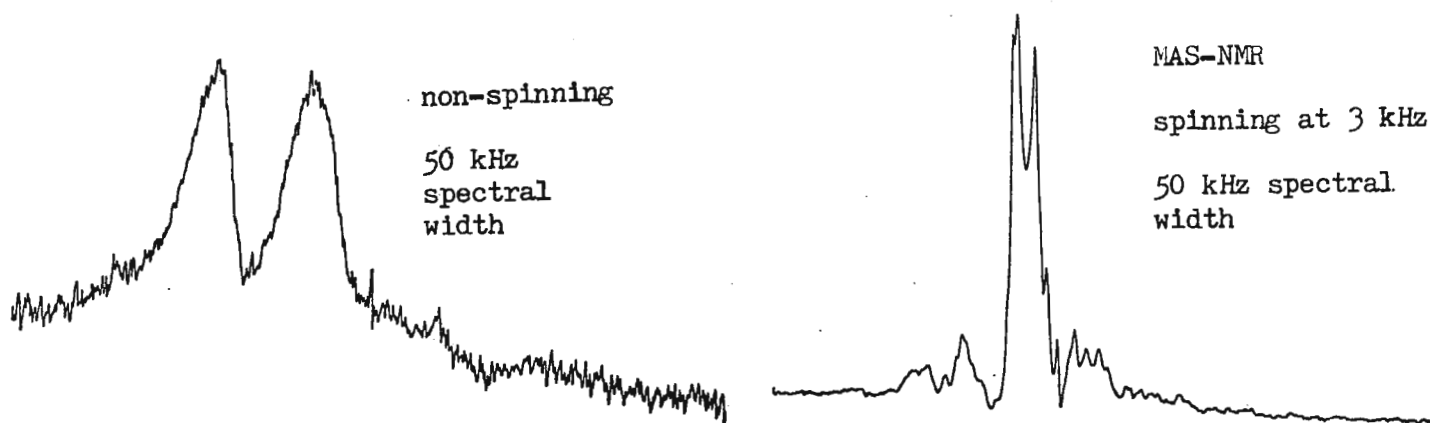


FIGURE 3: ^{23}Na NMR of $\text{Na}_4\text{P}_2\text{O}_7$ (same scale)

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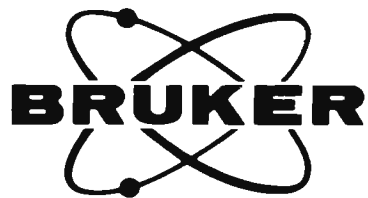
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School of Science

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20th November, 1981

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

Dear Prof. Shapiro,

Brisbane NMR Centre, CXP Pulse Programming Modifications
and ¹⁹⁵Pt CSA

David Doddrell has asked me to respond to your recent reminder which means your readers won't have to put up with any more of his CRAP for a while, at least. I felt it was appropriate first to mention the recent establishment of the Brisbane NMR Centre. This is a joint venture between University of Queensland, Queensland Institute of Technology and Griffith University, enabling hands-on access to high field/high power NMR equipment which would not have been financially possible individually. The Centre is situated at Griffith University, David is the Director and it is based on a Bruker CXP-300 spectrometer which is well-equipped for both multi-nuclear high resolution and high power work. Next year, the Centre should have access to a super wide-bore 200 MHz spectrometer as well. Other CXP owners may be interested in some of the work we have done to and with the CXP-300.

One substantial modification we made as soon as possible after installation was to the pulse programming capabilities. As CXP users will be aware, the programmer is limited to 8 pulse outputs, 4 for the observe transmitter ($\pm X$, $\pm Y$) and 4 for the proton decouplers ($\pm V$, $\pm W$) (both low and high power are phase controllable with recent Bruker modifications). However, these must also be used for acquisition triggering, receiver blanking and noise decoupler gating if used. Hence, in the worst case, there may be only five outputs for transmitter and decoupler pulses, which is insufficient for some recently developed multi-pulse sequences. To overcome this limitation Jim Field has multiplexed three of the decoupler pulses, V, -V and W, to end up with four additional pulses, V-V, VW, -VW and V-VW. One of these is used to replace the -W proton pulse which is then used exclusively for triggering and blanking. Two of the remaining combination pulses are used for attenuated CW and noise decoupling during acquisition. A consequence of this is that the LP decoupler mode commands are no longer active and decoupling has to be pulse programmed even for simple pulse sequences. Hence both pulse

programming and micro-programming are more tedious. As we have a number of users who operate the instrument in a routine manner only, the multiplexing can be switched off and programming still performed according to the Bruker documentation.

Other modifications underway include CHIRP frequency and composite pulse ^1H decoupling in order to compare their efficiency with the normal 180° phase shift noise decoupling, and spherical ^1H decoupling. The latter is noise decoupling using 90° phase shifts which doesn't provide more efficient decoupling but does provide better randomization of ^1H spins. Robin Bendall has shown this to be of value in multipulse sequences for editing ^{13}C spectra. Probes under construction include a large perfused organ ^{31}P probe and a solenoid coil double tuned ^{31}P cross-polarization probe. Perfused rat and guinea pig hearts have to date been examined in our tunable 20 mm Bruker probe. In the future, we hope to be able to examine hearts of larger animals to improve the time resolution of experiments.

One aspect of the CXP capabilities which is being well used is that of cross-polarization and magic angle spinning. We are using our ^{13}C CP/MAS probe for ^{29}Si and ^{195}Pt as well, with the former providing good spectra in short periods of time. Large CSA results in multiline ^{195}Pt CP/MAS spectra. However, our major interest is in this large CSA and the field dependent relaxation behaviour of platinum compounds in solution. Figure 1 shows that the CSA for $\text{Pt}(\text{acac})_2$ is ~ 1100 ppm. This is in good agreement with the value predicted by Lallemand¹ from variable field ^{195}Pt relaxation data.

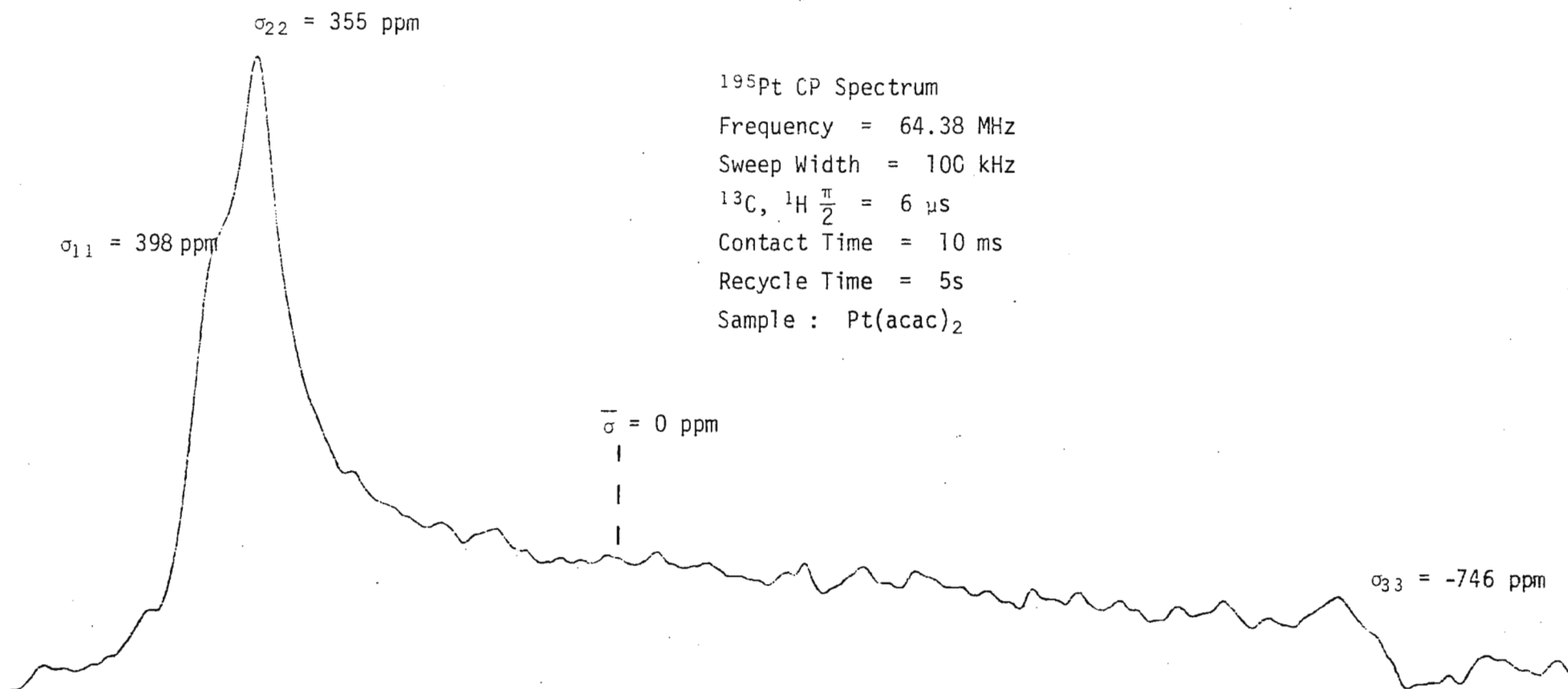
Please credit this contribution to David Doddrell's subscription.

Yours sincerely,



Peter Barron

¹ J.-Y. Lallemand, J. Soulie and J.C. Chottard, J.C.S. Chem. Comm., 1980, 436.



ENC Inc. Twenty-third Experimental Nuclear Magnetic Resonance Spectroscopy Conference
 Madison, Wisconsin, April 25-29, 1982

23rd ENC

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

Dear Barry:

I am enclosing an update on the first announcement of the 23rd ENC which appeared in the October issue of the Newsletter. A tentative program is given on the adjoining page. Requests for registration information should be made directly to R.G. Bryant at the address shown on this letterhead. The deadline for registration is March 15, 1982. As you can see from the schedule, Monday evening and Tuesday afternoon have been kept free of organized activity to provide more time for individual and small-group discussion.

Sincerely,

Nino

C.S. Yannoni
 Chair, 23rd ENC

Executive Committee

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 Monterey & Cottle Roads
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J. SCHAEFER

B.D. SYKES

D. TORCHIA

R.L. VOLD

J.S. WAUGH

23rd ENC, Madison, Wisconsin, April 25-29, 1982MorningAfternoonEveningMonday - April 26

Quadrupolar Nuclei
R.G. Bryant - Chair

Poster Session
D. Lankin - Chair

No formal
session

M. Bloom, S. Forsen,
P. Laszlo, E. Oldfield,
C. Springer

Tuesday - April 27

Solid-state NMR
C. Dybowski - Chair

No formal
session

Special Techniques

R.R. Ernst, R.G. Griffin,
P.M. Henrichs, L. Jelinski,
K. Zilm

M. Saunders plus
other speaker(s)

Wednesday - April 28

Sensitivity & Resolution
Enhancement in Liquids
A.N. Garroway - Chair

Poster Session
D. Lankin - Chair
Borg-Warner Research
Wolf & Algonquin Rds.
Des Plaines, IL 60018

Cocktail Party
and Banquet
C.P. Slichter
will speak

D.M. Doddrell, T.C. Farrar,
R. Freeman, L.D. Hall,
H.J. Jakobsen

Thursday - April 29

Multiple Quantum Coherence -
The Phenomenon and Experiment
J. Prestegard - Chair

G. Bodenhausen, R.R. Vold, A. Pines

NMR Imaging
P.C. Lauterbur - Chair

Speakers to be announced

UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD,
CAMBRIDGE,
CB2 1EW, U.K.
TELEPHONE (0223) 66499

17 December 1981

Dr B L Shapiro
Texas A & M University

Dear Dr Shapiro

SUDSY : A method for cleaning up difference spectra

For those of us fortunate to have very high field spectrometers, spin-decoupling difference spectroscopy is a good way of sorting out coupling connectivities in complex spectra : a control spectrum is subtracted from one with irradiation at a specific signal and the only response to appear should be from resonances experiencing decoupling. Unfortunately Bloch-Siegert (B.S.) shifts near the irradiation give rise to unwanted responses which severely limit the usefulness of the experiment. This is particularly so at low field, say less than 300 MHz. It occurred to us that as the shift near the irradiation is of a known, mathematically explicit, form we could correct for it.

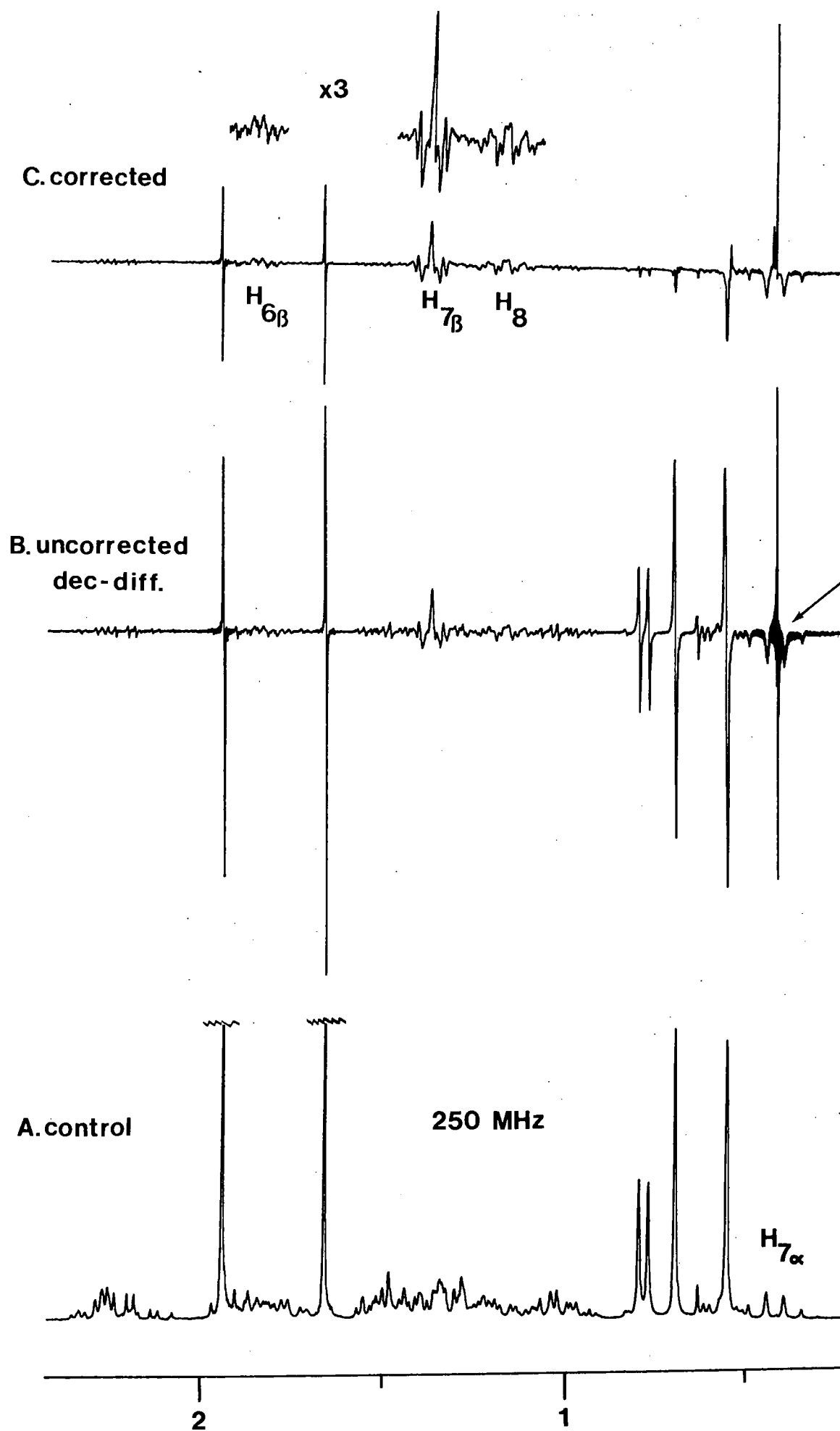
To our pleasure the correction works very well indeed, and allows the rescue and observation of decoupling responses which are otherwise swamped. It also gives a clue to improving n.O.e difference spectra.

When irradiation is turned on at ν_{irr} , a proton at ν_o is shifted by Δ Hz to ν_N . The size of the shift is given by

$$\Delta = \nu_N - \nu_o = \frac{K}{\nu_{irr} - \nu_o}$$

where K depends on decoupler power. By measuring sharp singlets in control and irradiated spectra, and fitting the shifts to the equation by linear regression we can get a value for K. This is then used to correct every data point in the irradiated spectrum :

(continued)



for each point at ν_N the position of ν_O is calculated, and the value of that point is determined by interpolation. The control is then subtracted from the corrected spectrum with the satisfying result shown. Above the control spectrum (of a progesterone) are shown an uncorrected and corrected difference spectrum. Near the decoupling, Bloch-Siegert suppression is about 95% complete. Further out it is much worse as the equation fails, but the effects are of course less serious to start with.

The correlation works best at lower fields where shifts are larger and easier to measure : we couldn't do it easily on our 400 MHz machine, but Henry Rzepa at Imperial College, London, kindly gave us time. All the n.m.r. processing and plotting were carried out on a mainframe IBM 370/165 in Cambridge, using home-written software, but no doubt similar interpolation and fitting routines could be written into NMR-dedicated computers. Simple linear shifts of control or irradiated spectrum can do a good job of removing those annoying dispersion responses from sharp signals in n.O.e difference spectra : the *source* may be either small phase or shift instabilities, but the *easiest* cure looks like linear shifts of 1-50 mHz, with interpolation between data points.

We hope to publish this soon, but meanwhile will be pleased to supply details to anyone who writes. All this work was done by John Merish, a graduate student of mine.

Yours sincerely,



JEREMY K M SANDERS

P.S. *SUDSY* is, of course,

Splendidly Uncluttered Difference Spectroscopy !



NICOLET
MAGNETICS
CORPORATION

A NICOLET INSTRUMENT SUBSIDIARY

December 22, 1981

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

Position Available - SUPERCONDUCTING MAGNET ENGINEER

Dear Barry:

Nicolet Magnetics has an immediate position available for a Superconducting Magnet Engineer. The desired applicant will report directly to the V. P. of Manufacturing while managing a production group. In addition, this individual will be responsible for new designs of Solenoid and Cryostat Systems as well as continuing engineering on current products.

The desired applicant should be experienced in the manufacture or design of high field superconducting magnets, and have some experience in management or supervision of personnel. A strong background in electrical engineering, mechanical engineering and physics or mathematics is recommended.

Nicolet Magnetics is a dynamic corporation where creativity and ingenuity go a long way. In addition to this, we offer very outstanding salaries and benefits. Please contact Ms. Toni Wilson for more information concerning this important position. We are an equal opportunity employer.

Sincerely,

Steve Mohr
Vice President, Manufacturing
NICOLET MAGNETICS CORPORATION

nmr / specnet

SYRACUSE UNIVERSITY

N.I.H. RESOURCE FOR MULTI-NUCLEI NMR AND DATA PROCESSING
DEPARTMENT OF CHEMISTRY, BOWNE HALL, SYRACUSE UNIVERSITY, SYRACUSE, NY 13210

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

**ANNOUNCING A New American Chemical Society Short Course/Experimental
Workshop in Modern NMR Spectroscopy, May 10-14, in Syracuse, New York.**

Dear Barry,

This new 5 day ACS Short Course consists of both lectures and laboratory sessions. The course, under the direction of Professors George C. Levy (Syracuse University), Frank A. L. Anet (U.C.L.A.), and Pierre Laszlo (University of Liege) will introduce and develop the concepts and methodology of modern multi-nuclei NMR Spectroscopy, including high field ^1H and ^{13}C NMR, 2D FT NMR, chemical applications of double quantum NMR, cross polarization methods, solids NMR, new data processing methods, and other current topics of interest. Guest lecturers will cover a number of these areas.

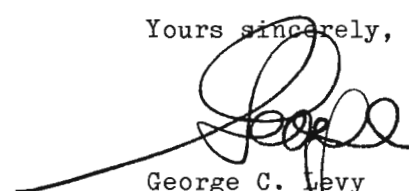
The course will be conducted at the Syracuse University NMR Laboratory. Demonstrations and experiments will access the laboratory's 360 MHz and 150 MHz widebore multi-nuclei FT NMR Spectrometers, as well as unique spectroscopic data processing capabilities available on the laboratory's computer network. Participants may request specific NMR data services during the Workshop/Short Course, **including runs on propriety materials**. The course fee is \$600 for participants not requesting NMR services, or \$800 for participants who wish to receive NMR services (limited to a maximum of 10 participants). Inexpensive housing is available and Syracuse is served by major airlines.

For information or registration write to:

Professor George C. Levy
Department of Chemistry
Syracuse University
305 Bowne Hall
Syracuse, New York 13210

[phone (315) 423-4026]

Yours sincerely,



George C. Levy
Professor of Chemistry

NMR/SPECNET

SYRACUSE UNIVERSITY

N.I.H. RESOURCE FOR MULTI-NUCLEI NMR AND DATA PROCESSING
DEPARTMENT OF CHEMISTRY, BOWNE HALL, SYRACUSE UNIVERSITY, SYRACUSE, NY 13210

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

NMR/SPECNET - A New Research Tool

Dear Barry,

This month we are initiating operation of NMR/SPECNET dial up services. Initially NMR/SPECNET will give users access to information about the N.I.H. Biotechnology Research Resource at Syracuse University, and also allow access to a powerful solution molecular dynamics program, MOLDYN. The MOLDYN program calculates overall and internal motional characteristics for molecules, fitting observed NMR relaxation data (T_1 's, NOE's, T_2 's or linewidths). MOLDYN supports varied models including anisotropic diffusion, restricted internal rotations, jump diffusion, etc. The program is extensively prompted for users.

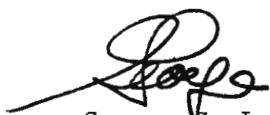
In the next 6-9 months NMR/SPECNET will expand capabilities to include remote spectroscopic data processing and a number of other unique features. Future TAMUNMR letters will cover these developments. In the meantime, if you want to gain access to NMR/SPECNET the phone numbers are:

(315) 422-3443	1200 baud*
(315) 422-3447	300 baud*

(* By mid 1983 both phone numbers should support either data rate.)

To sign on, use the trial USERNAME **NEWUSER**, and PASSWORD **SPECNET**. You will then be asked your actual name, etc and logged into the system. If you have any problems please call one of us.

Best regards from Snow Country.



George C. Levy
Resource Director



Charles L. Dumoulin
Operations Director



David J. Craik
Postdoctoral
Research Scientist



Instruments, Inc.

201 SAN ANTONIO CIRCLE, SUITE 152
MOUNTAIN VIEW, CALIFORNIA 94040
(415) 941-3804

11 December 1981

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

BRUKER INSTRUMENTS, INCORPORATED - POSITION AVAILABLE

Dear Barry:

We are looking for an individual with a strong nmr background to join the Bruker team in our California office.

Duties will include demonstration of superconducting nmr spectrometers to potential customers and development of applications support with present Bruker users.

Interested individuals should send their resume as soon as possible to the California office of Bruker Instruments or contact me directly at 415-941-3804.

Sincerely,

A handwritten signature in cursive script that reads "Malcolm R. Bramwell".
Malcolm R. Bramwell

MRB/vb

Bruker Instruments is an equal opportunity employer.



NICOLET
MAGNETICS
CORPORATION

A NICOLET INSTRUMENT SUBSIDIARY

December 12, 1981

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

PROBE ENGINEER POSITION AVAILABLE

Dear Barry,

We have a position available with Nicolet Magnetix Corp. for a person interested in doing research and development on Nuclear Magnetic Resonance and R.F. circuits. Experience building research quality NMR probes and the ability to test these probes in an NMR spectrometer is desirable. The candidate should be able and willing to do the detailed work necessary in the construction of prototype probes.

The applicant should have a minimum of a BA or BS in chemistry, physics or electrical engineering and a minimum of one year research experience as a lab technician or RA in an NMR related area or a higher degree in an NMR related area. We are an equal opportunity employer. For further information, please contact one of the undersigned.

Sincerely,

John Baldo

Glenn R. Sullivan

Baylor College of Medicine

NATIONAL HEART AND BLOOD VESSEL RESEARCH AND DEMONSTRATION CENTER
Division of Research

Departments of Medicine and Biochemistry
The Methodist Hospital, A601



January 5, 1982

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

Dear Barry:

RE: Postdoctoral Fellowship

I would like to bring to the attention of your readership the opportunities for postdoctoral research in the general area of lipid-protein interactions using magnetic resonance techniques. Our work involves a number of projects including the conformation of lipid-binding peptides, lipid dynamics in native and model plasma lipoproteins, and the structural role of carbohydrate moieties found on lipid-association proteins. Study of these systems is being pursued by low and high field NMR of enriched (^{13}C , ^{15}N) and naturally abundant (^1H , ^{13}C) systems.

The position requires prior experience in NMR. Expertise in peptide synthesis and/or lipid chemistry is desirable. The salary ranges from \$13,380 to \$18,000 depending on experience and qualifications. Renewal of the position for a second or third year is contingent on performance.

Interested candidates should send a curriculum vitae and arrange for three letters of recommendation to be sent directly to me.

Yours sincerely,

Joel

Joel D. Morrisett
Associate Professor

JDM/dm

Baylor College of Medicine is an Equal Opportunity Employer.

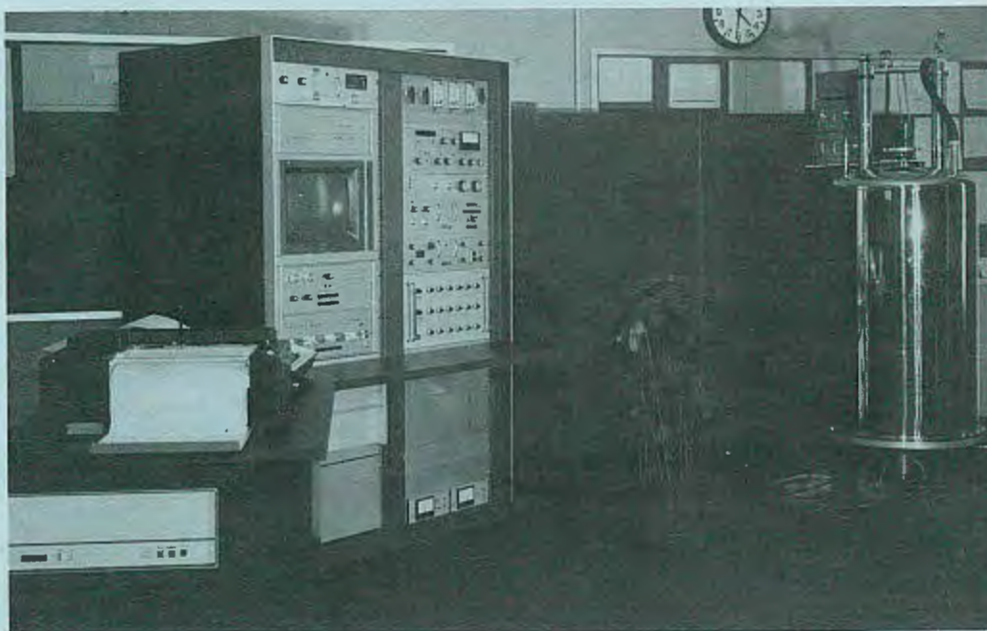
Nicolet Supercon FT-NMR Spectrometers

Uncompromising performance, limitless adaptability.

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- Automated T_1 and T_2 measurements.
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