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Newsletter

No. 258

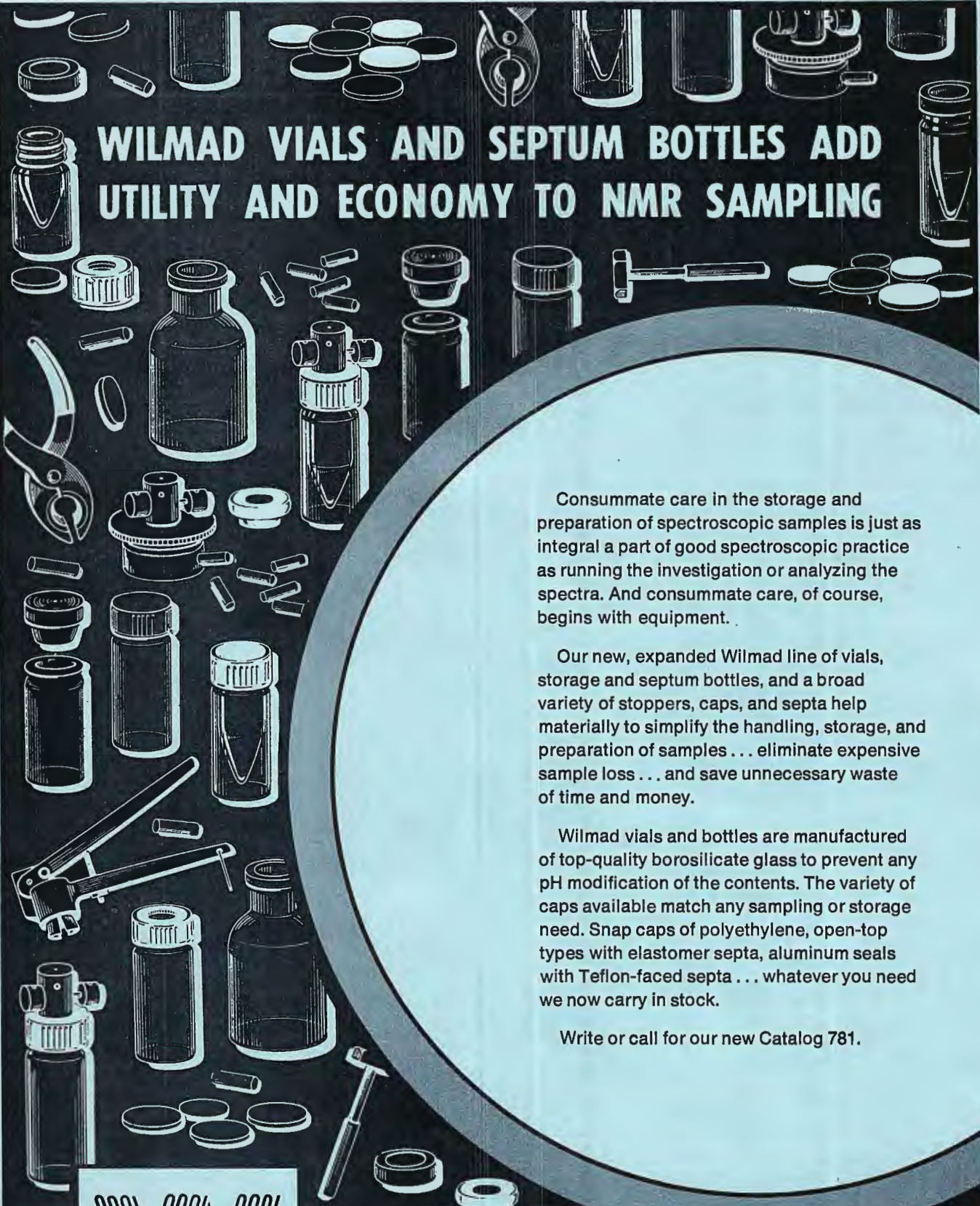
March, 1980

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DEADLINE DATES:	No. 259	7 April 198D
	No. 260	5 May 1980

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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# FT NMR was never "hard," only certain samples were.

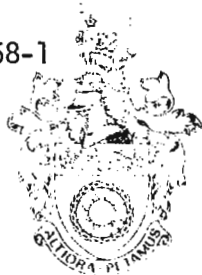
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Department of Chemistry  
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29th January, 1980

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

Dear Barry,

Vibrational corrections and the structures of oriented molecules

It has become customary to correct the structures derived from the analysis of n.m.r. spectra of oriented molecules for the effects of molecular vibrations. What is not made clear in carrying out this process is the fact that the magnitudes of these corrections may be in ~~some~~ doubt because of the lack of a complete knowledge of the force field governing the molecular vibrations: most force field calculations on planar molecules are confined to in-plane vibrations alone since there are generally insufficient data to define the out-of-plane vibrations.

This is illustrated for the case of 2,6-difluoropyridine by the results given in the Table. The vibrational corrections have been based on the best published force field (1). They demonstrate the large contributions from the out-of-plane modes of vibration which have large amplitudes. Nevertheless, it is precisely these which are least well defined. In fact it is the uncorrected structure derived from the  $D_{ij}$  which has the closest correlation with the microwave structure (2).

I hope that this will suffice to compensate for your final yellow ultimatum.

Yours sincerely,

*J.A. Ladd*

J.A. Ladd

References

1. S. Lui, S. Suzuki and J.A. Ladd, *Spectrochimica Acta* 34A, 583-587, 1978.
2. O.L. Stiefvater, *Z. Naturforsch.*, 30A, 1765, 1975.

Nuclei	Direct coupling Constant (Hz)	With in-plane vibrational correction	With out-of-plane vibrational correction	With total vibrational correction
2,3	-116.54	-119.99(+2.96)	-97.54(-16.3)	-100.99(-13.34)
2,4	-89.67	-89.81(+0.15)	-88.82(-0.95)	-88.96(-0.80)
2,5	-149.23	-149.34 (+0.08)	-148.22(-0.68)	-148.33(-0.60)
2,6	-272.14	-272.45(+0.11)	-271.86(-0.10)	-272.17(+0.01)
3,4	-1312.31	-1335.27(+1.75)	-1227.32(-6.48)	-1250.28(-4.73)
3,5	-340.57	-341.24(+0.20)	-332.13(-2.48)	-332.80(-2.28)

Values in parenthesis are the vibrational corrections  
expressed as %



February 13, 1980

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

Dear Dr. Shapiro:

SUBJECT: EPR Position Available

The EPR applications laboratory of Varian Associates, Palo Alto, California, has an immediate opening for a post-doctoral/research assistant. The program will involve the study of molecular motion and other applications of the EPR technique. Some collaboration with research groups at Stanford University should be anticipated by the successful applicant. This position could be renewable upon mutual agreement and may develop into a permanent staff position at Varian.

Interested applicants should send a resume and two letters of recommendation to: Dr. R. B. Clarksen, D-298, Varian Associates, 611 Hansen Way, Palo Alto, CA 94303. Varian is an equal opportunity employer.

Sincerely,

Richard Galetti  
Marketing Manager

Berlin, den February 7, 1980  
 Tel.: (030) 314-4171  
 Az.:

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

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2D Spectra from Stochastic Resonance  
Coupling Information from Third Order Frequency Kernel

Dear Professor Shapiro:

Saturation is well-known as a non-linear property of spin-systems. Cross-peaks in 2D NMR spectra constitute another type of non-linearity, since the linear response to two rf pulses is simply the superposition of two FID signals from which one cannot derive the connectivity of NMR transitions stemming from spin-spin coupling or chemical exchange. It should therefore be possible to obtain 2D spectra from the spin response to stochastic excitation with high enough power in order to drive the spin system out of the linear region (in CW NMR this is already warranted for the condition of optimum sensitivity). Who will be surprised that Richard Ernst has already suggested the possibility of such a procedure (1). But how to do it? We would like to present a preliminary account of our work in that direction.

The non-linear response of a system can be expanded as a series of convolution integrals of increasing order. For instance, the third-order contribution is

$$\int_{-\infty}^0 \int_{-\infty}^0 \int_{-\infty}^0 k_3(\tau_1, \tau_2, \tau_3) x(t-\tau_1) x(t-\tau_2) x(t-\tau_3) d\tau_1 d\tau_2 d\tau_3$$

where  $x(t)$  is the excitation time function. The so-called kernel  $k_3$  is a function in three dimensions. It is characteristic for the system and weights the products of the values of the excitation at three, in general, different times in the past.  $k_3$  is expected to decrease with  $\tau_i$  and is a measure of the "memory" of the system. A simple example for  $k_3$  is given in a paper which we will submit to JMR (2).

We find that in NMR the evaluation of the sampled response in terms of correlation integrals of  $n^{\text{th}}$  order is most conveniently performed in the frequency domain. The third-order frequency kernel for instance is given by

$$H_3(\nu_1, \nu_2, \nu_3) = \frac{\langle [\bar{Y}(\nu') - H_1(\nu') X(\nu')] X^*(\nu_1) X^*(\nu_2) X^*(\nu_3) \rangle}{\langle |X(\nu_1)|^2 |X(\nu_2)|^2 |X(\nu_3)|^2 \rangle}$$

$$\nu' = \nu_1 + \nu_2 + \nu_3$$

Cont'd...

and  $\langle \cdot \rangle$  denotes ensemble average.

The ensemble averages are built from  $N$  independent discrete Fourier transforms  $X_i(\omega)$  and  $Y_i(\omega)$  of the sampled time functions  $x_i(m)$  resp.  $y_i(m)$ ,  $t = m \cdot \Delta t$ . The latter are derived from the complete sampled input-output record  $\{x(m), y(m)\}$   $m = 1, \dots, M = 10^4 - 10^7$  by division into  $N$  consecutive sections each with  $M/N$  data points.

We have simulated the spin response to noise excitation using the density matrix formalism for a single line and an AB system. The results are

- (1) The first order frequency kernel  $H_1(\omega)$  is the common, one-dimensional NMR spectrum. With increasing rf power the NMR signal broadens like in CW NMR (cf. Ref.(3)).
- (2) No significant information has been found in the second order frequency kernel  $H_2(\omega_1, \omega_2)$ .
- (3) The three-dimensional third-order frequency kernel  $H_3(\omega_1, \omega_2, \omega_3)$  contains non-zero contributions in the plane defined by  $\omega_1, \omega_2 = -\omega_3$  ( $H_3(\omega_1, \omega_2, -\omega_2)$ ) which in fact can be identified as a 2D spectrum. Cross-peaks indicate the existence of indirect spin-spin coupling as shown in the figure.

The method is advantageous in that resolution and spectral width can be varied after the experiment by defining appropriate ensemble sizes  $M/N$  and applying digital filtering methods. On the basis of the same raw data, first the common 1D NMR spectrum is calculated and, second, the connectivity of lines may be checked by computing  $H_3$  at selected cross-points  $\omega_1, \omega_2, \omega_3 = -\omega_2$  where  $\omega_1$  and  $\omega_2$  are the frequencies known from the 1D spectrum. This may be of particular importance in cases where low sensitivity requires long measuring times. A more detailed account of this work will appear in Ber. Bunsenges., preprints are available to a limited number on request.

Sincerely yours,



Bernard Blümich



Dieter Ziessow

#### References

- (1) W.P.Aue, E.Bartholdi, and R.Ernst, J.Chem.Phys. 64, 2229 (1976)
- (2) B.Blümich and D.Ziessow, J.Magn.Res., to be submitted  
Saturation Lineshapes in Hadamard NMR Spectroscopy
- (3) E.Bartholdi, A.Wokaun and R.Ernst, Chem.Phys. 18, 57 (1976)

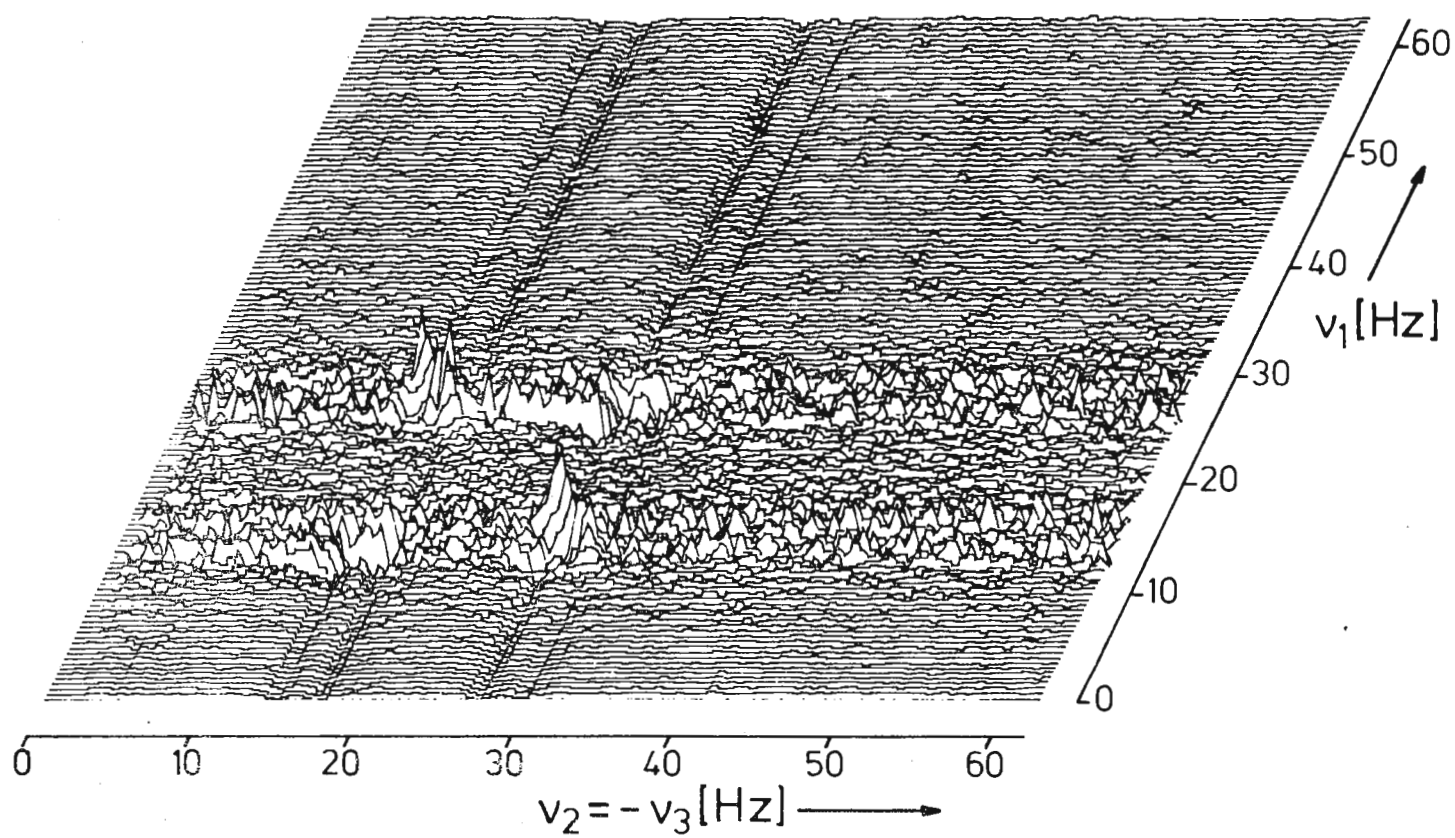
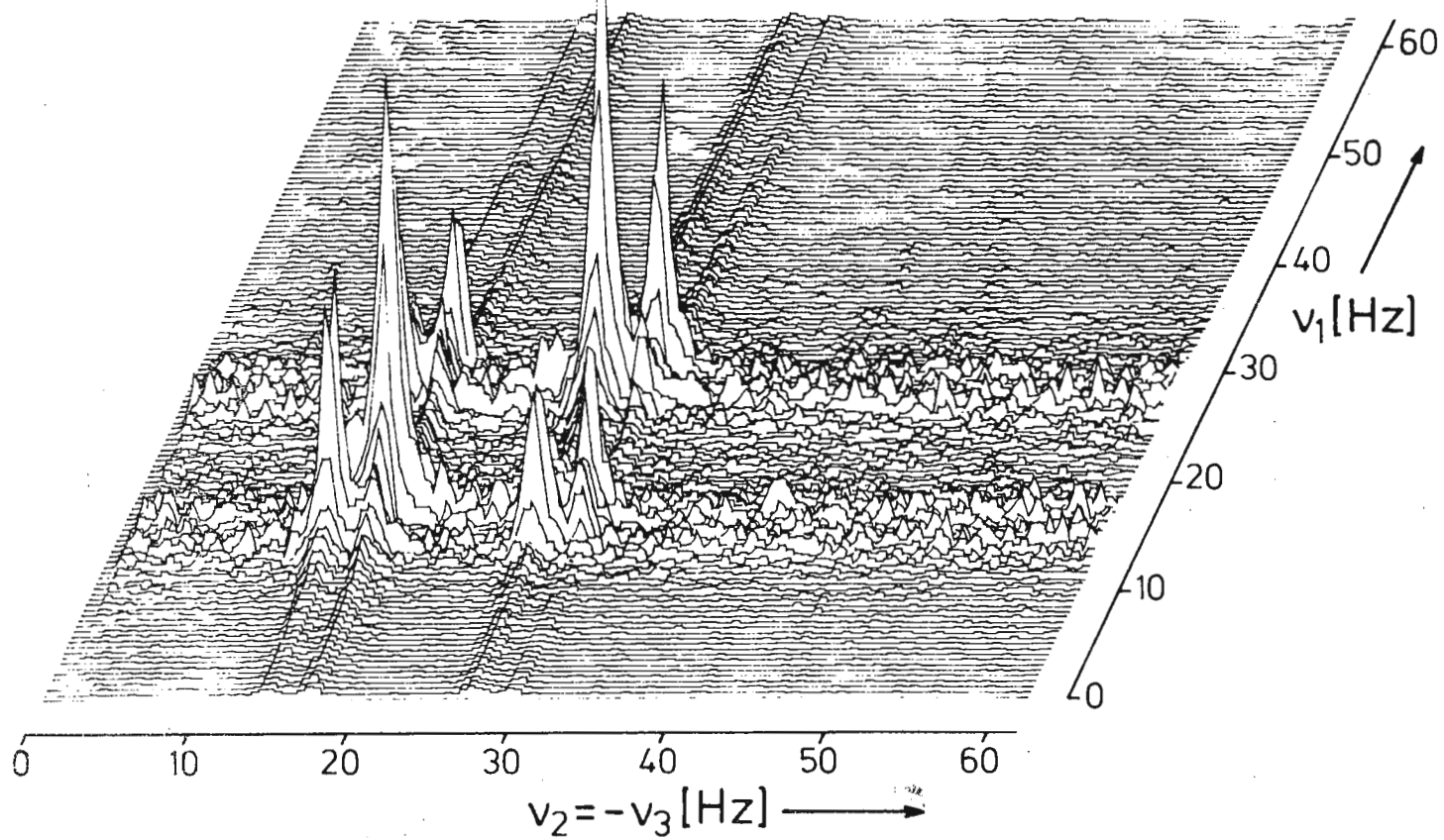
#### Legend to the Figure

Third order frequency kernel section for an AB spin system excited with Gaussian white noise with an rms flip angle of  $9.5^\circ$ . Calculation were based on 1Megawords ( $2 \times 20$ ) independent time data pairs  $x(m)$  and  $y(m)$  sectioned to give 16 kernel averages of 256 ensemble averages of each 128 frequency points.

Upper part: Top view of  $H_3$ , real part,  $128 \times 128$  points

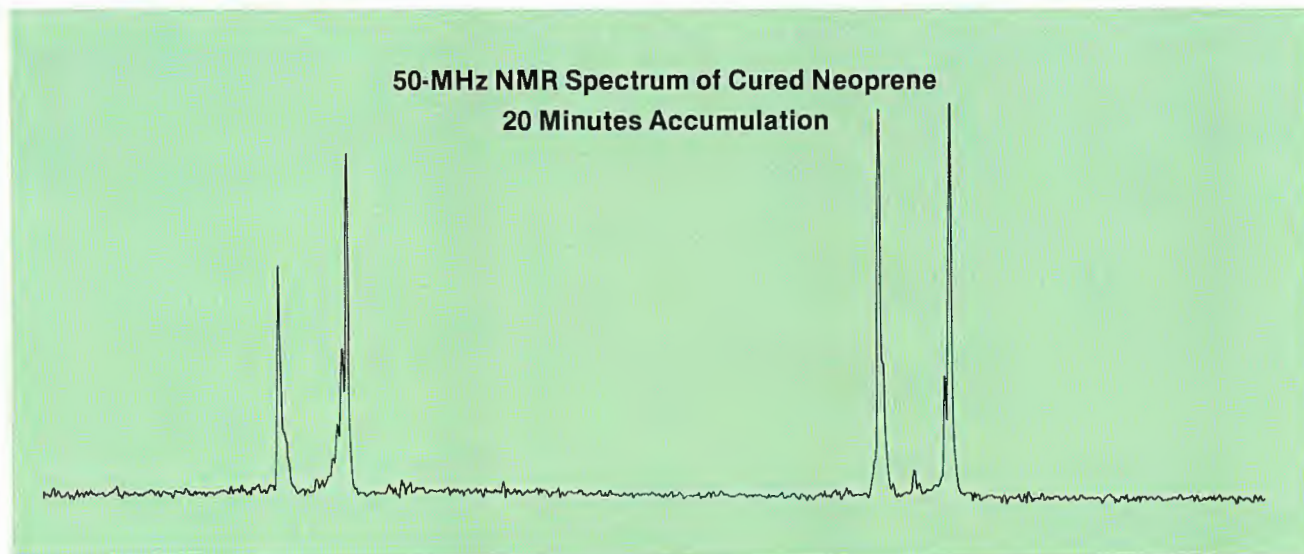
Lower part: Bottom view







# If you can't observe solids as readily as liquids on your superconducting FT NMR... ...you just don't have an XL-200!



<sup>13</sup>C spectrum of cured neoprene with carbon black\* in a Kel-F rotor using high-power gated decoupling (400 transients at 3-second intervals). The resolution has been enhanced by a Lorentzian-to-Gaussian transformation to bring out the fine structure. The width of the plot is 10 KHz. \*Sample courtesy of E. I. Du Pont de Nemours and Company

With the new <sup>13</sup>C solid-state accessory for the XL-200, you can spin solid or powdered samples at the magic angle, increase sensitivity using cross-polarization, and achieve efficient line narrowing with strong dipolar decoupling. Yet operation is surprisingly simple! You can introduce and eject the rotor pneumatically without disturbing the probe or the spinning axis adjustment. You monitor the spin rate on the spectrometer's built-in tachometer, just as in liquid-sample experiments. Front panel controls let you adjust optimal cross-polarization and decoupling conditions independently and conveniently.

There are other unique aspects to the XL-200 superconducting FT NMR Spectrometer, such as the data handling and spectrometer control system: a 13-bit ADC, which accommodates stronger signals on each transient; a standard 32K CPU, independent of the acquisition processor and programmed in PASCAL, a high-level, structured language; a built-in interactive 5M-word disk with dual platters; a large, flicker-free raster scan display.

The software, too, is exceptionally sophisticated. It permits multitasking (simultaneous acquisition, processing, printing, etc.) and queuing (automatic sequential execution of requested tasks) on the same or on different NMR experiments. You can also array parameters (up to three variables, including temperature) within a given experiment; generate your own convenient macro-commands;

create your own special or general-purpose pulse sequences in a simple, English-like code; even do your own computer programming in PASCAL.

Then there's the matter of the XL-200's broadband accessory which, with only a single probe for liquid samples, enables you to observe a host of nuclei (including <sup>13</sup>C) between 20 and 81 MHz. And there's the remarkable low-loss dewar system, which operates over three months on only 25 liters of liquid helium.

The XL-200 is in a class by itself—with a price tag and an operating economy that belie its advanced design.



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UNIVERSITY OF MINNESOTA  
TWIN CITIES

Department of Chemistry  
Kolthoff and Smith Halls  
207 Pleasant Street S.E.  
Minneapolis, Minnesota 55455

February 11, 1980

Professor B. L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, TX 77840

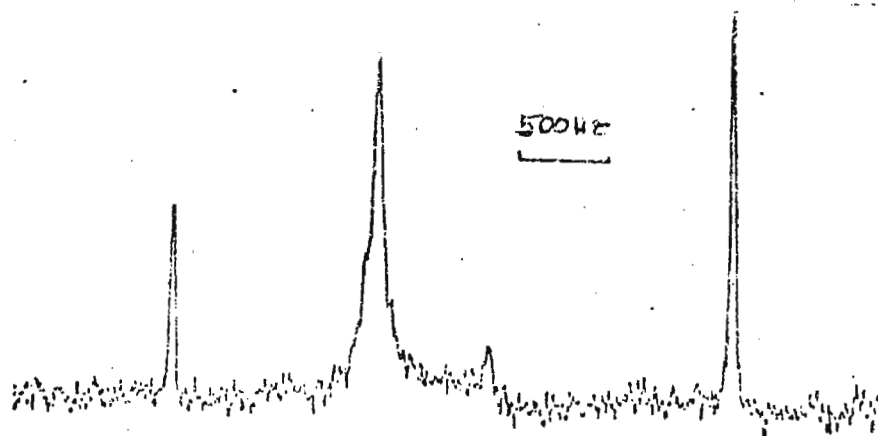
Re: Magic Angle Probe for XL-100/15

Dear Barry:

We have constructed a probe for our XL-100 capable of doing magic angle spinning and dipolar decoupling, but with no cross polarization. We are using an AR 60LA for  $^1\text{H}$  decoupling and the 100 W  $^{13}\text{C}$  Varian pulse card for a transmitter.

The spectrum is of hexamethylbenzene in a Delrin rotor. We plan to switch to Boron Nitride rotors in order to avoid the  $^{13}\text{C}$  resonance of Delrin, but more importantly, we have found that Delrin loses its mechanical integrity when the samples have some  $\text{CHCl}_3$  present.

We plan to present some results from our polymer-solvent studies at the ENC.



Sincerely,

*B.L.*

Robert M. Riddle

*L. J. Hedlund*

Lenas J. Hedlund





Professor B.L. Shapiro,  
Department of Chemistry,  
Texas A & M University,  
College Station,  
TEXAS 77845,  
USA.

Your reference

Our reference

Date 11 January 1980

Dear Professor Shapiro,

Application of Spin-lattice relaxation time measurements to the study of  
Litho-ionomer cement setting reactions.

Litho-ionomer cements are composed of polymeric acids and ion-leachable solids

(1). Their setting reactions in the example to be considered involve the extraction of metal cations from a glass. This forms a polymeric salt by an acid-base reaction with the polymeric acid. Precipitation of the salt causes the cement to set (2).

The chemical reactions are heterogeneous from the start, since the glass does not dissolve, and the end result is a covalent and ionically bound solid. However, high resolution NMR spectra can be obtained in the early reaction stages without recourse to solid-sample methods. We are interested in the mechanism of the setting reaction and spin-lattice relaxation time ( $T_1$ ) measurements should provide information on molecular and group dynamics during the initial stages of the setting reaction.

In the examples shown the  $^{13}\text{C}$ -NMR  $T_1$ 's were measured by the inversion-recovery method using a JEOL PFT-100 spectrometer, on a sample consisting of an Alumino Silicate glass and Polymeric Acid (ASPA). The latter was a 50% aqueous solution of a 2:1 copolymer of acrylic acid and itaconic acid together with some tartaric acid. Although some overlap in the  $^{13}\text{C}$ -NMR signals occurs from different structural elements of the acid system (see diagram), the  $T_1$  behaviour is explicable. The steady reduction in  $T_1$ 's of the tartaric acid CHOH groups, with little change in the  $T_1$ 's of the copolymer, indicates that of the tartaric acid is immobilised by association

with cations extracted from the glass while the copolymer remains unaffected. As salt formation proceeds a change in the relative chemical shift of itaconic branch chain carbonyls and tartaric acid carbonyls resolves their combined signal  $\odot$  into its components X, O.

Overall the behaviour is consistent with tartaric acid sequestering cations from the glass during the initial stages until the capacity of the tartaric acid is exceeded. A decrease in the copolymer's  $T_1$ s then follows corresponding to the onset of the transition to the set cement.

*H. J. Prosser*

H J Prosser

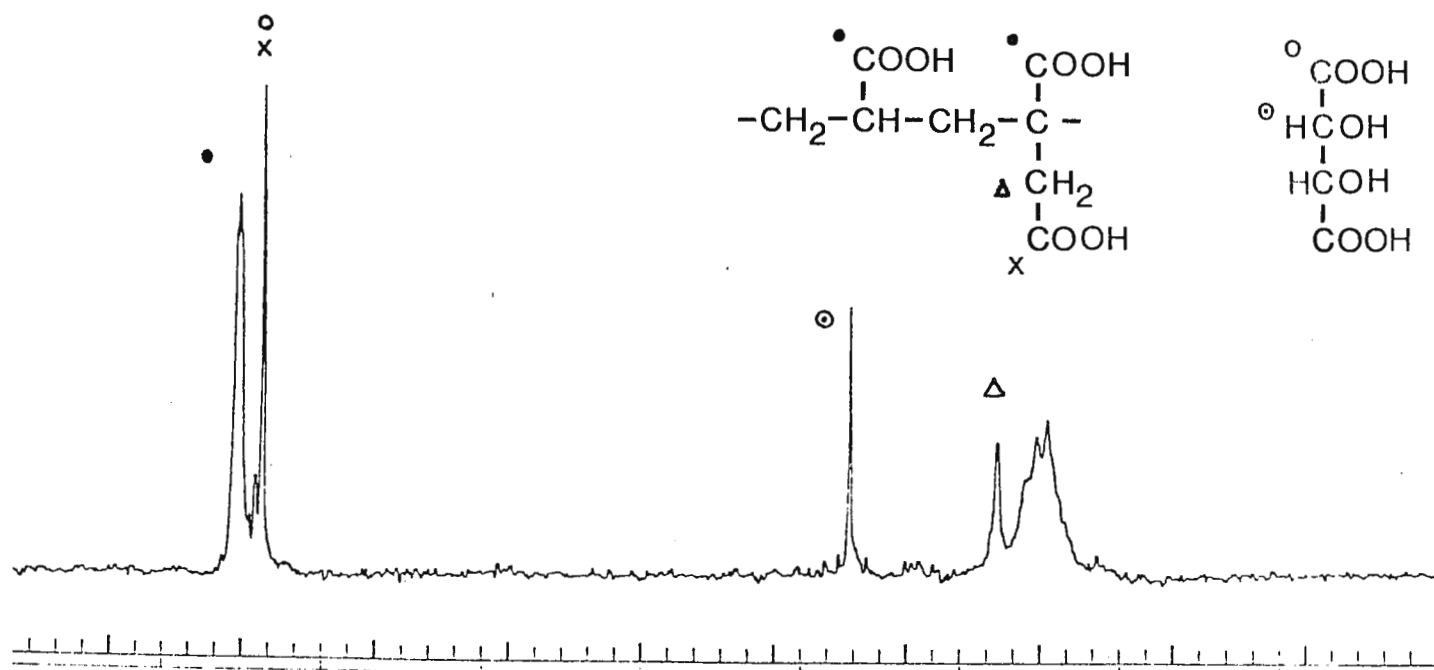
*A. D. Wilson*

A D Wilson

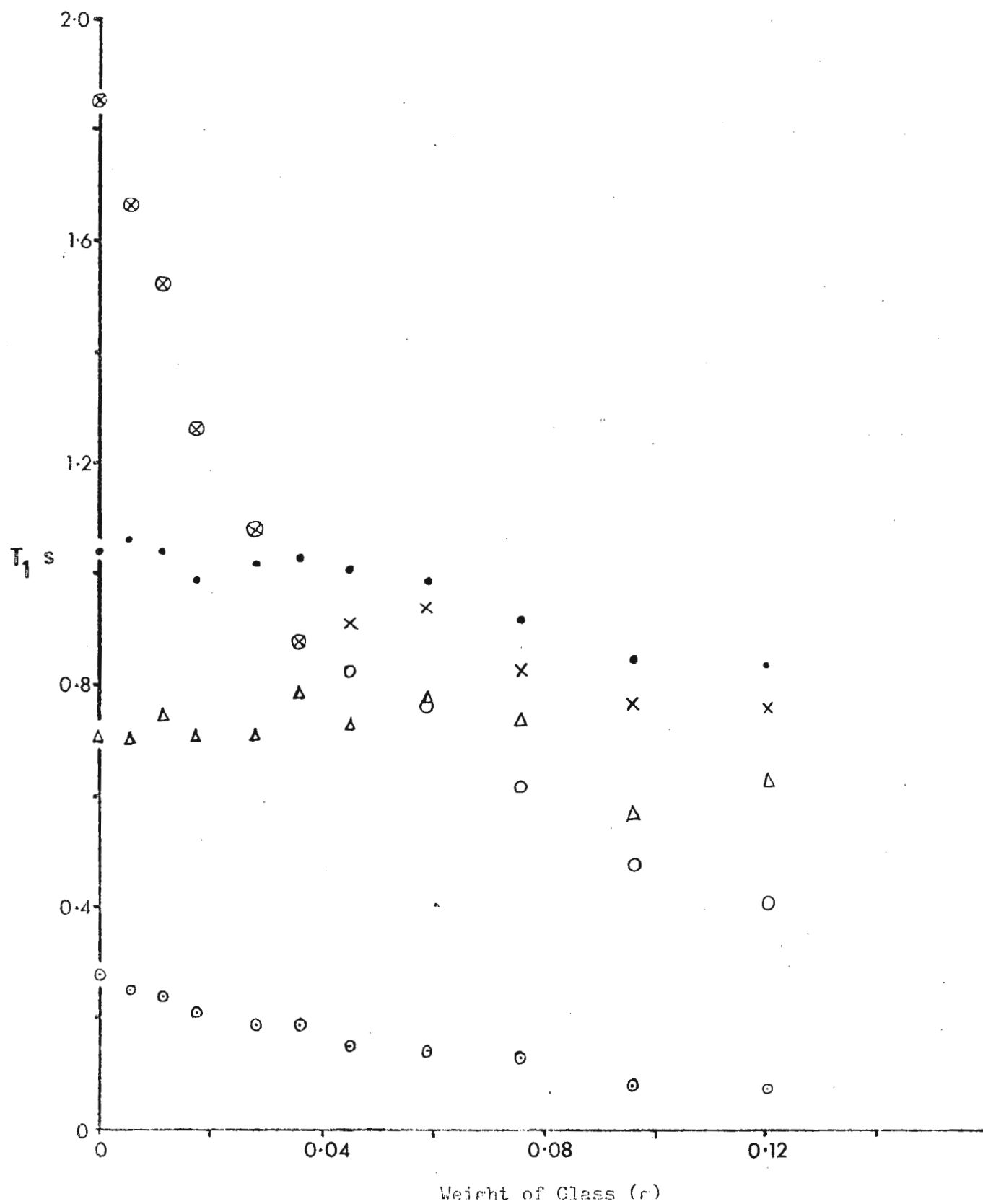
*C P Richards*

C P Richards

- 1) S Crisp and A D Wilson, Organolithic Macromolecular Materials, Applied Science, London 1977
- 2) H J Prosser and A D Wilson, J Chem Tech Biotechol, 29, 69, (1979)



Graph of Spin-lattice relaxation times against quantity of Glass  
added to 2.0% of Polymeric Acid solution





IN REPLY PLEASE QUOTE  
 REF.



# THE UNIVERSITY OF NEW ENGLAND

ARMIDALE, N.S.W.  
 Department of Organic Chemistry

20th February, 1980

Dr Bernard L. Shapiro,  
 Department of Chemistry,  
 Texas A&M University,  
 College Station, TX77843, U.S.A.

Dear Barry,

## *AB INITIO* CALCULATIONS OF BARRIERS TO INTERNAL ROTATION OF SOME AMIDES

N.m.r. has been widely used as a means of measuring experimentally the barriers to internal rotation of a variety of amides, and has yielded a quantity of interesting information about such rotational processes.

We have recently been calculating by *ab initio* SCF methods the heights of barriers to internal rotation in an attempt to understand the factors that determine the barriers. Previous *ab initio* calculations of the barrier to internal rotation of formamide and other simple amides about the C—N bond have mostly used experimental or "standard" ground-state bond lengths and angles, and assumed "rigid" rotation about the C—N bond. The "best" calculations would optimize both ground- and transition-state geometries, but such computations might soon become overwhelmingly expensive. We have made a thorough examination of the ground state of formamide (1) and a less extensive study of the transition state, and obtained (2) estimates of the barrier height close to the mid-point of the experimental range. In further partial geometry-optimization studies, we have found barrier heights for acetamide and *N*-methylformamide in reasonable agreement with experimental values. The ground states of formimide (diformamide) and diacetamide are predicted to be planar, and the *E,Z*-conformer to be preferred in both cases, strongly in the case of diacetamide, in agreement with experimental observations. The *Z,Z*-conformer in both cases is strongly destabilised by internal dipolar repulsion, whereas *E,E*-diacetamide is strongly destabilised by methyl-methyl steric interactions. Complete optimization of the geometry of the transition states for internal rotation of these molecules would be very profligate of computer time, but reasonable constraints imposed by reference to the simpler compounds mentioned above yield estimates of the barrier heights for internal rotation in reasonable agreement with n.m.r. values. In particular, that for diacetamide is *c.* 7 kJ/mol less than that for formimide, a result attributed to relief of steric strains present in the ground state of the former but not in that of the latter.

We believe the results of these calculations contribute to understanding of the experimental n.m.r. results.

1. N.R. Carlsen, L. Radom, N.V. Riggs, and W.R. Rodwell, *J. Am. Chem. Soc.*, 1979, **101**, 2233.
2. L. Radom and N.V. Riggs, *Aust. J. Chem.*, 1980, in the press.

Yours sincerely,

Noel V. Riggs



McMASTER UNIVERSITY

Department of Chemistry

1280 Main Street West, Hamilton, Ontario, L8S 4M1

Telephone: 525-9140

January 31, 1980

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

"Hidden Coupling Constants"

Dear Barry:

We've been using chemical shift correlated 2D NMR spectroscopy (1,2) with a  $90^\circ-t_1/2-90^\circ-t_1/2-F.I.D. (t_2)$  pulse sequence to help us solve the complicated proton NMR spectra of some oligoribonucleotides. This technique correlates the chemical shifts of connected (e.g. via scalar coupling) nuclei. A recent 2D spectrum of cytidyl -(3',5') - adenosine (CpA) surprised us by establishing a five bond connection between the CH-5 and the CH-1' protons, unobserved in the normal 1D spectrum.

Figure 1 shows part of the 1D  $^1H$  NMR spectrum of CpA at  $71 \pm 2^\circ C$ , plotted as a function of the normal frequency axis  $f_2$ . Figure 2 shows a slice through the corresponding 2D spectrum at the  $f_2$  frequency of the high-field transition of the CH-5 doublet. This  $f_1$  spectrum displays lines at both the sum and the difference of the  $f_2$  frequency of the CH-5 transition and the  $f_2$  frequency of any other connected transition. A proton transition is connected to another proton transition of a given nucleus A by either belonging to the same nucleus A or by belonging to a nucleus B which is coupled to nucleus A. In figure 2, lines 3 and 4 at  $\sim 10 Hz$  in  $f_1$  indicate a connection between the CH-5 transition and the two CH-1' transitions at  $\sim 20 Hz$  to higher field in  $f_2$  (see figure 1). If these lines were perfectly resolved, they would form a doublet of doublets with a large splitting (observed) due to  $^3J(H2'-H1')$  and a smaller splitting (unobserved) due to  $^5J(H5-H1')$ . The lines split by this latter coupling constant overlap and partially cancel in the  $f_1$  spectrum because they are of opposite phase - if the coupling constant was 0 Hz., they would cancel exactly.

The long range  $^5J_{H,H}$  coupling between these two nuclei is normally unresolved but has been observed in similar systems (3).

Please credit this to the account of J.I.A. Thompson.

Yours truly,

*Alex Bain*

A. D. Bain

*Jeremy R. Everett*

J. R. Everett

R. A. Bell

*R.A. Bell*

*Donald W. Hughes*

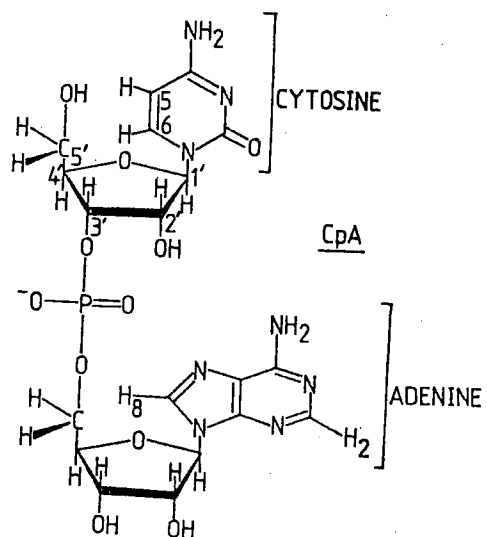
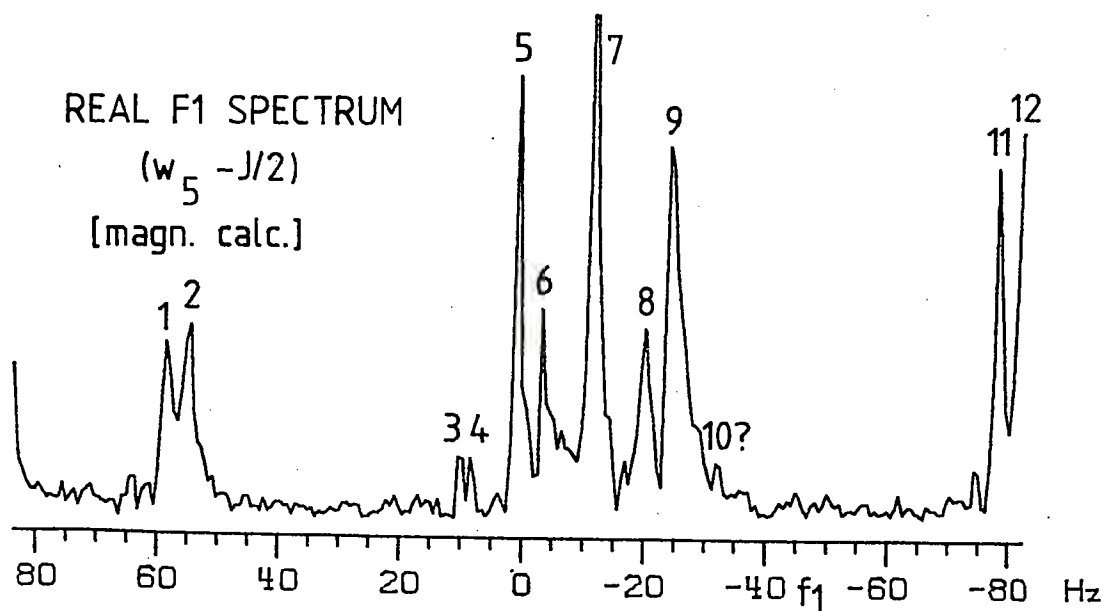
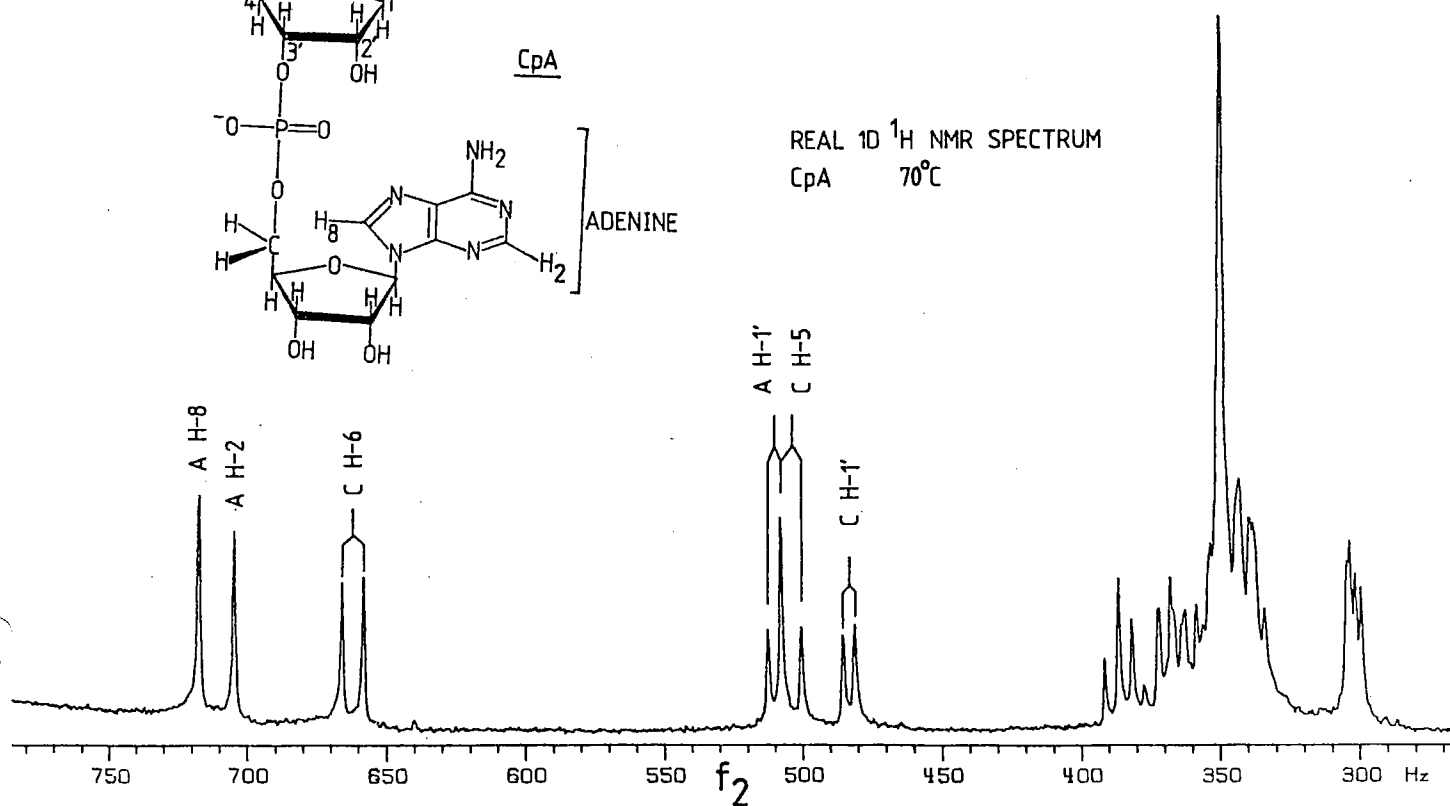
D. W. Hughes

1. K. Nagayama, K. Wüthrich and R.R. Ernst, Biochem. Biophys. Res. Commun. **90**, 305 (1979).
2. A.D. Bain, R.A. Bell, J.R. Everett and D.W. Hughes, J.C.S. Chem. Commun. (in press).
3. D.B. Davies, Prog. NMR Spectr. **12**, 135 (1978).

## REAL F1 SPECTRUM

(w<sub>5</sub> -J/2)

[magn. calc.]

REAL 1D <sup>1</sup>H NMR SPECTRUM  
CpA 70°C



UNIVERSITÉ D'OTTAWA

OTTAWA ONTARIO  
CANADA K1N 6N5

UNIVERSITY OF OTTAWA

DÉPARTEMENT DE CHIMIE

DEPARTMENT OF CHEMISTRY

February 1, 1980.

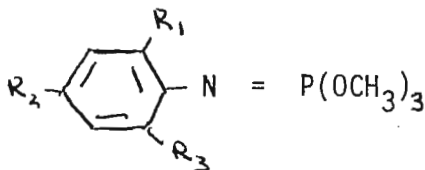
Professor B.L. Shapiro,  
Department of Chemistry,  
Texas A and M University,  
College Station, Texas  
77843, U.S.A.

TITLE: SOLVENT INDUCED S:N ENHANCEMENT IN  $^{15}\text{N}$  SPECTRA

Dear Barry;

We have recently completed the examination of the  $^{15}\text{N}$  spectra of a series of N-arylphosphorimidates to attempt to determine the dominant resonance interactions. This is a collaborative effort with Professor G.W. Buchanan of Carleton University and the results along with his  $^{13}\text{C}$  data on the same compounds should appear in Can. J. Chem., 1980.

I would like to describe one simple technique which we found very helpful in obtaining adequate signal/noise for the  $^{15}\text{N}$  spectra of the N-phenyl phosphorimide, I and its simple derivatives. ( $R_1, R_2, R_3 = \text{H or CH}_3$ )



It is well known that on irradiation of protons, the negative magnetogyric ratio for  $^{15}\text{N}$  leads to a theoretical maximum of -3.93 for the nuclear Overhauser enhancement factor in the case of purely dipole-dipole  $^1\text{H}$ - $^{15}\text{N}$  relaxation. Contributions from other mechanisms, however, can produce essentially zero  $^{15}\text{N}$  signal intensity and such mechanisms can be operative in which there are not directly bonded H's on N to facilitate dipole-dipole relaxation. One method used previously to overcome this problem is the addition of  $\text{Cr}(\text{acac})_3$ , but no beneficial effect of this reagent was observed for 1 - 5.

Considerable success was obtained, however, by use of a 3:1 volume:volume mixture of aniline:CHCl<sub>3</sub> in place of CDCl<sub>3</sub> as solvent. In the case of 1 for example, a tenfold increase in the signal to noise ratio was observed in the <sup>1</sup>H decoupled spectrum. Furthermore, no measureable solvent induced shifts or J<sub>p-N</sub> changes were noted between these two media. At least two factors may be operative to increase the signal to noise ratio. Additional protons in the medium will, on solute-solvent encounter, contribute to dipole-dipole relaxation of the <sup>15</sup>N nucleus, leading to a shortened T<sub>1</sub>. Also, as the protons are decoupled, an intermolecular nuclear Overhauser effect resulting from the dipole-dipole relaxation can occur.

One could in principle test for the relative contributions of each effect noted above by measuring the <sup>15</sup>N T<sub>1</sub>s and the n.O.e, but due to the lengthy time required for such experiments, they have not yet been carried out. Regardless of its origin this 100 fold decrease in time for accumulation should be attainable in many <sup>15</sup>N measurements involving nitrogen which lacks a directly bonded proton.

Yours sincerely,



Robert R. Fraser,  
Professor of Chemistry.

RRF/ma



## TUFTS UNIVERSITY

Department of Chemistry

February 22, 1980

Dr. B.L. Shapiro  
TAMUNMR Newsletter  
Texas A&M University  
College of Science  
College Station, TX 77843

"Z-80 Cross Assembler for RT-11 FORTRAN; Remote Correlation NMR"

Dear Barry:

We are now deeply involved in microcomputer networking of our Z-80 microcomputer board series MCB-16 with our PDP-11. One of the projects we are using this for is the acquisition of correlation nmr data from our EM-360L using the Z-80 with an analog-to-digital converter board, the sending of this data to the PDP-11 for processing and the sending of the processed data back for plotting and display.

Accordingly, we have developed a cross-assembler for the Z-80, written in standard FORTRAN which will take Z-80 assembly language code and translate it into a binary file which can be down-line loaded from the PDP-11 to the Z-80 using loading programs that we have developed. If anyone would be interested in a copy of this program, we'll send copies out for a small handling charge.

We hope to report on the results of the correlation experiment shortly.

Sincerely,

James W. Cooper  
Assistant Professor of Chemistry

JWC/lpl



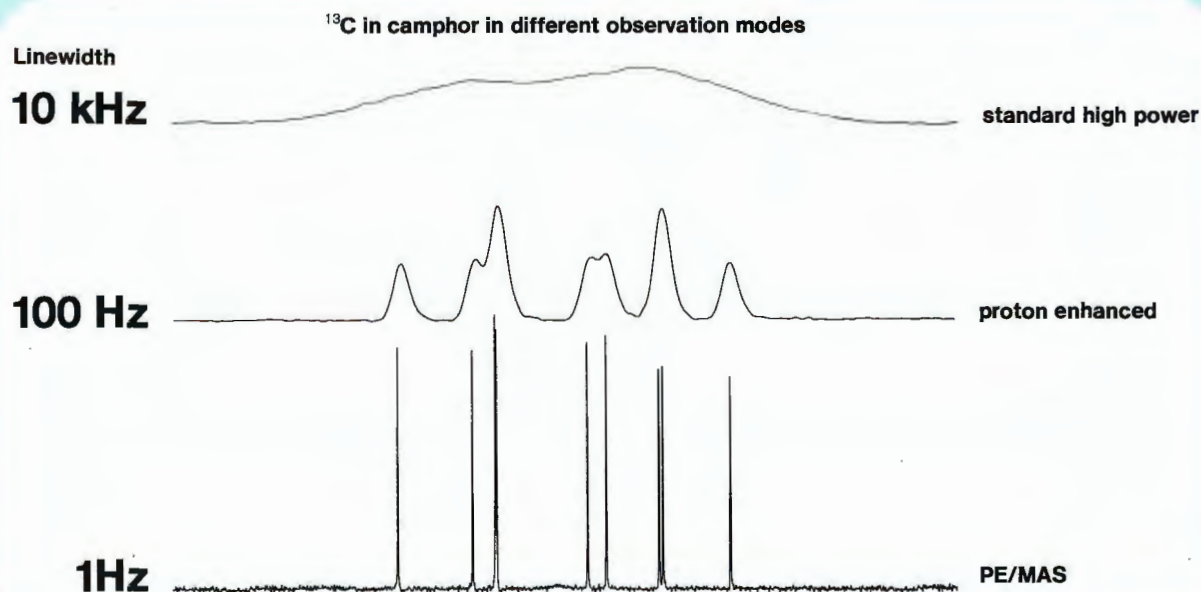
# Bruker $\equiv$ NMR NMR $\equiv$ Bruker

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Magic angle spinning with or without cross-polarization is just one of the many applications of the CXP series of pulse spectrometers, the most versatile instruments to date. No other instrument is capable of observing the full range of linewidths (from less than .1 Hz to several hundred kHz).

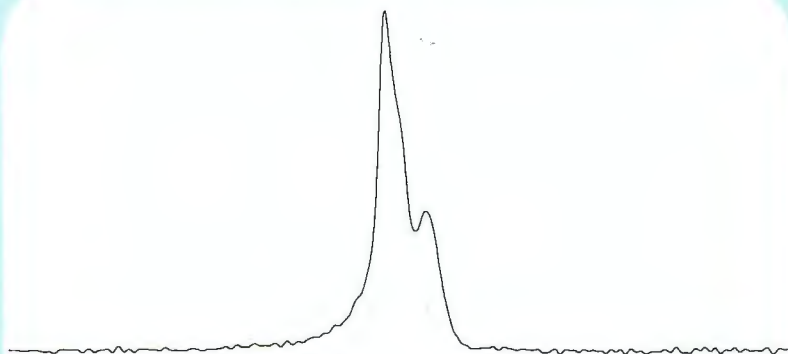
Unique features of the CXP spectrometer line for cross-polarization/magic angle sample spinning experiments comprise:

- a choice of magnets operating between 2.1 and 7 Tesla;
- highest spin-locking fields;
- rapid sample spinning;
- capability to observe a variety of nuclei (e. g. <sup>13</sup>C, <sup>15</sup>N, <sup>29</sup>Si, <sup>31</sup>P, <sup>113</sup>Cd);
- unmatched sensitivity
- a range of rotor sizes (6 to 13 mm o. d.);
- a flexible pulse sequence generator for experiments yet to be developed;
- ultrafast transmitter/receiver electronics.

The following spectra exemplify the potential of the BRUKER CXP pulse spectrometers:

#### **Polyethylene**

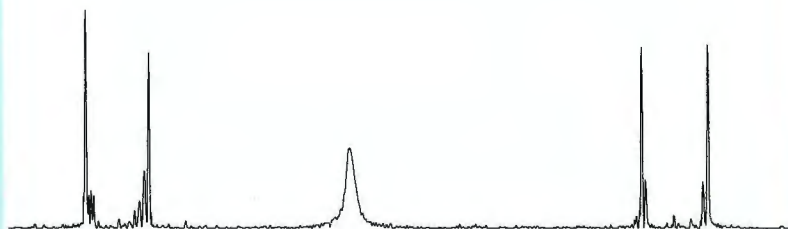
The resolution shown in the spectrum of this highly crystalline polymer required a decoupling field of 20 Gauss.



#### **Cured Neoprene with Carbon Black \*)**

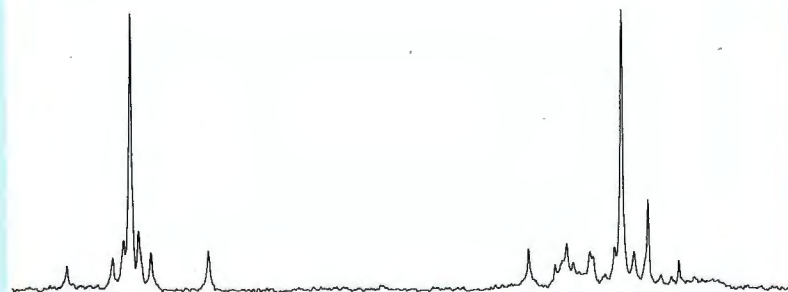
Soft plastics afford excellent S/N and resolution even in the absence of cross polarization and using low decoupling power (35W, BB-decoupling, 263 transients at 3.5 s recycle time, Gaussian resolution enhancement).

\*) sample courtesy of E. I. Du Pont de Nemours and Company.



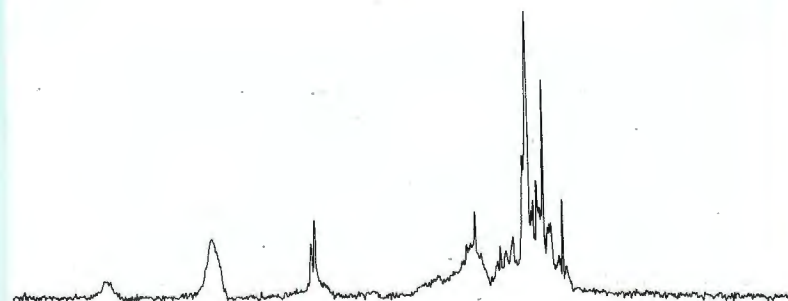
#### **Styrene Butadiene Polymer**

This complex polymer system afforded well separated interpretable lines in 30 minutes experimental time.

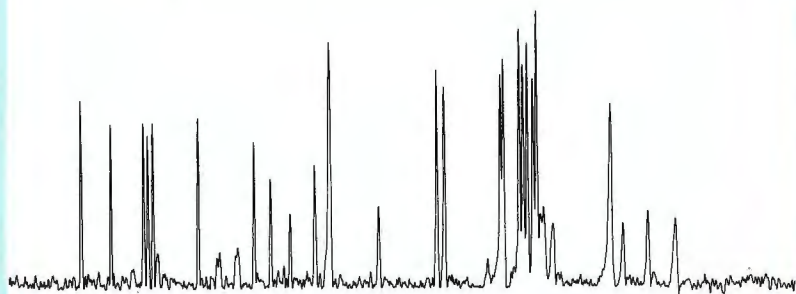


#### **Erythrocyte Ghosts**

Even this highly complex biological sample gave well resolved resonances.

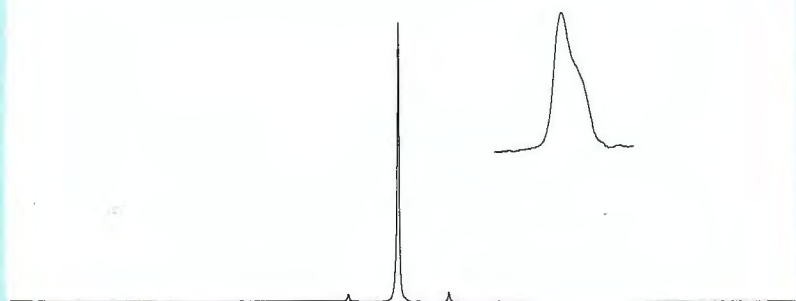






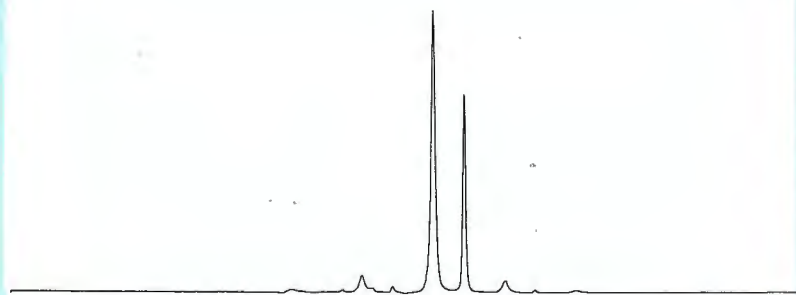
#### **Reserpine**

This <sup>13</sup>C CP-MAS spectrum demonstrates the feasibility of obtaining high-resolution spectra of complex organic molecules in the solid state. It is to be noted that chiral carbons can give rise to more than one signal, thus providing additional information. In this example, a new technique was applied for removal of rotational sidebands.



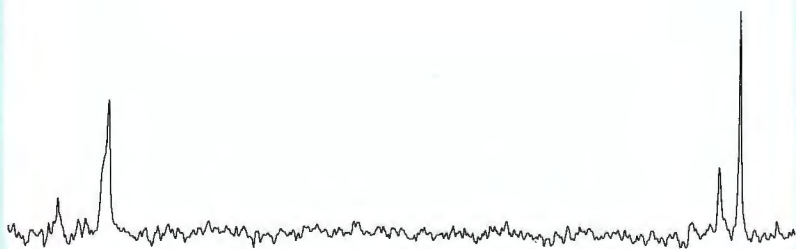
#### **Ammonium Dihydrogen Phosphate**

Magic angle spinning reduced the <sup>31</sup>P linewidth from 34 to 1.4 ppm.



#### **Mixture of Sodium Chloride and Sodium Nitrite Crystals**

This spectrum shows the chemical shift dispersion of <sup>23</sup>Na in the solid state. Magic angle spinning narrowed the lines to 2 ppm.



#### **Ammonium Nitrate**

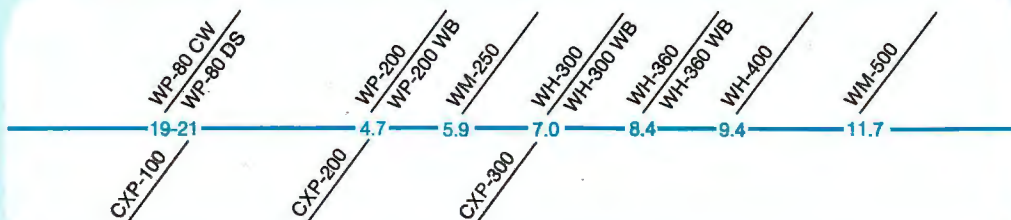
This natural abundance <sup>15</sup>N CP-MAS spectrum of solid ammonium nitrate narrows the nitrate resonance from 250 ppm to a few ppm. Interesting is the presence of two further lines probably belonging to a minor constituent.

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Department of Chemistry

The Florida State University  
Tallahassee, Florida 32306

19 February 1980

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

FSU IS ON THE WARPATH

Dear Barry:

For those readers of this newsletter who don't follow American collegiate football, Florida State's fighting Seminoles went on the warpath this year, finishing the regular season with a perfect 11-0 record. Meanwhile in the FSU NMR lab, another *SEMINOLE* is being prepared to go on a totally different kind of *WARPATH*. The *SEMINOLE* is, of course, our homebuilt 3.77 Tesla Sensitivity Enhanced Modular Instrument for Nuclei Of Low Enrichment; and the *WARPATH* is our newly designed Widespread Asynchronous Rapid Parallel Accurate Transfer Handler.

The *WARPATH* provides the data link between all of the computer resources available in the NMR laboratory at FSU. As its name implies, the *WARPATH* can be Widespread, allowing a total bus length of more than 1 km. The *WARPATH* is also Asynchronous in operation, allowing computers with widely differing internal clock frequencies to communicate with one another. This data network is definitely Rapid with a "burst mode" transfer rate of 190 kilobytes/second (over 3 orders of magnitude faster than a 1200 baud CRT!) and an overall file transfer rate of 50 kilobytes/second. Data rates such as these are achieved by operating in a byte-serial, bit-Parallel mode in which an entire byte (8-bits) of data is sent simultaneously. The Accuracy of the *WARPATH* is testified to by the fact that test transfers of many billions of bytes have been conducted and no bus related error has been detected. This accuracy is insured by the use of differential line drivers throughout the network.

To date, *WARPATH* interfaces have been built for Nicolet 1080's, the Data General Eclipse/Nova series of minicomputers, and Z-80 based S-100 microcomputers. The Nicolet and Data General interface is intelligent in its own right, containing a Z-80 microprocessor, buffer memory, and interface firmware. Since this interface requires only an 8-bit I/O port and 2 flag lines, it should be exceptionally simple to adapt to any of a number of other microcomputers as well.

The *WARPATH* and the rest of the FSU NMR lab will be open for tours and demonstrations during this year's ENC and everyone is welcome to come and look around (free souvenirs will not, however, be given away at the door!)

Best regards,

Dan Terpstra      George C. Levy

National Research Council  
CanadaConseil national de recherches  
Canada

Division of Chemistry

Division de chimie

File Référence

February 7, 1980

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

Correlation of Fluorine Chemical Shifts  
in Hexa-Coordinate Species

Dear Barry,

It has been shown that the equation

$$\delta F = pC + qT$$

will correlate the fluorine chemical shifts for species  $\text{SnF}_6-x\text{Ax}^-$ . (1)  $\delta F$  is the chemical shift of the particular fluorine from  $\text{MF}_6^-$ .  $p$  and  $q$  are the number of substituents cis and trans to that fluorine.  $C$  and  $T$  are parameters chosen for best fit. This equation is also obeyed for other central elements. Furthermore it is found that if one orders the ligands  $A$  according to  $C-T$  for that ligand for a particular central element the same order is maintained for all other central elements. The only significant exceptions can be explained by the availability of "d" orbitals on the central element. The data thus far are summarized in the Table.

Best wishes,

S. Brownstein

- (1) P.A.W. Dean and D.F. Evans, J. Chem. Soc.(A), 1154 (1968).  
(2) C. Merrill, S. Williamson, G. Cady and D. Eggers. Inorg. Chem. 1, 215 (1962)

A	Phosphorus	Arsenic	Niobium	Tantalum	Germanium	Tin <sup>(1)</sup>	Titanium	Sulfur <sup>(2)</sup>
Br <sup>-</sup>			17.5	13.5		23.7		83.2
Cl <sup>-</sup>	49.3		13.8	10.2		17.8		73.3
CN <sup>-</sup>	27.7	22.6			18.5	14.5		
CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	26.3	27.7	-38.2	-33.2	20.2	9.1		
FSO <sub>3</sub> <sup>-</sup>	22.5	22.2	-40.4	-33.5	19.8	7.8		16.4
ClO <sub>4</sub> <sup>-</sup>	21.8	22.1					65	
SCN <sup>-</sup>	20.7				16.4	10.4	59	
OCN <sup>-</sup>					11.1	5.5		
CF <sub>3</sub> COO <sup>-</sup>	14.8	11.9		-17.1	10.8	7.5	47	
NO <sub>3</sub> <sup>-</sup>					9.5			
N <sub>3</sub> <sup>-</sup>	12.5				9.4	5.0	22	
NO <sub>2</sub> <sup>-</sup>	11.4				7.3			
CH <sub>3</sub> COO <sup>-</sup>	5.3				4.0	2.6		



## BLUE HEN NMR COMPLEX

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

February 12, 1980

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

TITLE: Blue Chickens or Cold Turkey

Dear Barry,

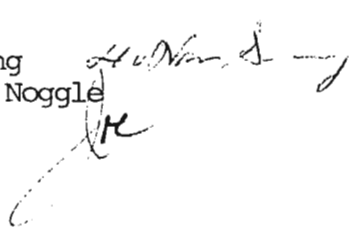
The NMR scene in Delaware has been brightened by two recent additions; viz. a Bruker WM250 spectrometer and Professor Lila G. Pease.

The spectrometer installation is not yet complete but those parts present are working well. The magnet came up smoothly and exceeded sensitivity and resolution specs on C-13 the first time (73 S/N on 10% EtBz and 0.1 Hz on Benzene, 10 mm CW decouple). One of our initial efforts on PVA (10% in CDCl<sub>3</sub>) is attached. Shown is the methine region of the <sup>13</sup>C NMR with more structure than we have been able to find in literature reports on this compound. The spectrum was run at ca. 50°C in about a half an hour. (We have not yet optimized pulse width or tuning so this is not a sensitivity test.)

The installation of Lila is more complete and at least as successful (S/N exceeds specs). She has been busily working on NMR of small model peptides and will presumably report on these at some future date.

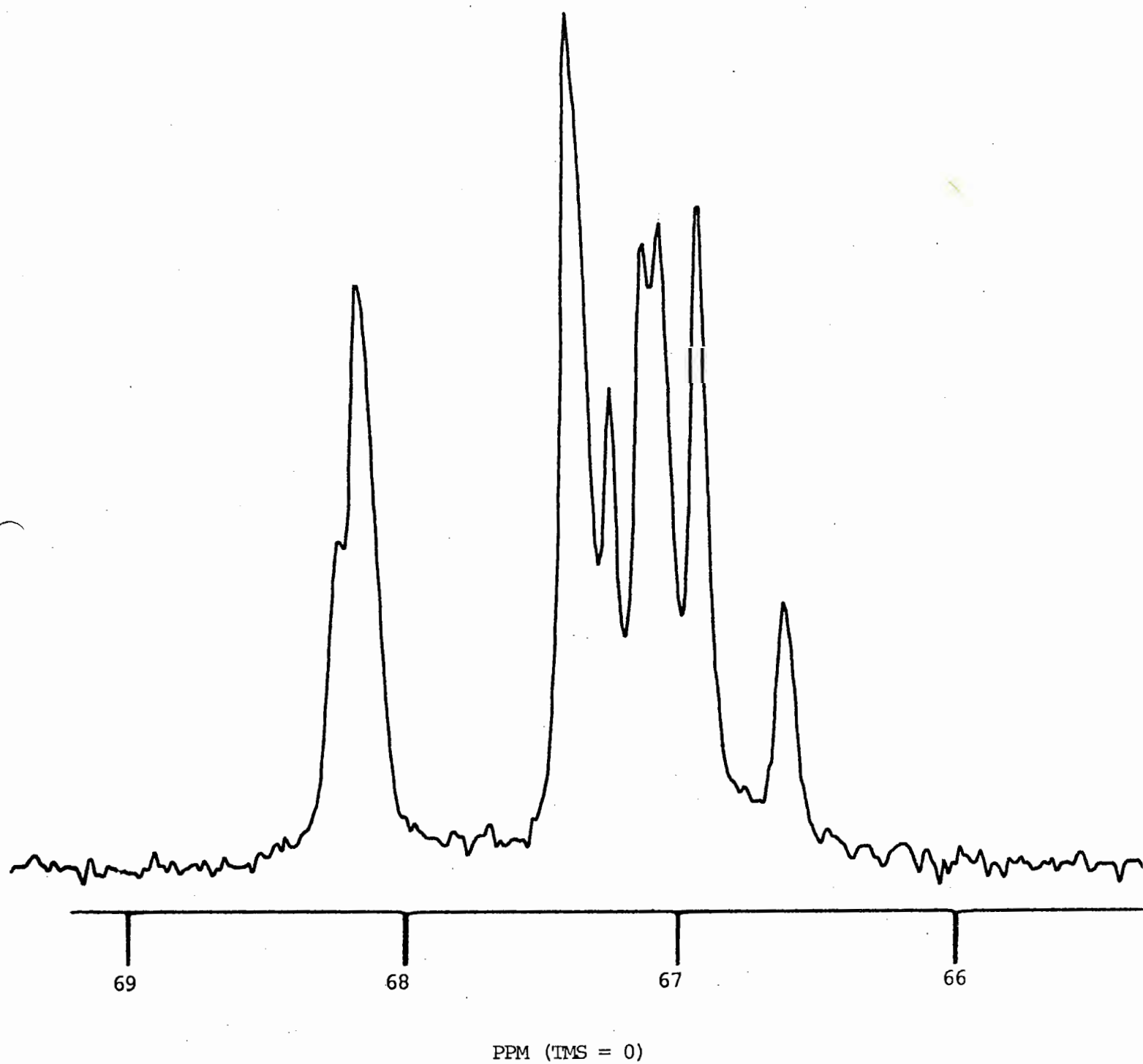
Yours very truly,

Ho-Nan Sung  
Joseph H. Noggle



nlw  
Attachment





Carbon-13 spectrum of atactic poly (vinyl acetate) at 62.86 MHz; methine region.



(303)491-6480

Colorado State University  
Fort Collins, Colorado  
80523

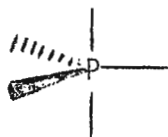
Department of Chemistry

February 13, 1980

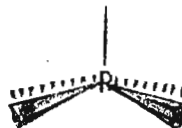
Professor B.L. Shapiro  
Department of Chemistry  
Texas A&M University  
College Station, Texas 77843Position Available. Solid-vs-Liquid  $^{31}\text{P}$  Shifts in Phosphoranes.

Dear Barry:

During the past dozen years considerable attention has been focussed in several laboratories on the five-coordinate phosphoranes, with limiting structures of the trigonal-bipyramidal (I) and rectangular pyramidal (II) types.  $^{31}\text{P}$  nmr chemical shifts have been applied extensively in the study



I



II

of such compounds in solution. As is often the case, the structural models on which interpretations of the solution-state nmr data have been based have been x-ray determined structures of crystalline samples. To examine the assumed relationship between the solid-state and solution-state structures, Larry Dennis (a postdoctoral in my group) has measured the  $^{31}\text{P}$  chemical shifts of eight of these type of compounds in the solid and solution states. For these phosphoranes the solid-state and solution  $^{31}\text{P}$  shifts ranged over 87 ppm, yet the difference between the solid-state and solution resonance frequencies for a given compound is in no case more than 3 ppm. Hence, we conclude that there are no major differences between the solid-state and solution structures of these compounds, and the x-ray determined structures of the solids serve as reliable models for interpreting solution data. The  $^{31}\text{P}$  chemical shifts of the solid samples were obtained at 24.3 MHz, using magic-angle spinning and cross polarization, on a home-built instrument based on a Varian HR-60 spectrometer.

A long-term position is available in our laboratory for an NMR INSTRUMENT SPECIALIST. The starting annual salary will be \$14,000 to \$20,000, depending on background, abilities and professional interests. The candidate must have a degree in science or engineering, with a strong background in nmr or in electronic instrumentation. The responsibilities will be weighted heavily toward the design, construction, modification and maintenance of nmr instrumentation, particularly for work on solids, but will also include technique development and research on solid fossil fuels. Applications should include curriculum vitae and bibliography and three letters of recommendation, and should be sent to Professor G.E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Application deadline is April 31, 1980. Starting date is May 15 - July 1, 1980. Colorado State University is an EEO/Title IX Employer. Equal Opportunity Office: 314 Student Services Building.

Sincerely,

*Gary E. Maciel*  
 Gary E. Maciel  
 Professor



DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

PUBLIC HEALTH SERVICE  
 NATIONAL INSTITUTES OF HEALTH  
 BETHESDA, MARYLAND 20205

February 5, 1980

Building 2, Room B2-08

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

Title: Postdoctoral Position Available

Dear Barry:

A postdoctoral fellowship has become available in my laboratory. For those interested in the type of work involved I refer you to my recent letter to this prestigious NMR Newsletter. The applicant should be a U.S. citizen, preferably with some postdoctoral experience in NMR applied to nucleic acids and/or proteins.

Yours sincerely,

*Jack S. Cohen*  
 Jack S. Cohen  
 Developmental Pharmacology Branch  
 National Institute of Child  
 Health and Human Development

UNIVERSITE LOUIS PASTEUR  
DE STRASBOURG

Strasbourg, le 15 Février 1980

INSTITUT DE CHIMIE

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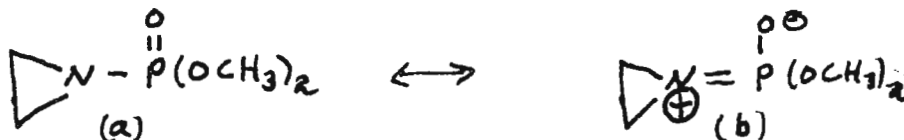
Professor B.L. SHAPIRO  
Department of Chemistry  
Texas A&M University  
COLLEGE STATION, TEXAS 77843  
U.S.A.

"Complimentarity of  $^{15}\text{N}$  and  $^{31}\text{P}$  Chemical Shifts  
in Cyclic Phosphoramidates"

Dear Barry,

In connection with our studies on structure and bonding in the title molecules<sup>(1,2)</sup>, we have examined the relationship between the  $^{15}\text{N}$  chemical shifts (relative to external  $\text{CH}_3\text{NO}_2$ ) and the  $^{31}\text{P}$  data (relative to external  $\text{H}_3\text{PO}_4$ ). The data are indicated graphically, and show a complimentarity effect.

The high field  $^{15}\text{N}$  shift in substituted aziridines has precedent<sup>(2)</sup>, and we attribute the deshielded  $^{31}\text{P}$  resonance in this material to the absence of back donation from the N lone pair, due to increased bond angle strain at N in the resonance form (b) indicated below.



- References: 1. Can. J. Chem. 57, 21 (1979)  
2. J. Org. Chem. 44, 1768 (1979).

Sincerely,

*G.W. Buchanan*

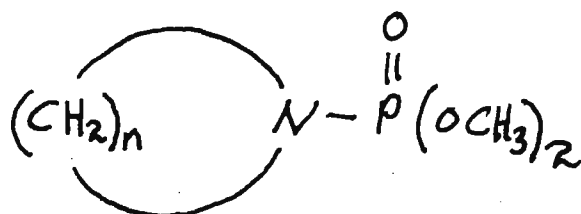
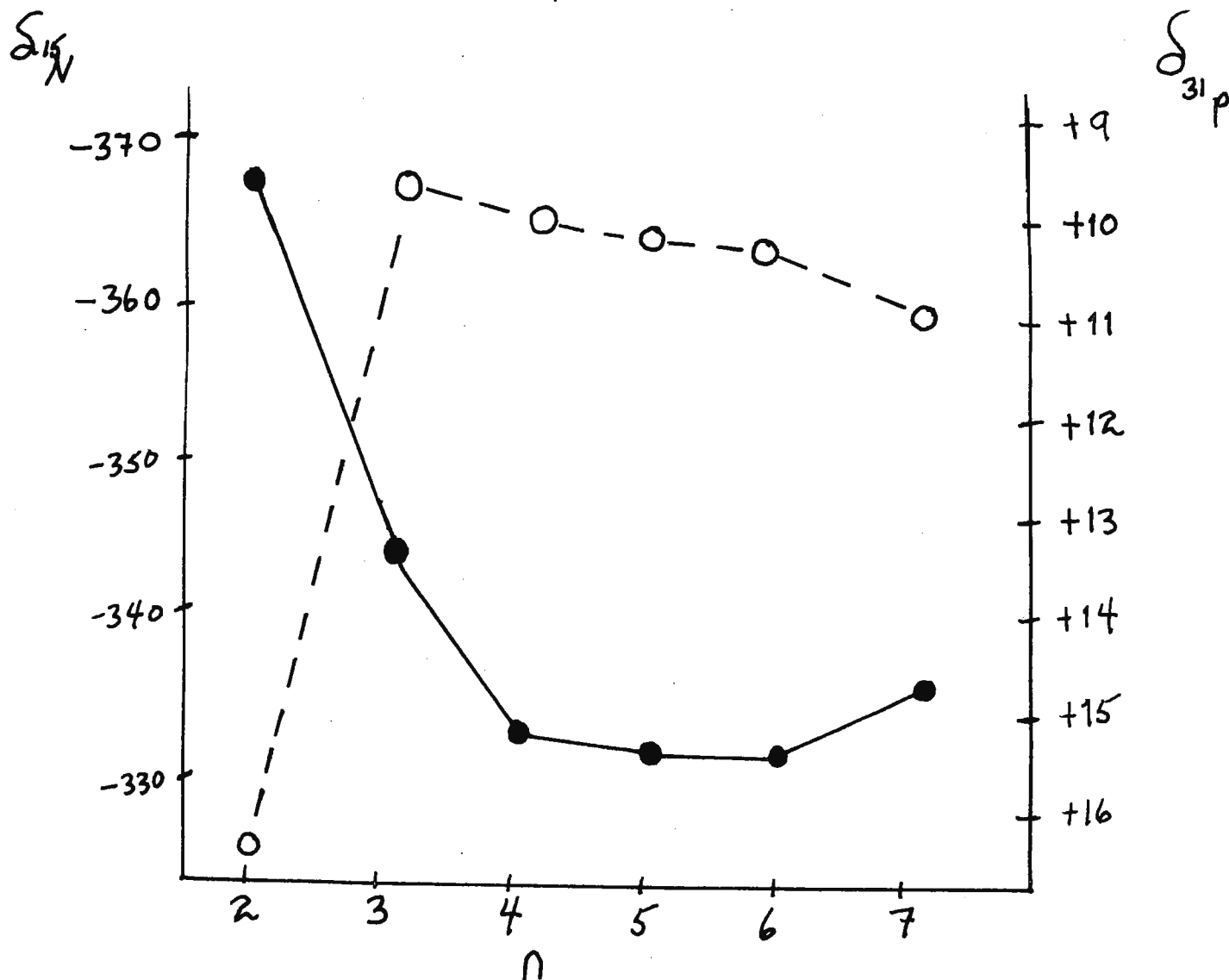
G.W. BUCHANAN

Professeur Associé



●  $\equiv \delta_N$  (vs  $\text{CH}_3\text{NO}_2$ )

○  $\equiv \delta_P$  (vs  $\text{H}_3\text{PO}_4$ )





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235 BIRCHWOOD AVENUE • CRANFORD, NEW JERSEY 07016

TELEX NO. 13-8840 • (201) 272-8820

February 20, 1980

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

Dear Barry:

LOWLY NMR

With the upsurge in interest of the down-frequency nuclei, and because many of our FX90Q owners are already using their low-frequency inserts, we thought that we should share some of our knowledge of specific details.

As many readers probably already know from their experience on less common nuclides, tuning a probe to a given frequency and observation of a signal from a sample containing a nucleus of that frequency are not necessarily always concurrent events. Hence, we have provided in the following table a list of benchmarks which we are using in our lab. In addition, the long  $T_1$ 's of lower frequency nuclides can occasionally alleviate the problem of deciding whether or not a signal is real. As is noted in the table,  $\text{AgNO}_3$  was doped with  $\text{Cr}(\text{acac})_3$  to shorten the long  $T_1$  of  $^{109}\text{Ag}$ . This would also be advisable with  $^{103}\text{Rh}$ , however, we did not wish to contaminate our sample for chemical reasons.

Large spectral widths are also inadvisable for anything but survey scans since the  $\pi/2$  pulses tend to be longer for the low frequency nuclides and the power distribution falls off rapidly at some point from the center {assuming QD and  $I(f) = \sin(\pi f t) / \pi f t$ }. This is particularly true with the inherent inefficiency of Helmholtz coils. On the FX90Q, our measured  $\pi/2$  pulse for  $^{183}\text{W}$  was 80  $\mu\text{sec}$  and for  $^{39}\text{K}$  was 78  $\mu\text{sec}$ , however, we are not using any specially tuned low frequency electronics. The low-frequency insert has a solenoid coil with an increased number of turns to match the low-frequency range but this coil is tuned utilizing the standard broad-band electronics module (normally 6 to 90 MHz). With this configuration, a delay time of 1 ms gives a flat base-line free of acoustic ringing.

Since we have only covered about half of the low-frequency nuclides, we would be interested in hearing about other benchmarks. Also, if anyone has been searching unsuccessfully at a higher-field for some lower-frequency nuclide, we would be happy to try at 90 MHz where the chemical shift dispersion is not as large.

Sincerely,



Dr. Michael J. Albright



Dr. Michael F. Kelly

MJA:MFK/mjd

## ONLY TABLE

LOW FREQUENCY NUCLIDES

<u>NUCLEUS</u>	<u>COMPOUND</u>	<u>CONCENTRATION</u>	<u>FREQUENCY (MHz)*</u>
$^{103}\text{Rh}$	$(\text{En})_3\text{RhCl}_3$	1 molal ( $\text{D}_2\text{O}$ )	2.843330
$^{73}\text{Ge}$	$(\text{Et})_4\text{Ge}$	50% V/V( $\text{C}_6\text{D}_6$ )	3.125720
$^{183}\text{W}$	$\text{Na}_2(\text{WO}_4)$	44% W/V( $\text{D}_2\text{O}$ )	3.733268
$^{109}\text{Ag}$	$\text{AgNO}_3 + \text{Cr}(\text{acac})_3$	2 molal ( $\text{D}_2\text{O}$ )	4.169744
$^{39}\text{K}$	KCl	3 molal ( $\text{D}_2\text{O}$ )	4.181275
$^{89}\text{Y}$	$\text{Y}(\text{NO}_3)_3$	1 molal ( $\text{D}_2\text{O}$ )	4.390792
$^{25}\text{Mg}$	$\text{MgSO}_4$	0.5 molal ( $\text{D}_2\text{O}$ )	5.485239
$^{67}\text{Zn}$	$\text{Zn}(\text{NO}_3)_2$	sat. ( $\text{D}_2\text{O}$ )	5.606640
$^{43}\text{Ca}$	$\text{CaCl}_2$	50% W/V( $\text{D}_2\text{O}$ )	6.030449

\* with TMS in  $\text{CDCl}_3$  at 89.604531 MHz



GORLAEUS LABORATORIA DER RIJKSUNIVERSITEIT TE LEIDEN  
SUB-FACULTEIT - SCHEIKUNDE

Wassenaarseweg 76

Postbus 9502

2300 RA Leiden

Telefoon 148333

toestel: 3921

Afdeling: Dr. J. Lugtenburg

Onderwerp:

LEIDEN, February 21, 1980

Prof. Bernard L. SHAPIRO

Department of Chemistry  
Texas A & M University

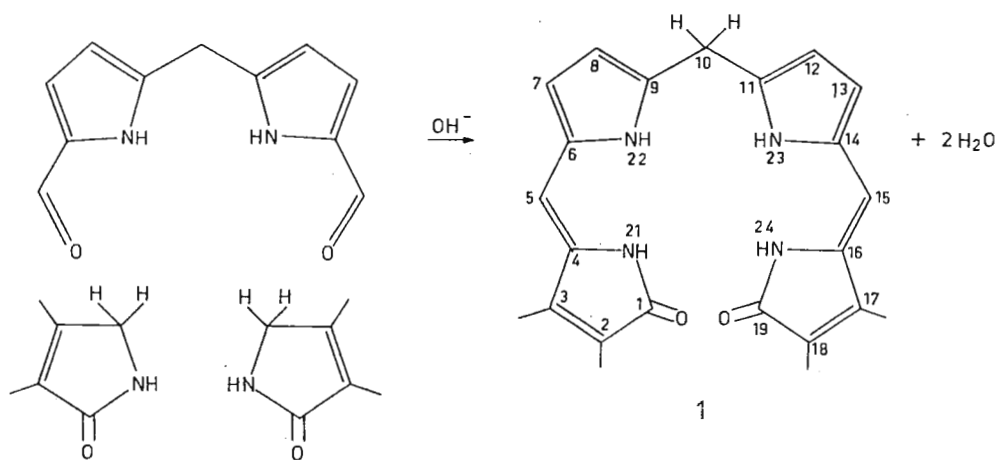
College Station,  
TX 77843

U.S.A.

Dear Professor Shapiro,

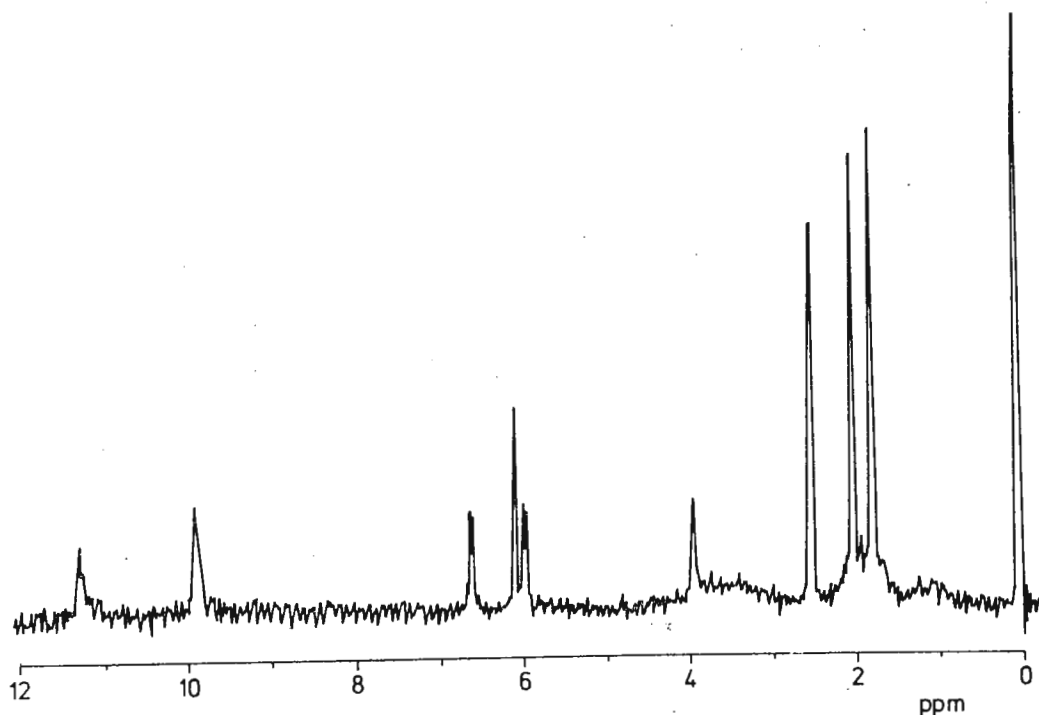
4,15-Z,Z - 2,3,17,18-Tetramethyl-10,23-Dihydro-1,19-[21 H, 24 H]-Bilindione

In continuation of our studies in the bilepigment field<sup>1</sup>, we needed a symmetrical bilirubin model with no substituents on the B and C rings. We were able to prepare 2,3,17,18-tetramethyl-10,23-dihydro-1,19-[21 H, 24 H]-bilindione<sup>2</sup> 1 in 90% yield by condensing 5,5'-diformyl-2,2'-dipyrrylmethane with 3,4-dimethylpyrrol-3-inone-2 in basic medium.



In theory 1 ( $\lambda_{\max}$  (MeOH) 406 nm, IR 3350  $\text{cm}^{-1}$  and 1655  $\text{cm}^{-1}$ , mass spectrum  $M^+ = 388 : \text{C}_{23}\text{H}_{24}\text{N}_4\text{O}_2$ ) can occur in three possible cis-trans isomeric forms: 4Z, 15Z; 4E, 15Z  $\equiv$  4Z, 15E; 4E, 15E. 1 must exist in either of the two symmetrical forms based on the number of lines in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum. 1 forms a complex with zinc acetate ( $\lambda_{\max} = 417$  nm), a property of Z derivatives<sup>3</sup>. The chemical shift of the 5-H and 15-H is in agreement with other cis derivatives<sup>1</sup>.

In the bilepigment field Z derivatives are thermodynamically more stable than E derivatives. We conclude that 1 exists in the 4Z, 15Z form. The assignment of signals in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of 1 is based on values of many related derivatives<sup>4</sup>.



$^1\text{H}$  NMR spectrum of 1 in DMSO  $\text{d}_6$  ref. TMS

	$\delta$	
2 + 18 $\text{CH}_3$	1.76 s	
3 + 17 $\text{CH}_3$	2.03 s	
5 + 15 H	6.04 s	
7 + 13 H	6.55 AB	
8 + 12 H	5.87 AB	$J_{AB} = 3.9 \text{ Hz}$
10 $\text{H}_2$	3.91 s	
21 + 24 H	11.3 broad s	
22 + 23 H	9.8 broad s	

$^{13}\text{C}$  NMR data of 1 (DMSO  $\text{d}_6$  ref. TMS)

	$\delta$	
1 + 19 C	171.78 s*	
2 + 18 C	124.40 s	
3 + 17 C	141.06 s	
4 + 16 C	130.81 s	
5 + 15 C	99.77 d	
6 + 14 C	126.32 s	
7 + 13 C	112.12 d	
8 + 12 C	108.42 d	
9 + 11 C	132.93 s	
10 C	26.00 t	
2 + 18 $\text{CH}_3$	8.22 q	
3 + 17 $\text{CH}_3$	9.37 q	

\*s,d, etc are the splitting patterns of these signals in the off resonance  $^{13}\text{C}$  NMR spectrum

References

1. J.A. van Koevinge Thesis Leiden 1978
2. H. Falk, K. Grubmayer and T. Schlederer  
Mh. Chem. 109 1191 (1978) These authors reported the synthesis of 1 by  
an other method, however they do not give any spectral data other than  
the parent peak in the mass spectrometer. Because of the extreme low so-  
lubility of their material in various solvents.
3. A. Gossauer, M. Blacha and W.S. Sheldrick  
J. Chem. Soc. Chem. Comm. 1976 764
4. V. Wray et. al. J. Chem. Soc. Perkin II 1979 1558.

Sincerely,

C. Erkelens,

J.A. de Groot

J. Lugtenburg

(cos

John

G. van

*UNIVERSITY of PENNSYLVANIA*

PHILADELPHIA 19104

*School of Medicine G3*DEPARTMENT OF  
BIOCHEMISTRY AND BIOPHYSICS

February 25, 1980

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

Dear Barry:

Is there still a place for peak detectors in pulsed NMR? Small dynamic range was a limitation which the present circuit is designed to overcome. Its dynamic range is about 40 dB, contrasted to about 20dB to be expected from a conventional peak detector.

The linearizing of the diodes is thanks to negative feedback: an old idea at lower frequencies but made to work here from 1 to 100 MHz. Feedback current flows from collector to base of the transistor, the hot-carrier diodes conducting on alternate half r.f. cycles. Negative feedback forces the base circuit to be at zero r.f. volts. The current in each of the diodes produces a voltage drop across its 68 ohm resistor, and this voltage is taken from one of the resistors and filtered to give the detector output. The current through the 68 ohms equals the current input from the transformer and is independent of the diode voltage drop, making the response linear. The drive circuit must be capable of delivering 50 mA peak-to-peak into a short circuit.

As far as biasing is concerned: The zener diode part of the circuit provides some forward bias for the hot-carrier diodes. The  $I_C$  set adjustment puts the collector current at 50 mA, conveniently measured as a 0.5 V drop across the 10 ohm emitter resistor. The D.C. offset control is important for good linearity at small signal levels and is adjusted to give 4.5 mV DC output when the r.f. input is zero.

The linearity is good over a 40 dB range at any frequency from 1 to 100 MHz. I define "good" as less than 5% deviation in output from the value which would be obtained by extending the long linear portion of

the response characteristic. The maximum linear output is about 1 volt, corresponding to about 50 mA peak-to-peak input.

Recovery from a 30 volt overload takes less than 5 microseconds. Transformer T<sub>1</sub> (1) can be 9 turns of No.26 AWG twisted pair on a Stackpole 57-9322 toroid, although experiments may be tried with different toroids and more or fewer turns.

Proper r.f. precautions must be observed such as keeping r.f. current-carrying leads short.

Please credit this to Dr. Mildred Cohn's subscription.

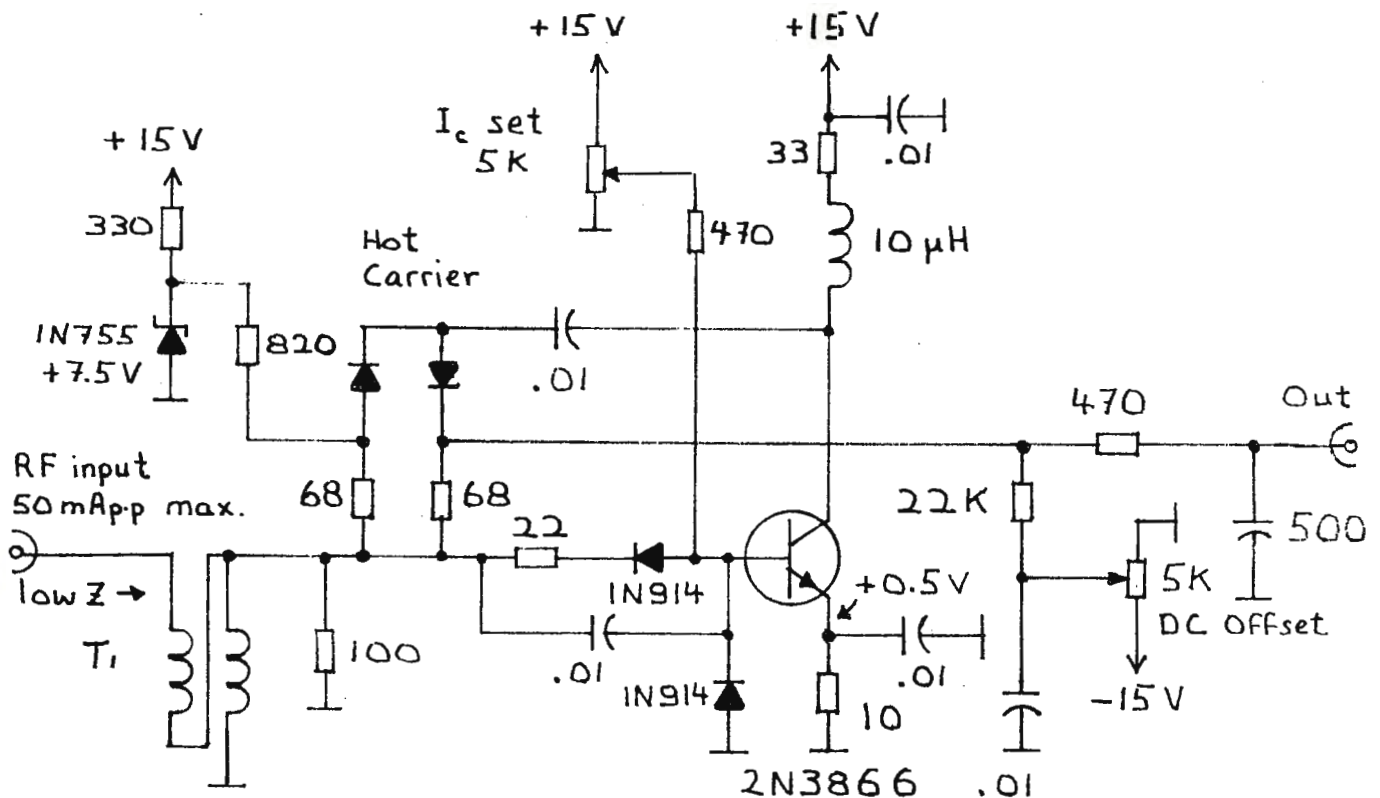
Sincerely yours,

*Jim*

James L. Engle

1. C.L. Ruthroff, Proc. IRE 47, 1337 (1959)

JLE/kb





## NORTHWESTERN UNIVERSITY

EVANSTON, ILLINOIS 60201

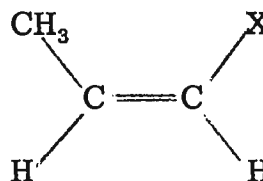
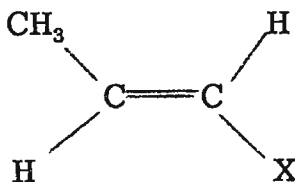
DEPARTMENT OF CHEMISTRY

February 25, 1980

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

Dear Barry:

We have been exploring the measurement of the barriers to C-CH<sub>3</sub> rotation by the Woessner method for the following systems (X is varied).



Although in general we used the isotropic expression, we found that the barriers from the anisotropic calculations were not appreciably different.

The toluene barriers correlate quite well with  $\sigma_I$  and very poorly with  $\sigma_R$ , so we eliminated hyperconjugation as the determining factor. The propene barriers also correlate well with  $\sigma_I$ . Interestingly, the rotational barriers correlate with the <sup>13</sup>C shifts of only the ortho carbons in the toluenes and of only the methyl-substituted carbon in the propenes. These results suggest that the major determining factor for these barriers is the electron density at these specific carbon atoms.

Sincerely,

Joseph B. Lambert

Ronald J. Nienhuis

Title: Rotational Barriers in Toluenes and Propenes

258-40

**9<sup>th</sup> INTERNATIONAL CONFERENCE ON MAGNETIC RESONANCE IN BIOLOGICAL SYSTEMS**

BENDOR, FRANCE.

Monday September 1st - Saturday September 6, 1980

**9<sup>ème</sup> CONFÉRENCE INTERNATIONALE DE RÉSONANCE MAGNÉTIQUE DANS LES SYSTÈMES BIOLOGIQUES**

Lundi 1er Septembre - Samedi 6 Septembre, 1980

*Please address correspondence to :*

PROFESSOR M. GUÉRON

COMABIO 9

ÉCOLE POLYTECHNIQUE

91128 - PALAISEAU CEDEX, FRANCE

Professor B. SHAPIRO  
Department of Chemistry  
Texas A. & M. University  
COLLEGE STATION, Texas 77843  
U.S.A.

Marseille, February 6th, 1980

Dear Professor Shapiro :

The 9th International Conference on Magnetic Resonance in Biological Systems (COMABIO 9) will be held Sept. 1-6, 1980 on the island of Bendor in the South of France. The scientific sessions will deal with proteins, oligopeptides, nucleic acids, membranes and studies of cells and organs. Relevant methods will be presented such as saturation transfer, photo-CIDNP, zeugmatography, etc... Poster sessions will be held concerning all subjects covered by the Scientific Program. Round tables will be organized on more controversial subjects. The number of participants is limited to 200. The Committee will try to select a distribution of younger as well as more experienced scientists. Students should include a short letter of recommendation from their supervisor. Funds have been provided to organizers specifically for the support of a few young scientists from Third-World Countries.

The final selection will be made by April 1st, 1980. The registration fee is FF 500. The cost of accomodation including breakfast and evening meal will be approximately FF 155 (double occupancy) and FF 210 (single). The Second Announcement has already been sent. Information can be obtained by writing to Prof. GUERON.

On behalf of the National Committee

Sincerely yours,



Patrick COZZONE  
Professor of Biochemistry

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DEPARTMENT OF CHEMISTRY

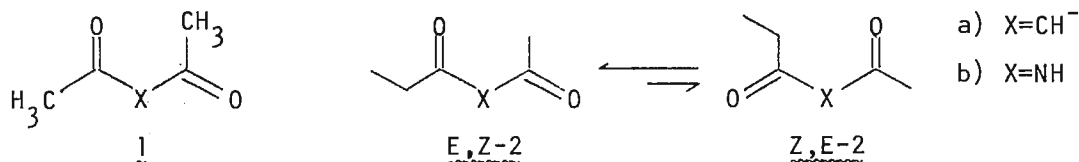
February 28, 1980

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

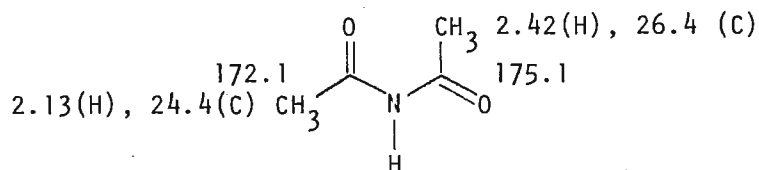
## $^1\text{H}$ and $^{13}\text{C}$ Chemical Shift Assignments in Imides and $\beta$ -Diketone Enolates

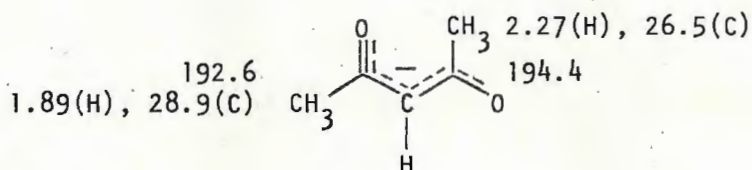
Dear Professor Shapiro:

We have been able to make  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift assignments to diastereotopic carbons and protons in the E,Z forms of imides and  $\beta$ -diketone anions 1a and 1b by examination of the spectra of the unsymmetrical homologs 2a and 2b.



Under conditions where only the E,Z form of 1 is observed the spectra of 2 exhibit resonances derived from major and minor isomers. We have assigned the E,Z and Z,E configurations to the major and minor isomers on steric grounds since the major isomer should have the less bulky methyl group in the sterically congested location near the carbonyl oxygen. On this basis we could determine the effect of stereochemistry in 1 and 2 on methyl  $^1\text{H}$  shifts and methyl and carbonyl  $^{13}\text{C}$  chemical shifts. The conclusions are summarized below.






This work is described in a paper which will appear in the Journal of Organic Chemistry. Preprints are available upon request.

I will very likely have a postdoctoral position available during the Summer or Fall of 1980. Interested applicants should send a resume and two letters of recommendation.

Sincerely yours,

  
 Morton Raban  
 Professor of Chemistry

"Postdoctoral Position available"

Dear Professor Shapiro :

A postdoctoral position is available in my laboratory for a one year period beginning October 1, 1980. It is renewable for another year. The work involves NMR studies on biological macromolecules and intact cells. Our wide-bore NT-200 System has P-31, C-13 and proton capabilities. Candidates should have a strong background in biochemistry and an interest in applying magnetic resonance techniques to biological systems. A working knowledge of french language (or a desire to learn french) would be appreciated.

The annual salary is attractive and depends on experience. Potential candidates should send me a resume before May 15, 1980 and arrange to have forwarded three letters of recommendation.

INSTITUT DE CHIMIE BIOLOGIQUE  
 LABORATOIRE DE BIOLOGIE PHYSICOCHIMIQUE

Sincerely yours,

UNIVERSITE DE PROVENCE  
 PLACE VICTOR HUGO - 13003 MARSEILLE

TEL. : (91) 62.15.54

Professeur P. J. COZZONE



Patrick COZZONE  
 Professor of Biochemistry



UNIVERSITY OF NEW HAMPSHIRE  
DURHAM, NEW HAMPSHIRE 03824

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

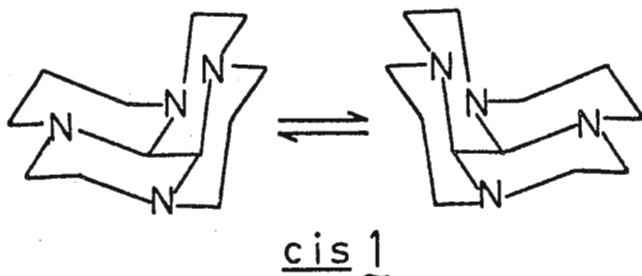
February 26, 1980

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

Dear Professor Shapiro:

Title: Dynamic  $^{15}\text{N}$  NMR of a Tetracyclic Tetraamine

In the course of our studies of stereochemistry and conformation of polycyclic polyamines, we have had the occasion to examine cyclam-glyoxal adduct 1 and related compounds by dynamic  $^{13}\text{C}$  NMR spectroscopy<sup>1</sup>.



$$\Delta G_c^\ddagger = 15.36 \pm 0.15$$

kcal/mole at  
 $57.5 \pm 3^\circ \text{C}.$

Only a very limited number of applications of  $^{15}\text{N}$  NMR to dynamic studies have been reported<sup>2</sup> due to the obvious limitations imposed by the low sensitivity of the  $^{15}\text{N}$  nucleus. Two nonequivalent pairs of nitrogens are exchanged upon interconversion of the two enantiomeric conformations of 1. Encouraged by the high barrier observed for this process by  $^{13}\text{C}$  and by the high effective nitrogen molarity available for solutions of 1, we have carried out a "brief" dynamic  $^{15}\text{N}$  study.

The spectrum of a 1.0 M  $\text{CHCl}_3$  solution of 1 at ambient probe temperature is a singlet at  $\delta = 45.3$  ppm (FX90Q at 9.04 MHz; spectral width = 5000 Hz; acquisition time = 0.819 sec; pulse delay = 5 sec; complete  $^1\text{H}$  decoupling; 10,000 pulses; line broadening =  $\sim 2$  Hz;  $\text{S/N} \sim 6/1$ ). Measurement was actually made utilizing a coaxial capillary of 1M  $\text{H}^{15}\text{NO}_3$  in  $\text{D}_2\text{O}$  for external reference and lock but the shift is reported relative to anhydrous liquid  $\text{NH}_3$  as recently recommended<sup>3</sup>. The results of lower temperature studies are shown in the figure below. (For these experiments coaxial acetone- $\text{d}_6$  was used for lock and the spectral width was decreased to 1000 Hz for increased



spectral resolution.) With the assumption that 22°C is within 5 degrees of the coalescence temperature, a  $\Delta G^\ddagger = 15.6 \pm 0.3$  kcal/mole is calculated, in reasonable agreement with the  $^{13}\text{C}$  NMR derived number.

Although I'm sure every lab in the country has its own trick for handling coaxial capillaries, I've included a diagram of an arrangement we've found to be particularly simple and convenient.

Please credit this contribution to the account of Kathleen Gallagher of the University Instrumentation Center here at UNH.

Best Regards,

*Gary R. Weisman*

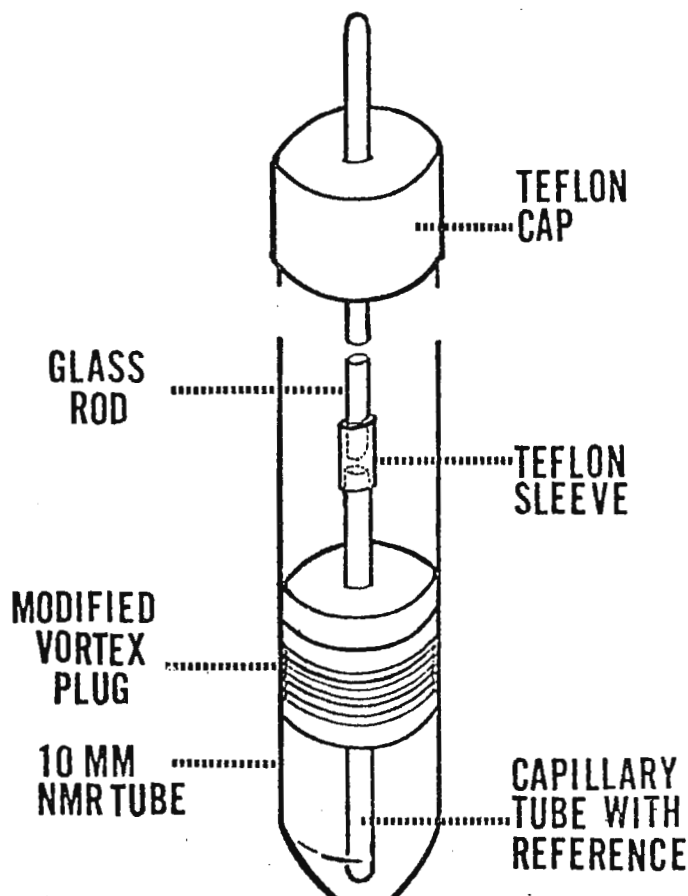
Gary R. Weisman  
Assistant Professor of Chemistry

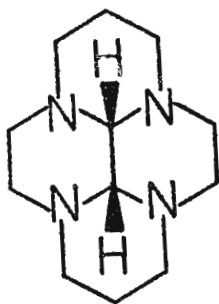
GRW:dd

Enclosure

#### References

- (1) G. R. Weisman, S. C.-H. Ho, and V. Johnson, Tet. Letters, 335 (1980).
- (2) Y. Nomura and Y. Takeuchi, Chem. Commun., 295 (1979).
- (3) G. C. Levy and R. L. Lichter, Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy, John Wiley and Sons, New York, 1979, p. 28-33.



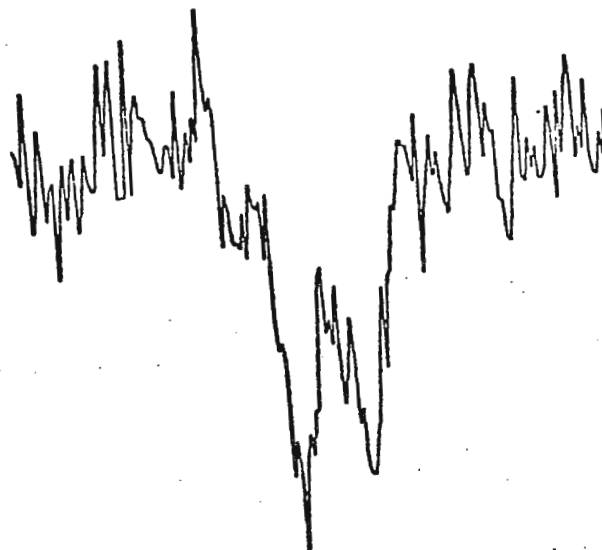


$^{15}\text{N}$  DNMR

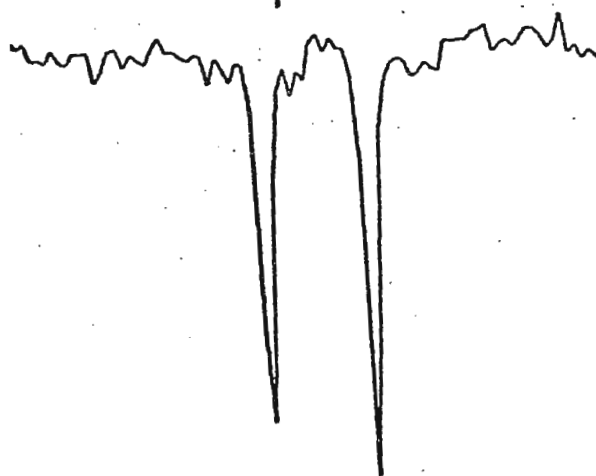
$s$   $\delta 45.3$  amb

$\Delta G_c^\ddagger = 15.6 \pm 0.3$  Kcal/mole

22°C.



2°C.



$\longleftrightarrow$   
7.3 Hz

INDIANA  
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UNIVERSITY



at INDIANAPOLIS

**PHYSICS DEPARTMENT** (38th Street Campus • Downtown Campus )  
1201 East 38th Street • 46205 • (317) 923-1321

February 22, 1980

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

TITLE: NMR Faculty Position

Dear Professor Shapiro:

Our department has a faculty position available for an NMR spectroscopist. The advertisement that is scheduled to appear in the March, 1980 issue of Physics Today is reproduced below:

Applications are invited for a position at the Associate or Assistant Professor level anticipated in the Department of Physics, Indiana University-Purdue University at Indianapolis (IUPUI). The applicant should have experience in Nuclear Magnetic Resonance at the Assistant Professor level or equivalent and an interest in biological or medical applications of NMR. It is expected that he or she would initially collaborate with existing groups currently working on high-resolution NMR or imaging. Options exist to interact with ESR groups or the Biophysics division. Preference will be given to persons who can help develop an undergraduate or masters level laboratory in biological physics and are willing to interact with the Indiana University School of Medicine component of IUPUI. Submit applications to Professor B. D. Nageswara Rao, Department of Physics, IUPUI, 1125 E. 38th Street, Indianapolis, Indiana 46205. IUPUI is an Equal Opportunity Employer.

We would appreciate your bringing this to the attention of TAMU readers.

Sincerely yours,

B. D. Nageswara Rao



# TECHNISCHE HOGESCHOOL DELFT

## Laboratorium voor Technische Natuurkunde

Prof. Dr. Bernard L. Shapiro  
 Department of Chemistry  
 Texas A&M University  
 COLLEGE STATION, TX 77843  
 U.S.A.

Uw kenmerk      Uw brief van      Ons kenmerk      Datum      Delft, Lorentzweg 1  
 JS/mvs/56      13th February 1980      Doorkiesnummer (015) 78 5394

### Onderwerp

Joint ISMAR-AMPÈRE International Conference on Magnetic Resonance,  
Delft (Netherlands), 25 - 30 August 1980

Dear Professor Shapiro,

In TAMU NMR NEWSLETTER, No. 245, dated February 1979, a brief announcement was inserted on the Joint ISMAR-AMPÈRE International Conference on Magnetic Resonance. Below you will find further information on the above Conference.

Last January the Registration Bulletin for the Conference was distributed to all people having reacted to the first announcement. In this Registration Bulletin a.o. the following details are given:

### SCIENTIFIC PROGRAMME

The Conference will encompass theory, applications and instrumentation of the whole range of Magnetic Resonance and Relaxation as applied in Physics, Chemistry, Biophysics and Biochemistry. The possibility of contributions in the fields of dielectric and ferro-electric relaxation will also be considered.

The preliminary programme includes the following Invited Lectures:

B. Bleaney (U.K.): Enhanced NMR in rare earths.

R. Freeman (U.K.): Some Developments in Two-Dimensional Fourier-transform NMR.

W.N. Hardy (Canada): Magnetic Resonance of Atomic H at low Temperatures.

R. Kaptein (The Netherlands): High Frequency NMR in Biological Systems.

K. Möbius (B.R.D.): Non-proton ENDOR and TRIPLE Resonance of Radicals in Solution.

J.R. Norris (U.S.A.): Electron Spin-Echo on the primary Reactants and Events of Photosynthesis.

D.D. Osheroff (U.S.A.): NMR as a probe of the remarkable ordered phases of  $^3\text{He}$ .

Y. Roinel (France): Nuclear Magnetic Ordering in LiH.

R.Z. Sagdeev (U.S.S.R.): Novel Aspects of CIDNP.

W.S. Veeman (The Netherlands): Relaxation in Polymers as studied by HR-solid state NMR.

H. Alloul (France): Resonance in disordered Magnetic Systems (Spin-glasses).

J.J. Katz (U.S.A.): The NMR-Spectroscopy of Compounds and Systems  
of unnatural Isotopic Composition.  
W.S. Moore (U.K.): Spin-Imaging.  
E.T. Lippmaa (U.S.S.R.): HR-solid state NMR-Spectroscopy.  
R.E. Richards (U.K.): NMR-studies of whole biological tissue.  
J. Seelig (Switzerland): Recent NMR-studies of biological membranes.  
(not yet known): Whole-cell NMR.

About 100 Short Communications will be included in the programme in  
at most 4 parallel sessions. A period of 20 minutes will be allotted  
to each contributed paper, including a brief discussion. A poster  
presentation will be on Monday, Tuesday and Thursday, from 15.30 -  
17.15 hrs. About 100 posters can be presented each afternoon.

#### CALL FOR PAPERS AND POSTERS

There already has been a call for papers. Because this call reached  
many participants after the closing date mentioned in that call, short  
abstracts (5 - 10 lines) can be submitted until April 30, 1980, to the  
Congress Office.

The ISMAR-AMPÈRE Organizing Committee is responsible for the selection  
of the contributions to be presented as a Short Communication or as a  
Poster. Authors will be informed about the decision concerned in the  
beginning of June, 1980; details about the presentation will be sent  
then. The abstracts of accepted contributions (posters and short  
communications) will be included in the Congress Programme.

#### FEE

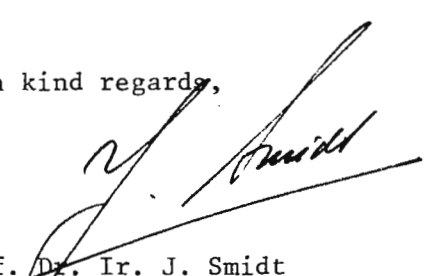
Advance registration (before June 15, 1980)	Hfl. 225,--
Late registration (after June 15, 1980)	Hfl. 250,--
Accompanying persons	Hfl. 45,--
For the subscribers to the Bulletin of Magnetic Resonance this will be:	
Advance Registration (before June 15, 1980)	Hfl. 200,--
Late Registration (after June 15, 1980)	Hfl. 225,--
Accompanying persons	Hfl. 45,--

People having interest in the ISMAR-AMPÈRE Conference and wishing to  
receive a Registration Bulletin should apply to:

ISMAR-AMPÈRE 1980  
c/o KIVI  
P.O. Box 30424  
2500 GK THE HAGUE  
The Netherlands

In the meantime, I remain,

with kind regards,

  
Prof. Dr. Ir. J. Smidt  
Chairman Organizing Committee



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Lecturers: E. D. Becker (Bethesda), R. R. Ernst (Zurich), R. Freeman (U.K.), R. K. Harris (East Anglia), U. Haeberlen (Heidelberg), G. E. Maciel (Colorado), P. Mansfield (Nottingham), M. Mehring (Dortmund), A. Pines (Berkeley), K. Packer (East Anglia), E. W. Randall (London), D. L. VanderHart (Washington), J. Waugh (Massachusetts). A few additional lecturers may be included in the program.

Language: All lectures and discussions will be held in English.

Participation: Attendance at the Institute will be limited. Applications to participate in the Institute are invited from all countries, although preference will be given to applicants from NATO countries.

Grants: A limited number of grants in partial support of travel and living expenses will be available to selected participants from NATO countries who cannot obtain adequate support from other sources.

Accommodation: Participants receiving NATO support will be accommodated in the TANKA VILLAGE HOTEL where all technical sessions will be held.

Further Information: For further details and application forms, contact:

Dr. T. Axenrod  
Department of Chemistry  
The City College of CUNY  
New York, N.Y. 10031  
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or

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