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Newsletter

No. 266

November, 1980

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DEADLINE DATES:	No. 267	1 December 1980
	No. 268	5 January 1981

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

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

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NMR DISCUSSION GROUP

RKH/JH

UNITED KINGDOM

8th October, 1980.

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

FIFTH INTERNATIONAL MEETING ON NMR SPECTROSCOPY

Dear Barry,

I am writing to let TAMU NMR Newsletter readers have some details about the next International Meeting arranged by the British NMR Discussion Group. This will take place at the University of Exeter, in south-western England, during the period 12 - 17 July 1981. The following half-day symposia and plenary lectures have been arranged:

Symposium

Multi-nuclear magnetic resonance:
spin- $\frac{1}{2}$ nuclei

Intact biological systems

Heterogeneous systems

Multinuclear magnetic resonance:
quadrupolar nuclei

Applicable theory

Dynamic Processes

Techniques (two half-day symposia)

Plenary lecturers

E.A.V. Ebsworth
W. Von Philipsborn

R.G. Shulman
P. Mansfield

H. Pfeiffer
J.J. Fripiat

G.E. Maciel
S. Forsen

R.R. Vold
G. Binsch

P. Laszlo
A.E. Merbach

E. Lippmaa
R.R. Ernst
D.I. Hoult
U. Haeblerlen
R. Freeman

.....Cont.

.....Cont.

There will, as usual, be poster sessions and some contributed talks. Anyone wishing to contribute in either of these ways should write to me. However, for details of registration, accommodation, social events etc. and for an application form, prospective participants should write to:-

Dr. J.F. Gibson
Royal Society of Chemistry
Burlington House
London W1V 0BN
England.

Consideration of the list of plenary lecturers indicates that an excellent meeting is to be expected. See you there?

Yours sincerely,

Robin

PROFESSOR R.K. HARRIS

(Chairman: NMR Discussion Group)

**HERCULES INCORPORATED**

RESEARCH CENTER • WILMINGTON, DELAWARE 19899 • TELEPHONE: 302-995-3000

October 2, 1980

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

Dear Barry:

"FOOT POWERED EM-390 NMR AND A REPORT THAT
NMR IS ALIVE AND WELL AT HERCULES INCORPORATED"

For the physically well-coordinated spectroscopist who happens to have either a Varian EM-390 or EM360-L NMR, the following modification may be of interest. Shown in the attached drawings are two foot switches which are very simply added to the existing spectrometer. The first switch [a Linemaster Clipper foot switch momentary DPDT available from Herbach & Rademan (Cat. No. L2-029); 401 E. Erie Avenue; Philadelphia, PA 19134] is used to override the recorder forward or reverse scan switch located on the bed of the spectrometer next to the recorder. The second switch, a double sided or dual switch [Linemaster Executive Dual Side DPDT, Herbach & Rademan (L2-042) \$17.40] is used to control alternately the integrator reset and the integrator hold functions. The installation is such that when not in use the instrument functions as a plain vanilla EM-390.

Now some people (other than the piano or organ players in the readership) are probably asking why the trouble to put in foot switches? Ah ha! we reply, they prove to be most convenient for freeing one's hands to write down data taken from say a digital voltmeter connected across the external recorder jacks (or oscilloscope vertical input leads) during integration. Thus the left hand may be used to move the recorder and the right hand may be used to write down numbers or vice versa. This may be done most conveniently by using one foot to hold an integral value (voltage) or cancel the same

Dr. Barnard L. Shapiro

October 2, 1980

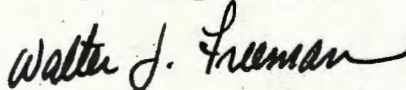
and the other foot to halt or start the forward recorder drive. In this way, integral steps in a spectrum may be successively integrated many times while simultaneously measuring the height of the step (in volts). If this is done ten times for instance, allowing a few seconds between readings for relaxation (spins and operator), the column of numbers can be added and the decimal point shifted to give an average value. The precision goes up, and repetitive quantitative procedures are less burdensome. This technique is particularly fine for kinetic studies and for routine quantitative analysis. Also the recorder release switch is convenient for those who shim the old-fashioned way (a la A-60) on a sharp line by successive tracings.

A minor drawback may occur if you are left handed. In this case, the system still works but is less effective due to the right-handed console bed. Another problem may occur for those who are less coordinated (do you trip a lot, do poorly in some sports such as ping pong? Are you hopeless with a yo-yo?) However, with the proper attitude this type of operation may be therapeutic.

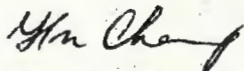
On another note, we should like to announce that Jacques Reuben has joined the NMR group at Hercules where he is settling in "to the joys of spectroscopy for profit".

Lastly, we wish to report that our wide bore Nicolet NT-360 NMR is functional. We had experienced some major problems operating at elevated temperatures for extended periods but that difficulty seems to have been resolved. Multinuclear capability is in and working. We will report more on this system later.

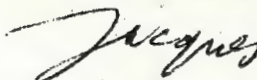
Very truly yours,



W. J. Freeman



H. N. Cheng



J. Reuben
Analytical Division
Development Department

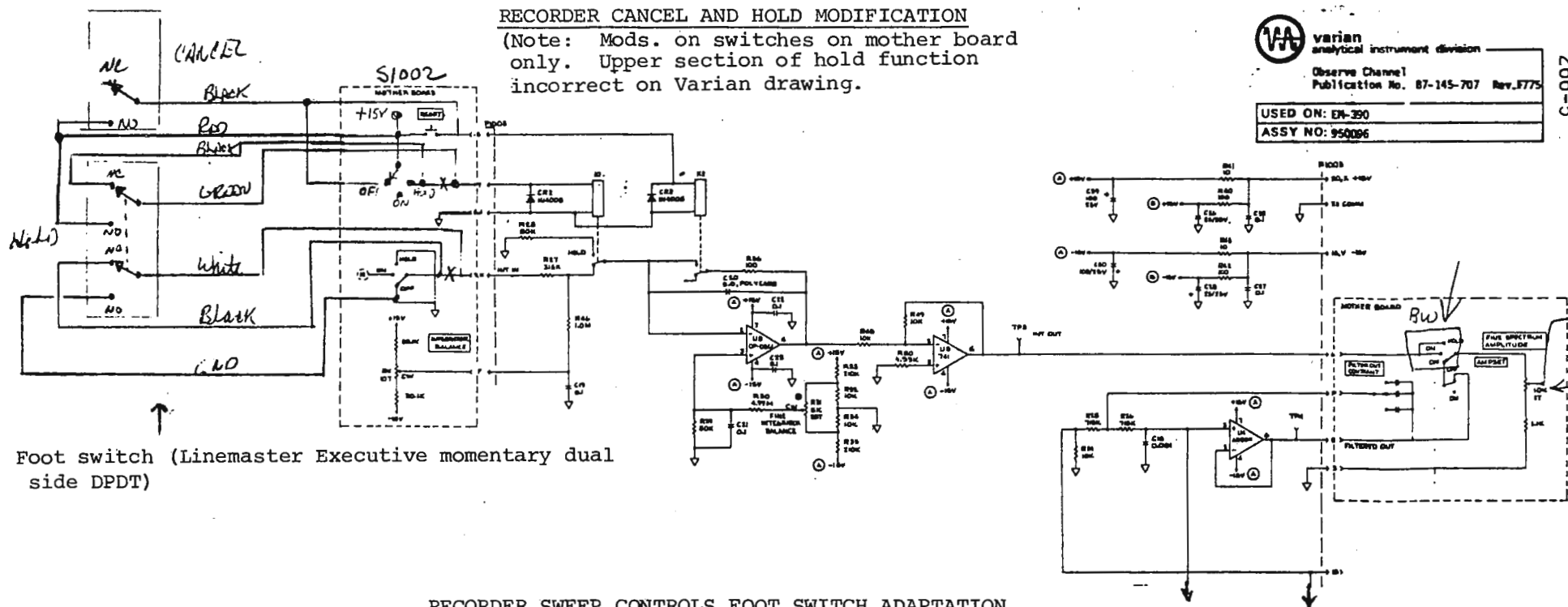
WJF
HNC:gtg
JR

RECORDER CANCEL AND HOLD MODIFICATION

(Note: Mods. on switches on mother board only. Upper section of hold function incorrect on Varian drawing.)

varian
analytical instrument division
Observe Channel
Publication No. 87-145-707 Rev. 8775
USED ON: EM-390
ASSY NO: 950096

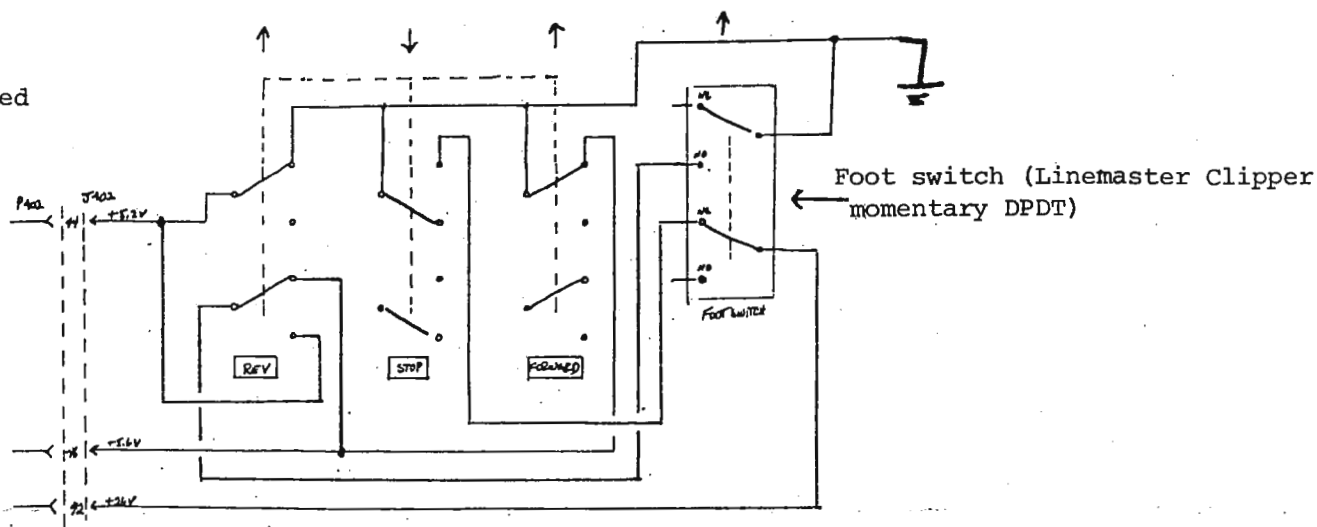
266-5



RECORDER SWEEP CONTROLS FOOT SWITCH ADAPTATION

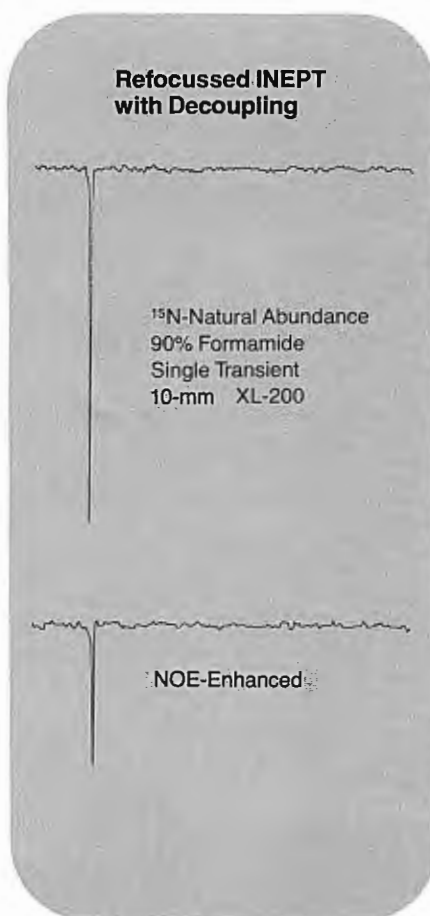
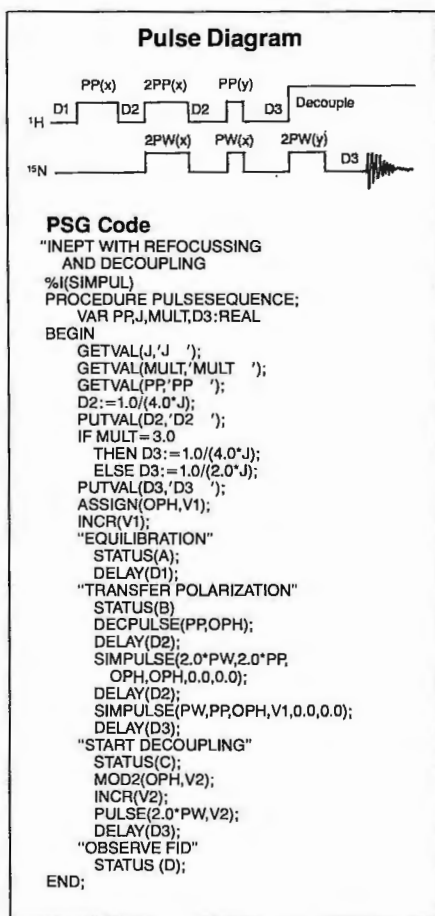
(Note: Switches shown in off position)

Further construction details
available from authors if needed



Recorder Control Switchboard, Varian Part No. 87-145702F (950114C)

How much do you know about the Varian XL-200?



Almost everyone knows about the XL-200's reliability and ease of operation. But are you aware of its power, flexibility and sophisticated research capabilities?

Beneath its basic exterior, the XL-200 offers you true research power to perform complex experiments.

For example, you can frequently obtain enhanced sensitivity from low- γ nuclei through INEPT sequences on the XL-200. See: Freeman and Morris, *J. Amer. Chem. Soc.*, **102**, 72 (1979); and, Morris, *J. Amer. Chem. Soc.*, **102**, 428 (1980).

Illustrated here is a simple implementation of these ideas.

The XL-200's Pulse Sequence Generation capabilities were used to perform the enhanced sensitivity experiment above. Acquisition Processor features are another important benefit for XL-200 owners.

Pulse Sequence Generation

- PASCAL language-based code with resident compiler
- English-like sequence code
- Error checking compiler
- Large text library for source code storage
- Sophisticated editor for convenient programming in PASCAL
- Use of PASCAL statements within sequence code
- Simple PSG components such as:

PULSE	OFFSET	SPAREON	HLV
OBSPULSE	DELAY	SPAREOFF	DBL
DECPULSE	IFZERO	DECPHASE	ADD
SIMPULSE	LOOP	RCVRON	SUB
STATUS	DECR	RCVROFF	MOD2
ASSIGN	INCR	RND	MOD4
- Ability to specify and vary phase and receiver off-times dynamically
- Use of indirect variables for phase control
- Up to three nested loops for repetitive action
- Ability to execute simultaneous observe and decoupler pulses
- External device control under sequence control
- Use of floating-point parameter format
- User-creation of new delay, pulse, frequency, integer and flag parameters
- Flexible branching within sequences
- Ability to phase-shift within a pulse with no dead times
- Use of math statements for sequence timing calculations

- Complete separation of sequence code from parameter sets
- Dynamic variable calculations
- Use of indirect parameter labels in sequence code
- User control of parameter display characteristics
- **Example sequences**
 - Standard two-pulse
 - Carr-Purcell-Meiboom-Gill T2
 - Quadrupole echo
 - Cross-polarization
 - Multiple-contact cross-polarization
 - Selective excitation
 - Quadrature selective excitation
 - INEPT
 - INEPT with refocussing and decoupling
 - PREP
 - J-Cross polarization
 - Refocused J-cross polarization
 - Noise off-resonance spin echo
 - Inversion-recovery spin echo
 - Multiple quantum 2D
 - Proton-carbon correlated 2D
 - Heteronuclear enhanced 2D
 - Double quantum ^{13}C - ^{13}C spectroscopy

Acquisition Processor

- Independent 32-bit arithmetic bit-slice 32K CPU
- 50-nanosecond hardware timing
- Software-programmed for highest flexibility

- FIFO architecture for event streaming at 50-ns resolution
- State-of-the-art LSI construction
- 50-kHz spectral widths standard
- Pulse timing to 0.1 microsecond
- Automatic filter selection
- Four observe phases under CPU control
- Four decoupler phases under CPU control
- Explicit and relative mode phase selection
- Quadrature detection
- Single or double precision acquisition with 32-bit data path
- Direct periodic data save to non-volatile memory
- Transmitter and decoupler frequencies under CPU control
- Decoupler gating under CPU control
- Decoupler modulation under CPU control—CW, noise, square wave and external
- Decoupler modulation frequency under CPU control
- Decoupler high/low power switch under CPU control
- Precision decoupling power in 60 one-dB steps below one watt under CPU control
- Computer controlled VT
- Low/High and High/Low VT mode switch under CPU control
- Up to three simultaneously arrayable acquisition parameters
- Dynamic phase selection in multi-transient data collection
- 48-bit microprogram specialized instruction set
- Noise amplitude and scaling limit checking
- Lock/VT/high noise interlocks

In NMR research the XL-200 is first among first-class spectrometers. Following are lists of other features that make the XL-200 your logical choice for complex and sophisticated research NMR.

Standard Features

- Computer controlled VT
- $^{19}\text{F}/^1\text{H}$ 5-mm VT probe
- ^{15}N - ^{31}P 10-mm VT broadband probe
- ^1H universal transmitter cards for observe, decouple and lock
- Built-in printer, plotter, keyboard, TV display and 5M-word dual disk
- 32K acquisition processor memory
- 32K main CPU memory
- Large, calibrated chart paper
- Interactive display knobs
- Autolock for automatic locking, even after sample change
- Pulsed/timeshared lock modes
- Universal fixed and broadband rf transmitters with interchangeable functions
- 3-month helium hold-time with only 25 liters needed for refill, including transfer loss
- 14-day nitrogen hold-time—45 days with optional refrigerator
- Welded dewar
- 25-watt rf transmitter output—200-watt pulse amplifier
- 10- μsec ^1H 90° pulse/15- μsec ^{13}C 90° pulse
- Internal ^2H lock
- Pushbutton PROM-based program loading
- Disk-based data system
- Flicker-free TV display with graphics capability
- Simplified 1-meter probe tuning
- 0.4 to 1.6 MHz offset synthesizer
- 13-bit ADC

Accessories

- ^{19}F transmitter
- Large sample and 5-mm broadband probes
- Nitrogen refrigerator
- Magnet power supply
- Maintenance kit
- Magic-angle/cross-polarization solids probes

Data System

- PASCAL language
- State-of-the-art operating system
- Disk-based using modular design software concept
- Concurrent and sequential PASCAL
- Floating-point data and math format
- Multitasking-simultaneous acquire, plot, print, display, parameter entry
- Queuing of acquisitions, plots, prints and calculations
- Spooling of plots and prints
- Disk-resident data tables
- Separate FID and spectral storage
- System resident PASCAL compiler for user programming
- User access to data files

- Expandable user-defined command and parameter architecture
- Floating-point or integer transform
- Convolution difference/gaussian apodization functions
- Parameter set libraries
- 2D transform
- Plot graphics
- T1, T2, 3-parameter least-squares-fit analysis programs
- Spin simulation
- LAOCOON with magnetic equivalence
- User-definable disk libraries
- PASCAL system source code availability
- NOE calculation
- Add-subtract-convolution spectral manipulation



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October 9, 1980

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

Dear Dr. Shapiro:

High Output Magic Angle Spinning Speed Monitor

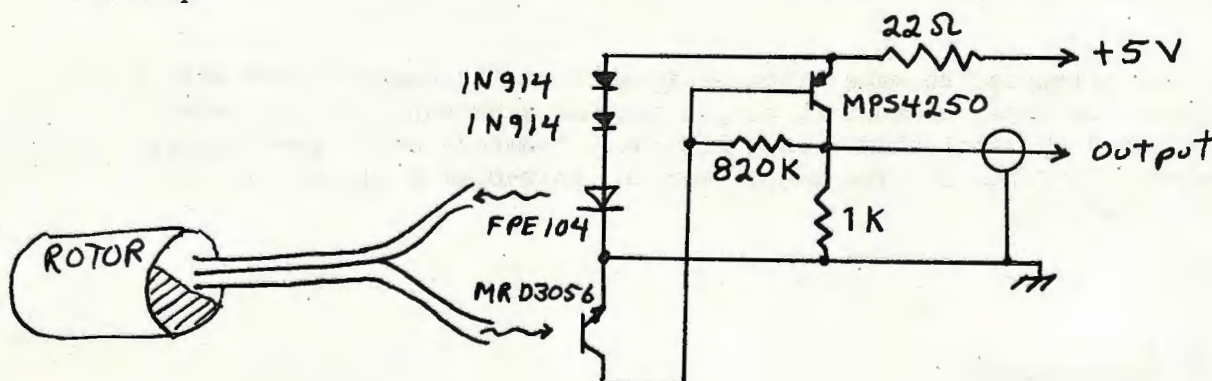
The diagram below illustrates a very low noise highly sensitive circuit for monitoring high speed magic angle spinning. The output is of sufficient amplitude and clarity for direct counting at the highest attainable speeds without the use of audio filters and amplifiers. A narrow beam IR emitting diode (Fairchild, FPE 104) is used because of its greater efficiency; hence one half of the end of the rotor must be painted to reflect IR and one half must be blackened. White enamel paint is a satisfactory reflector of IR, but improved rejection of "white" light noise may be obtained by using a bright, deep red enamel to reflect IR. A Y-type bifurcated glass fiber light pipe with 6 mm² total cross sectional area was used. A smaller light pipe could be used with some loss in sensitivity. Plastic fiber light pipes were found to be very susceptible to strain related failure. Low cost surplus Y-light pipes suitable for bench testing are available from Poly Paks, Inc., South Lynnfield, Mass. Custom made non-magnetic versions are available from Welch Allyn, Inc., Skaneateles Falls, NY.

Please credit this to Dr. Paul Ellis' subscription.

Sincerely,

F. David Doty
Research Associate

FDD:lep





Pharmaceutical Products Division

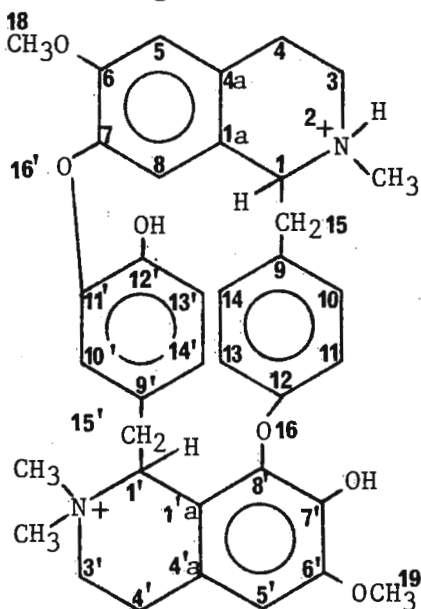
Abbott Laboratories
North Chicago, Illinois 60064

September 26, 1980

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

Dear Barry:

"Suggested ^{13}C NMR Assignments for (+)-Tubocurarine Chloride"



We recently had an occasion to examine more thoroughly the ^{13}C NMR of (+)-tubocurarine chloride. Previous proton work (TAMUNMR-162-24) noted that the protons on the para-substituted aromatic ring H-10, H-11, H-13 and H-14 are sharp at ambient temperature, but broaden at higher temperatures. ^{13}C NMR studies show analogous results in that four protonated aromatic carbon resonances broaden at higher temperatures. This study was reported in TAMUNMR 222-12.

We have now attempted to make other assignments. Assignments were made by comparison with model compounds, single frequency decoupling experiments and calculated chemical shifts from benzene. Chemical shift assignments are reported in Table I. The sample was run in D_2O with dioxane as an internal reference.

Sincerely,

Ruth S. Stanaszek
Ruth S. Stanaszek

RSS:dmp



Table I

<u>Assignment</u>	<u>Chemical Shift (δ)</u>	<u>Assignment</u>	<u>Chemical Shift (δ)</u>
C-12	s 156.3 ^a	C-5	d 119.0
C-6'	s 150.4	C-13	d 116.9
C-11'	s 149.3	C-8	d 115.5
C-8'	s 148.0	C-10'	d 113.6
C-6	s 145.8	C-11	d 112.6
C-7	s 142.3	C-5'	d 109.7
{ C-12'	s 138.1	C-3	t 68.5
{ C-9'	s 137.8	C-1	d 64.9
C-10	d 134.5	{ OCH ₃ (18)	q 56.9
C-14	d 131.4	{ OCH ₃ (19)	q 56.2
{ C-9	s 130.8	C-3'	t 54.7
{ C-4'a	s 129.6	2' (NCH ₃) ₂	q 54.7
{ C-1a	s 125.5	C-1'	d 51.7
C-14'	d 128.3	C-15	t 46.1
C-13'	d 123.8	2(NCH ₃)	q 40.7
{ C-4a	s 121.5	C-15'	t 40.0
{ C-7'	s 121.2	{ C-4	t 23.7
{ C-1'a	s 120.5	{ C-4'	t 23.7

^aOff-Resonance Spin Decoupling experiment.

INSTITUT FÜR PHYSIK DER UNIVERSITÄT BASEL

CH - 4056 Basel (Switzerland)

October 6, 1980

EXPERIMENTELLE KERNPHYSIK

Klingelbergstrasse 82, Telefon 061 - 44 22 80

Prof. Dr. P. Diehl

Postdoctoral Position Available.

Dear Barry,

I will have funds available for a postdoctoral position for one year beginning in spring or summer 1981. The work will involve NMR-research in oriented molecules. We have a multinuclear FT-spectrometer (WH 90 DS, Bruker). The salary amounts to Swiss Francs 39'000.- per year. There is no travel allowance. Any person interested should write to me as soon as possible.

Sincerely yours

Peter

Prof. Dr. P. Diehl

266-11
Prof. V.F. Bystrov
USSR Academy of Sciences
Shemyakin Institute
of Bioorganic Chemistry

Ul. Vavilova 32
Moscow 117312 USSR

Professor Bernard L. Shapiro
Department of Chemistry
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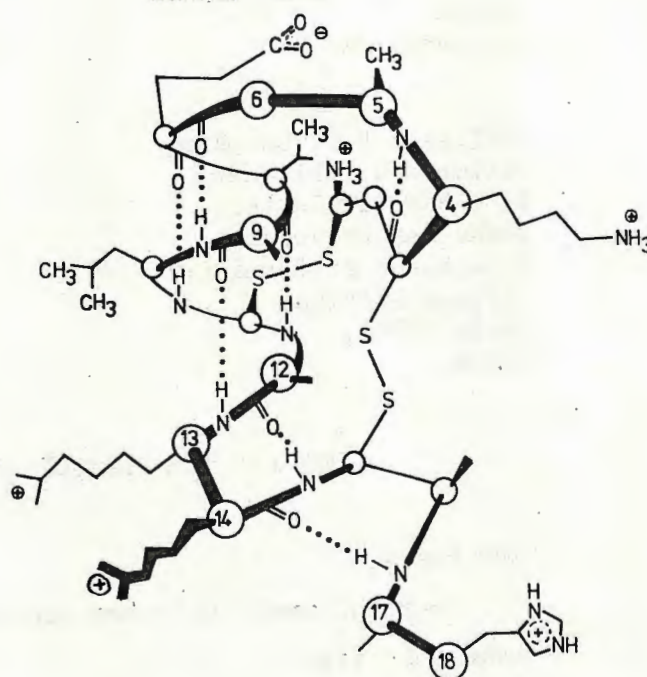
Title: Apamin Conforma-
tion

August 26, 1980

Dear Barry:

At last after consideration of assigned proton NMR signals (1,2) we arrived to a solution conformation of apamin (see Figure) - honey bee venom polypeptide neurotoxin which consists of 18 residues interconnected with two disulphide bridges 1-11 and 3-15 (3). When analyzing the NMR parameters (see Table) attention is captured by the three or even four residues in succession (10, 11, 12 and possibly 13) with both very slow amide $\text{NH} \rightarrow \text{ND}$ exchange ($t_{1/2} < 14$ hours) and low values of $\text{H}-\text{NC}^\alpha-\text{H}$ proton couplings (3.0-5.9 Hz). Both of these features are inherent to polypeptide right-handed helical structure. Thus it was assumed that the 10-13 fragment is incorporated in a helix and its backbone NH 's are H-bonded to the carbonyls of $n - i$ residues ($i = 3, 4, 5$ for 3_{10} -, α - and π -helices). By model building it was found that only α -helix could be constructed due to steric hindrances introduced by disulphide links. The presence of α -helical region in apamin is supported by CD and laser Raman spectra and by secondary structure prediction. In building of apamin spatial structure other features of NMR study (1,2) were also taken into account: chemical shift pH-dependences, effect of Gd(III) ion binding, torsional ϕ angles estimated from H-H and C-H couplings, effect of selective chemical modification of apamin on NMR parameters. Thus evaluated apamin spatial structure better explains available spectroscopic data than recently theoretically predicted structures (4-6).

Apamin residue	$^3J_{\text{HNC}^\alpha\text{H}}$	Amide NH $t_{1/2}$, h
Cys-1	-	-
Asn-2	9.5	< 0.1
Cys-3	5.2	0.2
Lys-4	7.6	4
Ala-5	6.8	11
Pro-6	-	-
Glu-7	6.9	0.1
Thr-8	8.5	4
Ala-9	2.7	< 0.1
Leu-10	5.5	20
Cys-11	5.9	14
Ala-12	3.0	26
Arg-13	4.2	> 100
Arg-14	3.5	2.7
Cys-15	5.4	26
Glu-16	7.1	0.5
Glu-17	6.8	11
His-18	6.9	< 0.1



References:

1. J. Magn. Res. 30, 151 (1978); Bioorgan. Khim. (USSR) 6, 840 (1980).
2. TAMU NMR Newsletters 249-21, 259-28.
3. E. Habermann, Science 177, 314 (1972).
4. P. N. Mel'nikov, E. M. Popov, Bioorgan. Khim. 6, 21 (1980).
5. R. C. Hider, U. Ragnarsson, FEBS Lett. 111, 189 (198).
6. B. Busetta, FEBS Lett. 112, 138 (1980).

With best regards,

Sincerely yours,

Vladimir

Vladimir Bystrov

School of Chemical Sciences
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RKH/JH
Your Ref. BLS/KS

3rd October, 1980.

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

NMR AND THE PERIODIC TABLE/NMR COMPUTER PROGRAM LIBRARY

Dear Barry,

Your coloured reminders provoke a response along two somewhat trivial lines this time.

Firstly, readers of TAMU NMR Newsletter may be interested in the attached "NMR Popularity Graph" of the elements, collated for the 2½ years 1978 - mid 1980. I am endeavouring to maintain a computer listing of NMR references concerning nuclei other than the five most-popular ones (^1H , ^{13}C , ^{15}N , ^{19}F and ^{31}P), compiled from the American Chemical Society's "CA Selects" on NMR. The listing may be ordered by computer according to mass number and the result plotted on a histogram as shown. According to my reckoning, the "top ten" consist of the five mentioned above plus (in order) ^2H , ^{29}Si , ^{17}O , ^{23}Na and ^{77}Se , with ^{59}Co behind. However, I should point out that although I try to be reasonably comprehensive, I have to make some arbitrary choices, and the following comments apply:-

1. I exclude "Diss Abs." and some similar types of "publication".
2. I have endeavoured to make it a chemistry-based graph, so I exclude articles I judge to be physics (e.g. on metals and alloys). I do, however, include articles on solid-state NMR of chemical relevance.

.....Cont.

...../Cont.

3. I try to include all articles giving chemical shifts or relaxation times of the nuclei listed, including those obtained by INDOR and related techniques. However, I exclude papers giving coupling constants of the nuclei listed which were obtained from spectra of the popular nuclei (^1H) etc.
4. The histogram probably grossly underestimates ^{11}B and ^{14}N studies, since I only began "collecting" references for these nuclei recently. Moreover, my coverage of the 1978 literature is probably not very comprehensive.

I am willing to send TAMU NMR Newsletter readers a copy of the complete list (in order of mass number), which can act as a kind of supplement to a well-known book (the chapters of which are not included in the histogram). However, I shall have to charge the sum of £10 per copy to cover the expenses (send in advance if possible please). Currently there are a total of 410 references, which produce exactly 500 allusions to different nuclei on the histogram.

All this reminds me of my former computing activities in compiling a Library of NMR Computer Programs, now containing over 40 programs. I'm not sure I've ever informed TAMU NMR Newsletter readers that I handed over the Library operation (with relief) to the Science Research Council Daresbury Laboratory about a year ago. Therefore anyone wanting a copy of the 1979 Manual (as far as I know, still free!) and later bulletins, or details/copies of the programs, should write to:-

Dr. W. Smith
NMR Program Library
SRC Daresbury Laboratory
Daresbury
Warrington
Cheshire WA4 4AD
England

I trust this "contribution" ensures I continue to receive the TAMU NMR Newsletter.

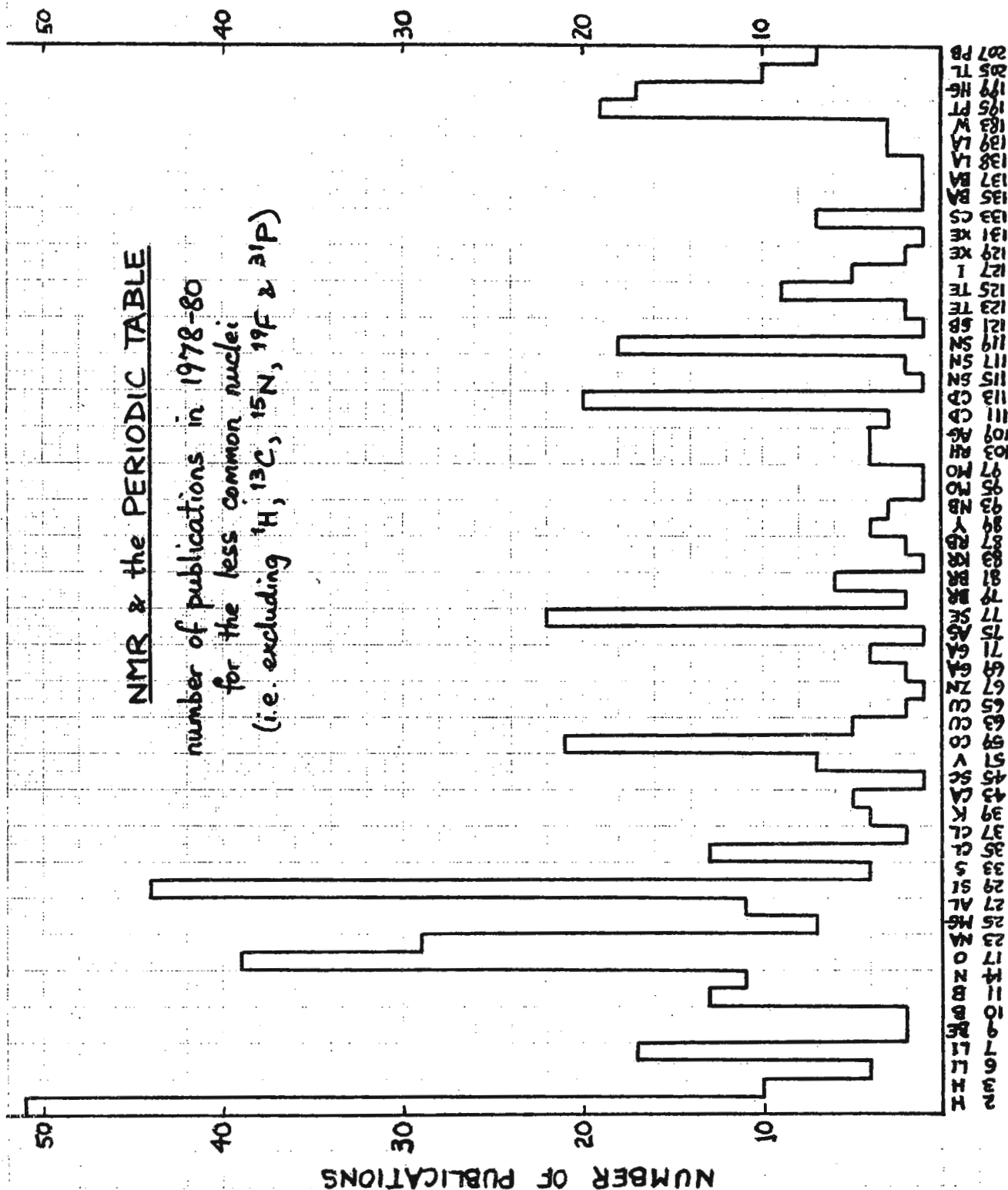
With best wishes,
Yours sincerely,

Robin

PROF. R.K. HARRIS

NMR & the PERIODIC TABLE

number of publications in 1978-80
for the less common nuclei:
(i.e. excluding ^1H , ^{13}C , ^{15}N , ^{19}F & ^{31}P)



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CENTRAL RESEARCH & DEVELOPMENT DEPARTMENT
EXPERIMENTAL STATION

October 7, 1980

Professor Bernard L. Shapiro
Department of Chemistry
Texas A&M University
College Station, Texas 77843Paramagnetic Susceptibilities Measured by NMR

Dear Professor Shapiro,

Recently, we have been measuring magnetic susceptibilities of paramagnetic materials by proton NMR in our Bruker SXP100 spectrometer. The idea is based on the observation made 25 years ago (1-3) that the liquid in the annulus in a coaxial tube arrangement (see Figure 1) gives rise to a broad resonance signal with two peaks, owing to the fact that the field experienced by the molecules in the annulus is nonuniform. The separation between the two peaks is a function of the volume susceptibilities of the materials used and also of the geometrical dimensions. We fill the inner tube with the magnetic material to be measured and if its volume susceptibility, χ_v , is much larger than that of the glass and the diamagnetic liquid, and if the tubes are infinitely long, the separation ΔH of the two peaks relative to the applied field H_0 is given by

$$\Delta H/H_0 = 4\pi\chi_v r_o^2/r_m^2, \quad (1)$$

where r_o is the inner radius of the inner tube, and r_m is the mean radius of the annular liquid. The volume susceptibility is in cgs units per cm^3 , or cm^3/cm^3 , i.e. it is dimensionless. Unfortunately, this splitting is only obtained when the direction of H_0 is perpendicular to the tube axis, which makes the experiment not well fitted for the usual geometry of a supercon. Sample spinning does not improve the resolution of the spectrum. In fact, if the spinning rate were faster than the peak splitting the spectrum would collapse to a single peak.

We have successfully measured susceptibilities between 2×10^{-6} and 3×10^{-5} cgs/ cm^3 with splittings of 1.5 to 22 kHz in a 90 MHz spectrometer, using a 7.5 mm tube inside a 10 mm tube. For instance, Cr_2O_3 gave 24.3×10^{-6} cgs/g which agrees well with the literature value of 25×10^{-6} cgs/g.

A practical problem is deviation from ideal geometry, including the loose definition of r_m in the formula. One way to get around this problem is by calibrating with a known paramagnetic solution (e.g. MnSO_4). The line shape can also be predicted theoretically. The signal is a superposition of single



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peaks arising from all the volume elements of the liquid, where each peak is shifted according to its position with respect to the paramagnetic material. In the geometry defined in Fig. 1, the shift of the volume element with cylindrical coordinates z, r, ϕ is given by

$$\Delta H(z, r, \phi) = \pi \chi_V \frac{r_o^2}{r^2} H_o \frac{z_1}{\sqrt{r^2 + z_1^2}} \left[\frac{3r^2 + 2z_1^2}{r^2 + z_1^2} \cos^2 \phi - 1 \right] \\ + \pi \chi_V \frac{r_o^2}{r^2} H_o \frac{z_2}{\sqrt{r^2 + z_2^2}} \left[\frac{3r^2 + 2z_2^2}{r^2 + z_2^2} \cos^2 \phi - 1 \right].$$

One obtains the actual line shape by integrating over the volume of the liquid that contributes to the NMR signal (i.e. that is confined in the rf coil). Figure 2 shows the predicted value of r_m for infinitely long tubes, an inner tube with I.D. = 7.0 mm and O.D. = 7.5 mm, and an outer tube with varying I.D. Figure 3 shows the effect of finite heights. Plotted is the predicted normalized splitting for varying height of the paramagnetic sample, where the liquid and the paramagnetic material line up at the bottom, and the height of the liquid is 15 mm (inner tube: I.D. = 7.0, O.D. = 7.5 mm, outer tube: I.D. = 9.5 mm). The splittings in Figure 3 are normalized to the splitting one would get for infinitely long tubes.

Yours sincerely,

Alexander J. Vega

AJV/kac
Attach.

¹C. A. Reilly, H. M. McConnell, and R. G. Meisenheimer, Phys. Rev. 98, 264a (1955).

²M. Garcia Morin, G. Paulett, and M. E. Hobbs, J. Phys. Chem. 60, 1594 (1956).

³J. R. Zimmerman and M. R. Foster, J. Phys. Chem. 61, 282 (1957).

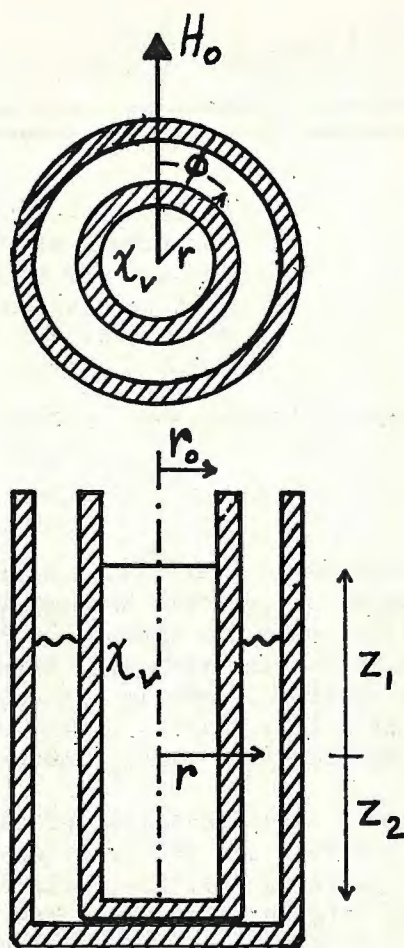


Fig. 1

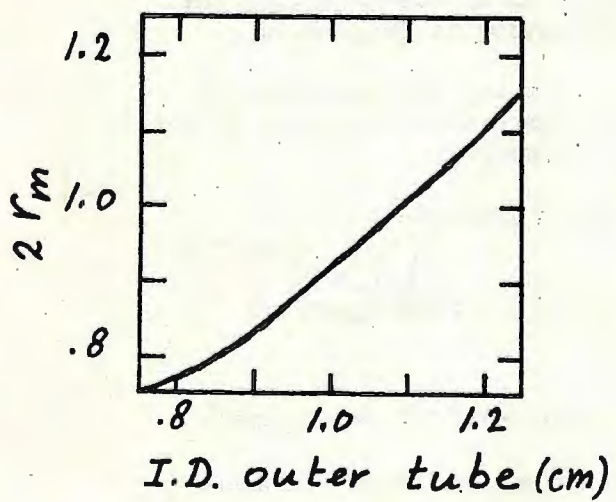


Fig. 2

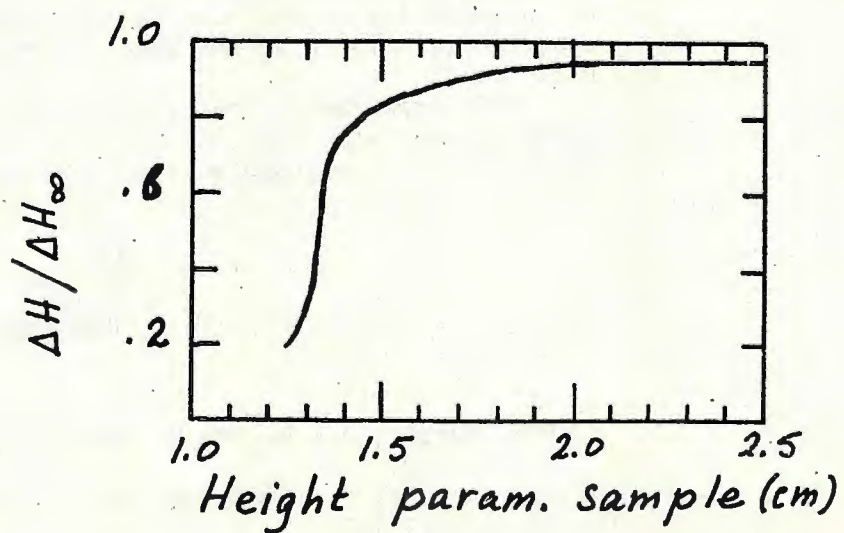


Fig. 3



Wageningen

Department of Molecular Physics

Your reference

Your letter of

Our reference 80/375, MH/RD

Date October 8, 1980

Enclosures

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

Subject Magic angle spinning NMR of tobacco mosaic virus

Dear Professor Shapiro,

In a recent TAMU NMR Newsletter (1), a description has been given of a high-resolution solid state NMR spectrometer with magic angle spinning possibilities at Dr. Veeman's laboratory in Nijmegen, the Netherlands. It is noteworthy that this beautiful home-built machine with excellent specifications is not only capable of measuring NMR spectra of solids. Also spectra of *solutions* of viruses, like tobacco mosaic virus (TMV), can be obtained without any problem.

TMV, which consists of 2140 identical protein subunits and a single strand of RNA, has been the object of study in our laboratory for the last couple of years (2-4). Conventional high resolution NMR is limited for this large particle that has a molecular weight of 42×10^6 . The overall rotational motion of TMV is so slow, that strong line broadening results. In ^{13}C NMR only 10 % of the carbons (which, by the way, are indicative for internal motions within the virus) are observed (3).

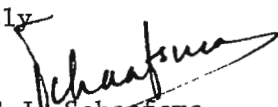
As is shown in Fig. A, which was obtained in very close collaboration with Dr. Veeman, proton enhanced magic angle spinning ^{13}C NMR gives well-resolved spectra of TMV in solution. This spectrum has practically as much detail and intensity as is obtained with TMV that is dissociated in RNA and free protein subunits (Fig. B, cf. Ref. 3).

This experiment clearly demonstrates that the NMR technique has grown up now to a stage in which no longer limitations are present for applications to supramolecular biological systems.

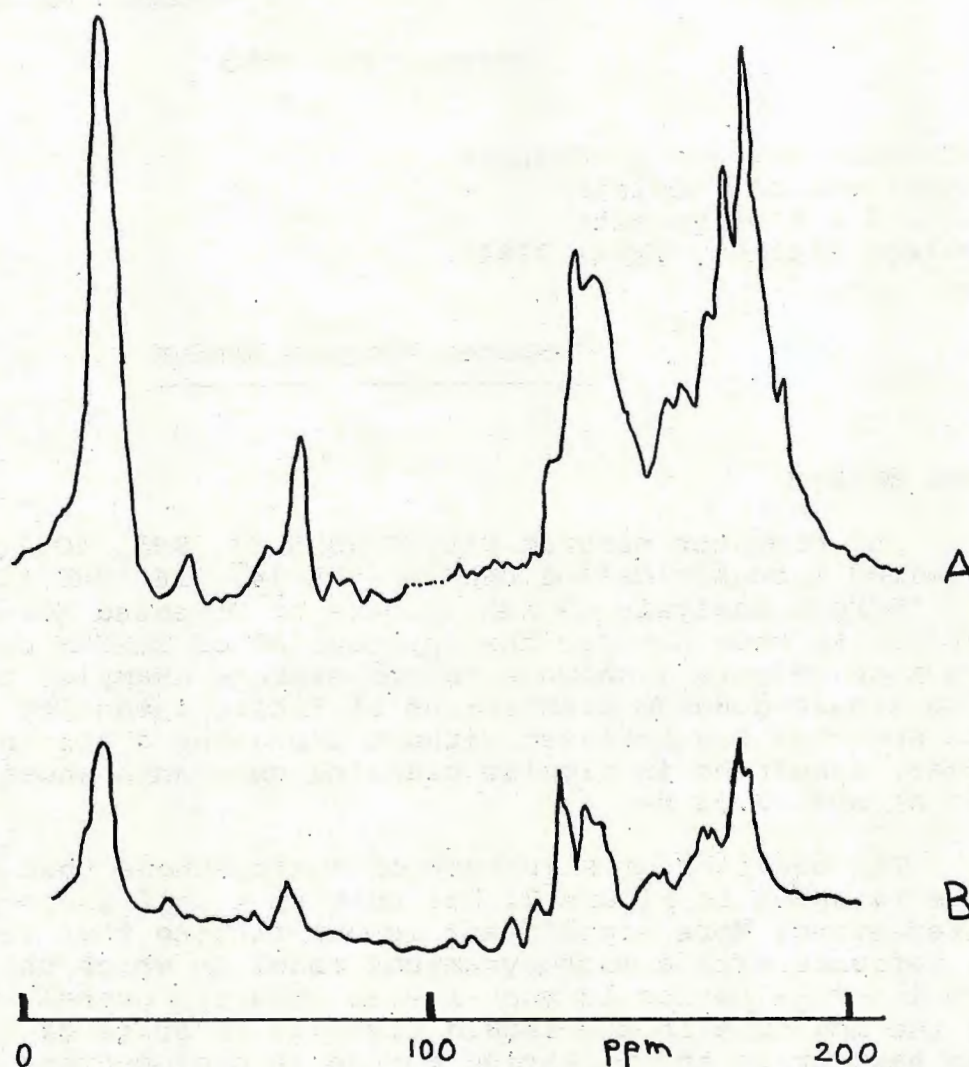
Yours sincerely


M.A. Hemminga

&


T.J. Schaafsma

1. E.M. Menger, J.W.M. van Os and W.S. Veeman, TAMU NMR Newsletter 255(1979)3.
2. J.L. de Wit, M.A. Hemminga and T.J. Schaafsma, J. Magn. Resonance 31(1978)97-107.
3. J.L. de Wit, N.C.M. Alma-Zeestraten, M.A. Hemminga and T.J. Schaafsma, Biochemistry 18(1979)3973-3976.
4. J.L. de Wit and T.J. Schaafsma, FEBS Lett. 92(1978)273-275.



- A. 45 MHz proton enhanced and decoupled magic angle spinning ^{13}C NMR spectrum of natural abundance TMV in phosphate buffer pH 7.0 at room temperature. Conditions: TMV concentration: approx. 200 mg/ml; spinning rate: 3.4 kHz; cross-polarization time: 1 ms; 50 000 accumulations.
- B. Broadband ^1H decoupled 90.5 MHz ^{13}C NMR spectrum of dissociated TMV-protein and RNA in phosphate buffer pH 11 at 30 $^{\circ}\text{C}$. Conditions: concentration 60 mg/ml; repetition time: 1 s; 50 000 accumulations.

DIVISION OF CHEMISTRY AND PHARMACY
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INSTITUTE OF ORGANIC CHEMISTRY
KARLSTRASSE 23

GERHARD BINSCH
PROFESSOR OF THEORETICAL ORGANIC CHEMISTRY

October 10, 1980

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

Computer Program DANSOM

Dear Barry:


Our computer program DAVINS (JMR 37, 395, 409 (1980)) has now acquired a cousin called DANSOM (OMR 14, 226 1980)). The name stands for "Direct Analysis of NMR Spectra of Oriented Molecules". We were curious to know how far the application of DANSOM could be pushed in practice. Figure 1 shows a rather extreme example, consisting of 2930 single-quantum transitions of finite intensity in absorption. The spectrum was analyzed without assigning a single one of those lines, resulting in dipolar coupling constants whose standard errors are at most 0.02 Hz.

The equilibrium structure of cyclopentene that comes out of this is shown in Figure 2, but that in itself is not so terribly interesting. More significant is our finding that the results are at variance with a microdynamical model in which one assumes that the internal motion is much faster than the overall reorientation of the molecule in the liquid crystal, in spite of the fact that the barrier to the puckering motion in cyclopentene is only 2.77 kJ/mol. If correct, this would mean that the past attempts to exploit nematic-phase NMR for conformational analysis must be in error and that the seeming agreement between the experimental results and those calculated on the basis of such a model must have been spurious. We conclude that the theoretical treatment of the results on conformationally mobile molecules in general requires an infinite number of orientation tensors (submitted to Mol.Phys.).

Sincerely yours,



David S. Stephenson



Gerhard Binsch



Figure 2. Calculated equilibrium structure of cyclopentene.



NAVAL RESEARCH LABORATORY

WASHINGTON, D.C. 20375

IN REPLY REFER TO:

6120-483:ANG:mbr

22 October 1980

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

Gain Fluctuations in a Solid State RF Amplifier

Dear Barry:

Polarization transfer in liquids by coherent rotating frame cross-polarization (1-3) places stringent demands on the stability of the rf transmitters. The two rf amplitudes γB_1 , each much greater than J , should be settable (and stable) to within some fraction of J . For $^{15}\text{N}-^1\text{H}$ cross-polarization at an rf field strength of 2 kHz and a value of 80 Hz for a typical directly bonded NH pair, the rf field amplitudes should be matched to within about 1% or 0.1 db. (These restrictions do not apply to adiabatic methods (4) which avoid the amplitude match problem altogether.)

In the course of these experiments, we found that the matching condition would occasionally jump, remain constant at a new level for minutes or longer, and then return to nearly the initial state. The source of this problem was traced to a solid state broad band power amplifier in which the outputs of parallel transistor stages are summed together.

The enclosed chart recording shows the rectified output of this malfunctioning amplifier (T) as well as the input which has been amplified by a separate power amplifier (R). Also shown is the schematic of the test facility. The gain was quite steady for eight hours before this incident. Over the course of 18 hours, four similar fluctuations occurred. No line voltage fluctuations were observed by a Dranetz 606 disturbance analyzer during the recording period. A separate test showed that the dc power supply in the rf amplifier was not responsible for this behavior. We speculate that one or more transistors failed intermittently, with consequent loss of gain.

The intermittent nature of this failure makes it impractical to observe by oscilloscope, except by a most obsessional observer. Such an intermittent gain fluctuation, here of the order of 12% in voltage

6120-483:ANG:mbr
22 October 1980

(25% in power), leads to severe reduction of NMR signal amplitudes in cross-polarization, although this effect may be completely unnoticed in conventional FT (single pulse) experiments. We have no assurance that ours is an isolated problem and commend tests of long-term transmitter stability to other spectroscopists. It is our understanding that such tests are not commonly performed by the manufacturers.

Gerry

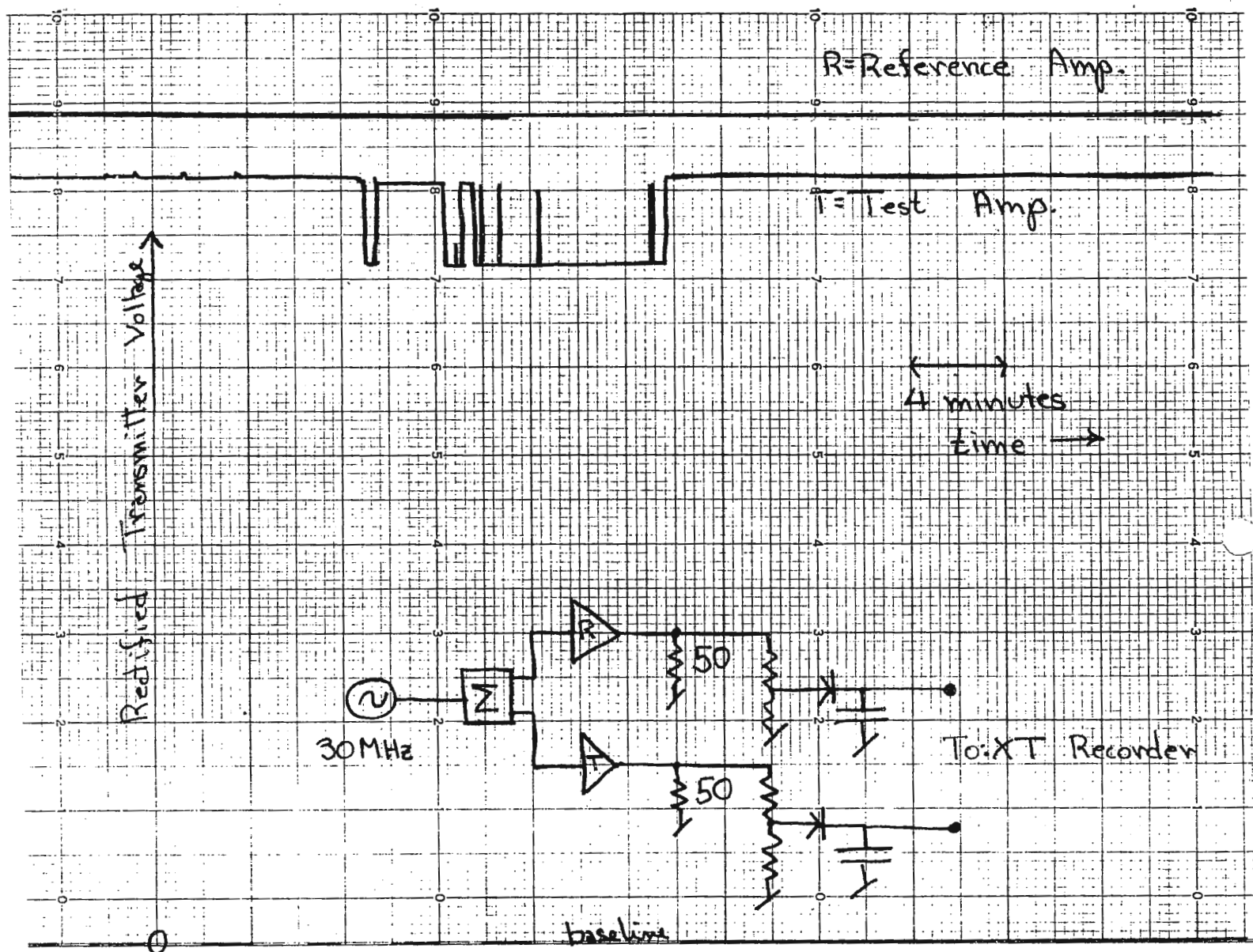
G. C. Chingas
Polymeric Materials Branch
Chemistry Division

Sincerely yours,

Al

A. N. Garroway
Polymeric Materials Branch
Chemistry Division

1. R.D. Bertrand, W. B. Moniz, A. N. Garroway and G. C. Chingas, J. Am. Chem. Soc. 100 5227-5229 (1978).
2. R. D. Bertrand, W. B. Moniz, A. N. Garroway, and G. C. Chingas, J. Magn. Reson. 32, 465-467 (1978).
3. G. C. Chingas, A. N. Garroway, R. D. Bertrand and W. B. Moniz, J. Magn. Reson. 35, 283-288 (1979).
4. G. C. Chingas, A. N. Garroway, W. B. Moniz and R. D. Bertrand, J. Am. Chem. Soc. 102 2526-2528 (1980).



A 'gain fluctuation incident' in a solid state rf power amplifier. The chart shows the rectified rf output (voltage) from the transmitter (T) under test and a similar reference (R) amplifier. During this 18 hour test, four similar incidents were observed. The small (ca 1%) fluctuations seem to be precursors to the major instability. Both amplifiers were operated well within recommended limits and systematic interchange of splitter output ports, dummy loads, rectifiers and chart recorder amplifiers all indicted the test amplifier. (For clarity the chart recording has been darkened by hand.)



Wageningen

266-28

Department of Molecular Physics

Your reference

Your letter of

Our reference 80/379, MH/RD

Date October 8, 1980

Enclosures

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

Subject Varian XL-100 for sale

Dear Professor Shapiro,

At the end of this year we will be replacing our Varian XL-100 system by a Bruker CXP-300 spectrometer. The XL-100 system is therefore for sale (as a whole, or in parts) for approximately 5 - 10 % of the original value.

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Yours sincerely,

M.A. Hemminga & P.A. de Jager

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SCHOOL OF PHARMACY
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY

SAN FRANCISCO, CALIFORNIA 94143

October 22, 1980

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

Title: Distance Geometry for NMR

Dear Barry,

Gordon Crippen (now a colleague of yours) and I have been developing a computer program that might be of some interest to the NMR community. The basic idea is to generate molecular structures that are consistent with experimental constraints. There are a number of programs aimed at this problem, proceeding from quite different mathematics. Our particular approach uses matrix methods from a field of mathematics called distance geometry. The input data are distances (or angles) between atoms (or united atoms) along with some assessment of experimental errors. Known chiral centers can also be specified.

The program returns a number of structures (i.e., center of mass, principal axes coordinates) that meet the constraints to some predetermined limit. For 50-150 atoms or united atoms the computer costs have been a few dollars per structure on the computers available to us (CDC 7600, IBM 370/165). Minicomputer (PDP-11/70, VAX) versions are being tested.

The advantages of this program seem to be:

- (1) Reasonable geometric structures are produced quite efficiently.
- (2) Inconsistent constraints are identified.
- (3) "Local" minima problems are much reduced compared to energy optimization techniques.

The disadvantages that we know of include:

- (1) We will not produce a best-fit to chemical shifts or relaxation times - our approach requires distances for input. Hence the program is most likely to be useful for those doing coupling constants and NOE experiments.
- (2) We do not guarantee "low" energy structures, however, the program output can be coupled to an energy minimization routine as desired.

- (3) We have no proof that the method must always find a solution; that is some local minimum troubles may remain. These have been rather minor in the problems we have seen so far.

The general approach is described in G.M. Crippen and T. Havel, *Acta Cryst.* A34, 282 (1978); I.D. Kuntz, G.M. Crippen, and P.A. Kollman, *Biopolymers* 18, 939 (1979). An NMR application is given in G.M. Crippen and N. Oppenheimer, *Int'l. J. Peptide Protein Res.*, in press, 1981. Werner Braun and Kurt Wuthrich have made a number of modifications (private communication).

An "export" version of the program in Fortran, prepared by Timothy Havel, is available. If anyone is interested, please contact either Gordon or me for further details.

Sincerely,

Tack

Irwin D. Kuntz
Professor of Pharmaceutical Chemistry

IDK:ja



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EQUIPMENT FOR SALE

(1) *NMR spectrometer. Proton Fourier-Transform. Varian/Nicolet HR/TT-220.* Consists of 5.2 T superconducting magnet, proton probe, additional quadrupole field correction shim set, Varian HR-220 console with variable temperature controller, Nicolet TT-220 accessory with NIC-1083 computer, disk drive, teletype.

(2) *NMR spectrometer, Multinuclear Fourier-Transform. Extensively modified Bruker HX-90-2.* Consists of 2.1 T 12" electromagnet, power supply, 10kW refrigerated cooling unit, Bruker console, variable temperature controller, PFP external deuterium lock system, Nuclear Advancement 7-40 MHz broad band probe and accessory, FT timing accessories, ENI 350L amplifier, Adret 1-70 MHz synthesizer, about 10 probe inserts, Nicolet 1074/ DEC PDP 8/e data system, teletype, computer controlled x-y recorder, paper tape reader/punch, audio filtering system, crystal filter.

Both instruments are fully operational and in very good condition. It would be preferred to sell the instruments as complete operating units, but bids for portions of the instruments will be considered. Instruments will be available after Feb., 1981.

Please address any bids or pricing enquiries to Mr. James J. Stewart, Superintendent of Purchasing, The Rockefeller University, 1230 York Avenue, New York, NY 10021. (212)360- 1313.

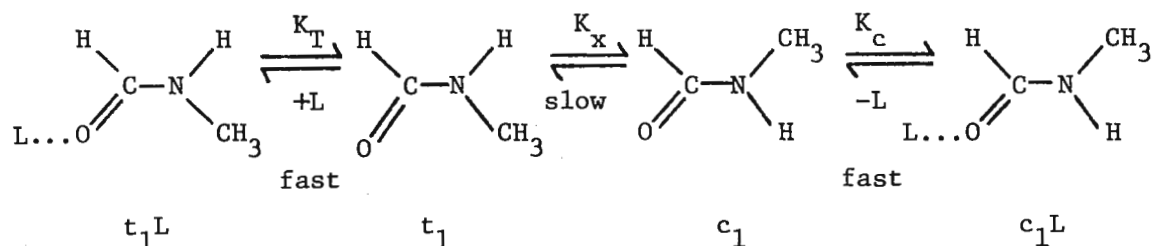
October 28, 1980

Professor B.L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77843Perturbing *Cis/Trans* Equilibria using Lanthanide Shift Reagents.

Dear Barry:

Continuing our studies of the interaction of lanthanide shift reagents (LSR) with amides¹, we attempted to unravel the complex equilibria present when LSR is added to a solution of N-methylformamide (NMF) in CCl₄. In addition to *cis* and *trans* NMF monomers, the 1:1 and 2:1 complexes of each isomer with the LSR, Eu(fod)₃, are expected to be present. Furthermore, Eu(fod)₃ dimerizes in CCl₄ solution. Other species which may be present are the n-mers resulting from the amide self-association via hydrogen bonding.

Of special interest to us was the fact that the *cis:trans* isomer ratio in NMF, which is 8:92 in the absence of LSR², becomes 50:50 at a LSR:NMF molar ratio (L_0/S_0) of approximately 0.4. However, even though this indicates a large increase in the population of *cis* species, a plot of δ vs. L_0/S_0 (Figure 2, ref. 1) for the N-methyl protons reveals much larger lanthanide-induced shifts for *trans* as compared with *cis* isomers ($S_0 = 0.1 \text{ M} = \text{stoichiometric concentration of NMF}$). In order to explain these results, a model was proposed which takes the following equilibria into account



where L = unbonded LSR and the dimerization of the LSR, $L + L \xrightleftharpoons{K_L} L_2$ is included. Slow and fast refer, of course, to the NMR time scale and $(t_1 + t_1L)$ and $(c_1 + c_1L)$ are proportional to the integrated intensities of the *trans* and *cis* N-methyl proton signals, respectively. The chemical

Northern Illinois University

shifts of these signals are

$$\delta_{trans} = \frac{t_1 L}{t_1 + t_1 L} \Delta_T \quad \text{and} \quad \delta_{cis} = \frac{c_1 L}{c_1 + c_1 L} \Delta_C$$

where Δ_T and Δ_C are the limiting shifts of the *trans* and *cis* complexes. The stoichiometric concentration of LSR is $L_0 = L + L_2 + t_1 L + c_1 L$.

Even though the problem has been reduced to 1:1 complexes only and the effects of amide hydrogen bonding by self-association has been assumed to be small, six parameters must be determined: K_T , K_C , K_X , K_L , Δ_T and Δ_C . However, $K_X = (c_1 + c_1 L):(t_1 + t_1 L)$ as $L \rightarrow 0$ and literature values may be used for K_L .

Nonlinear regression analysis yields values for Δ_{cis} and Δ_{trans} for the N-methyl protons of the NMF isomers which are quite close to the values found for Δ_2 for the N-methyl protons in N,N-dimethylformamide (5.2 and 11.4 ppm respectively¹). Thus the LSR probably binds in a similar manner to the two structurally similar amides. However, in NMF, the values found for K_C are much larger than those for K_T , indicating a much more negative free energy of binding of LSR to the *cis* isomer, possibly for steric reasons. Since one of the principal assumptions in the use of LSR to determine molecular geometrics in solution is that the complexation does not disturb the molecular conformation(s), we plan to study further those modifications of geometry which do occur.

To our knowledge, an analysis of this type, which includes measurement of the continually changing isomer ratio as well as the chemical shifts, has not been done before. We note that a similar equilibria shift has been observed in N-methylacetamide and two other secondary amides in LSR/ $CDCl_3$ solutions.³

Sincerely,

Lori

Laurine L. Graham

1. L.L. Graham, *Org. Magn. Reson.* **14**, 40 (1980).
2. L.A. LaPlanche and M.T. Rogers, *J. Amer. Chem. Soc.* **86**, 337 (1964).
3. R.A. Fletton, G.F.H. Green and J.E. Page, *J.C.S. Chem. Comm.*, 1134 (1972).



INDIANA UNIVERSITY

DEPARTMENT OF CHEMISTRY

 Chemistry Building
 Bloomington, Indiana 47405
 812-337-5513

October 28, 1980

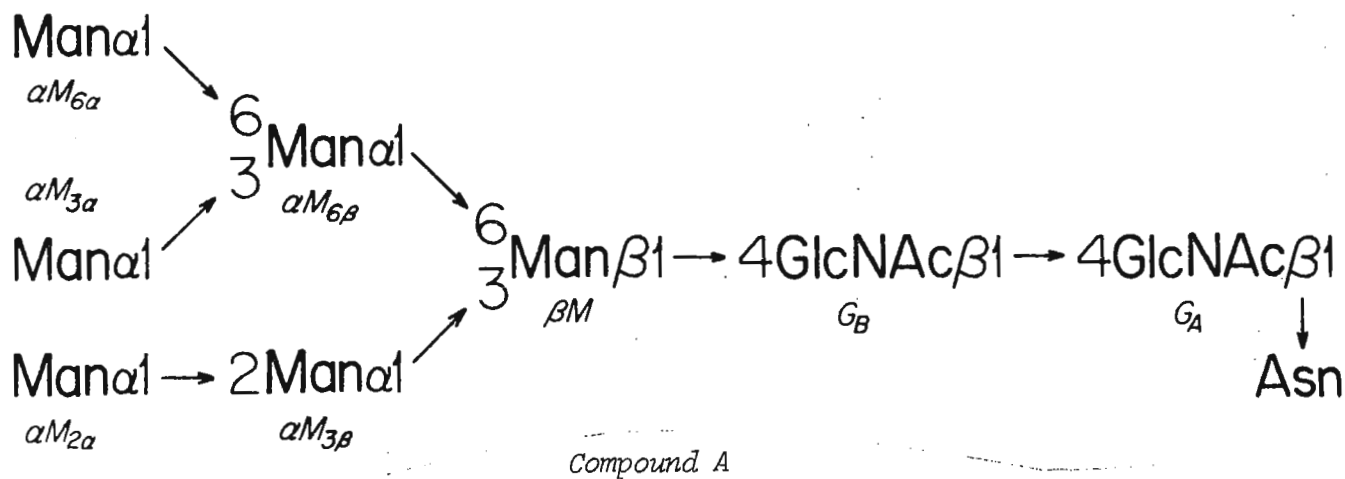
 Professor Barry L. Shapiro
 TAMU NMR Newsletter
 Department of Chemistry
 Texas A & M University
 College Station, Texas 77843

 KINETICS OF α -MANNOSIDASE ACTION ON VARIOUS
 α -D-MANNOPYRANOSYL LINKAGES

Dear Barry:

This is a progress report on one aspect of our studies of glycoproteins and glycopeptides by ^{13}C NMR.

We find that ^{13}C NMR spectroscopy is a practical method for following the kinetics of enzymatic digestion of individual carbohydrate residues of glycopeptides and for determining the structures of the products of partial digestions. Specifically, we have studied the jack bean α -mannosidase digestion of the hen ovalbumin glycopeptide $\text{Man}\alpha 1 \rightarrow 6(\text{Man}\alpha 1 \rightarrow 3)\text{Man}\alpha 1 \rightarrow 6(\text{Man}\alpha 1 \rightarrow 2\text{Man}\alpha 1 \rightarrow 3)\text{Man}\beta 1 \rightarrow 4\text{GlcNAc}\beta 1 \rightarrow 4\text{GlcNAc}\beta 1 \rightarrow \text{Asn}$ (*Compound A*). We find that the reported "rule" that jack bean α -mannosidase hydrolyzes $\text{Man}\alpha 1 \rightarrow 2\text{Man}$ and $\text{Man}\alpha 1 \rightarrow 6\text{Man}$ linkages at least 15 times faster than $\text{Man}\alpha 1 \rightarrow 3\text{Man}$ linkages [Tai, T., Yamashita, K., Ogata-Arakawa, M., Koide, N., Muramatsu, T., Iwashita, S., Inoue, Y., and Kobata, A. (1975) *J. Biol. Chem.* 250, 8569-8575] is not of general validity. Although the $\text{Man}\alpha 1 \rightarrow 2\text{Man}(\alpha)$ linkage of *Compound A* is the first one to be digested, the $\text{Man}\alpha 1 \rightarrow 3\text{Man}(\beta)$ linkage is hydrolyzed next, faster than the $\text{Man}\alpha 1 \rightarrow 6\text{Man}(\alpha)$ linkage. The $\text{Man}\alpha 1 \rightarrow 3\text{Man}(\alpha)$ linkage is hydrolyzed very slowly.



Consider the effect of α -mannosidase on *Compound A*. Fig. 1 shows the region of *O*-linked anomeric carbons in the spectrum of this compound (50 mM sodium acetate, pH 4.4) before the addition of α -mannosidase. The other spectra of Fig. 1 show the corresponding spectral region at various intervals (indicated in hours at the right of each spectrum) after addition of α -mannosidase. Each indicated interval is the time between addition of α -mannosidase and the mid-point in the accumulation of each spectrum (each spectrum is the result of 0.4 h of signal averaging). In the analysis of our results we have used not only the regions of *O*-linked anomeric carbons, but also the rest of each spectrum. However, the regions of nonanomeric carbon resonances contain interfering peaks from the two pyranose anomers of the liberated free D-mannose. We eliminated the interfering resonances by digital subtraction of a spectrum of dilute aqueous D-mannose (with 50 mM acetate) at anomeric equilibrium.

The anomeric carbon region after 2.4 h of treatment with α -mannosidase (Fig. 1G) clearly indicates the presence of four *O*-linked anomeric carbons, which strongly suggests a fairly homogeneous $(\text{Man})_3(\text{GlcNAc})_2\text{Asn}$ molecule. The chemical shifts of the anomeric carbons indicate one $\text{Man}\alpha 1 \rightarrow 3\text{Man}$ linkage (103.5 ppm) and one $\text{Man}\alpha 1 \rightarrow 6\text{Man}(\beta)$ linkage (101.1 or 101.7 ppm) in addition to the $\text{Man}\beta 1 \rightarrow 4\text{GlcNAc}$ (101.7 or 101.1 ppm) and $\text{GlcNAc}\beta 1 \rightarrow 4\text{GlcNAc}$ (102.6 ppm) linkages. Because the resonance at 103.5 ppm is consistent with both a $\text{Man}\alpha 1 \rightarrow 3\text{Man}(\alpha)$ and a $\text{Man}\alpha 1 \rightarrow 3(\beta)$ linkage, we can conclude on the basis of Fig. 1G that, after 2.4 h of α -mannosidase treatment, *Compound A* has been converted either into $\text{Man}\alpha 1 \rightarrow 6(\text{Man}\alpha 1 \rightarrow 3)\text{Man}\beta 1 \rightarrow 4\text{GlcNAc}\beta 1 \rightarrow 4\text{GlcNAc}\beta 1 \rightarrow \text{Asn}$ or into $\text{Man}\alpha 1 \rightarrow 3\text{Man}\alpha 1 \rightarrow 6\text{Man}\beta 1 \rightarrow 4\text{GlcNAc}\beta 1 \rightarrow 4\text{GlcNAc}\beta 1 \rightarrow \text{Asn}$. However, examination of the region of nonanomeric carbon resonances clearly proves that the latter structure is the only one present.

The fact that we obtain essentially pure $\text{Man}\alpha 1 \rightarrow 3\text{Man}\alpha 1 \rightarrow 6\text{Man}\beta 1 \rightarrow 4\text{GlcNAc}\beta 1 \rightarrow 4\text{GlcNAc}\beta 1 \rightarrow \text{Asn}$ after 2.4 h of α -mannosidase digestion of *Compound A* indicates that α -mannosidase removes $\alpha\text{M}_{3\beta}$ much faster than $\alpha\text{M}_{3\alpha}$. However, examination of the spectra of Fig. 1 recorded before that of Fig. 1G shows that $\alpha\text{M}_{3\beta}$ is actually hydrolyzed faster than $\alpha\text{M}_{6\alpha}$. In other words, the $\text{Man}\alpha 1 \rightarrow 3\text{Man}(\beta)$ linkage is digested even faster than the $\text{Man}\alpha 1 \rightarrow 6\text{Man}(\alpha)$ linkage. Details will be presented in a manuscript.

In summary, ^{13}C NMR is very useful for examining structures of partially cleaved species produced during the action of glycosidases on oligosaccharides, glycopeptides, and glycoproteins. Furthermore, the use of ^{13}C NMR as a monitoring technique makes it practical to quench a glycosidase reaction at a time appropriate for isolating molecules that would be difficult to prepare by other methods.

Sincerely,

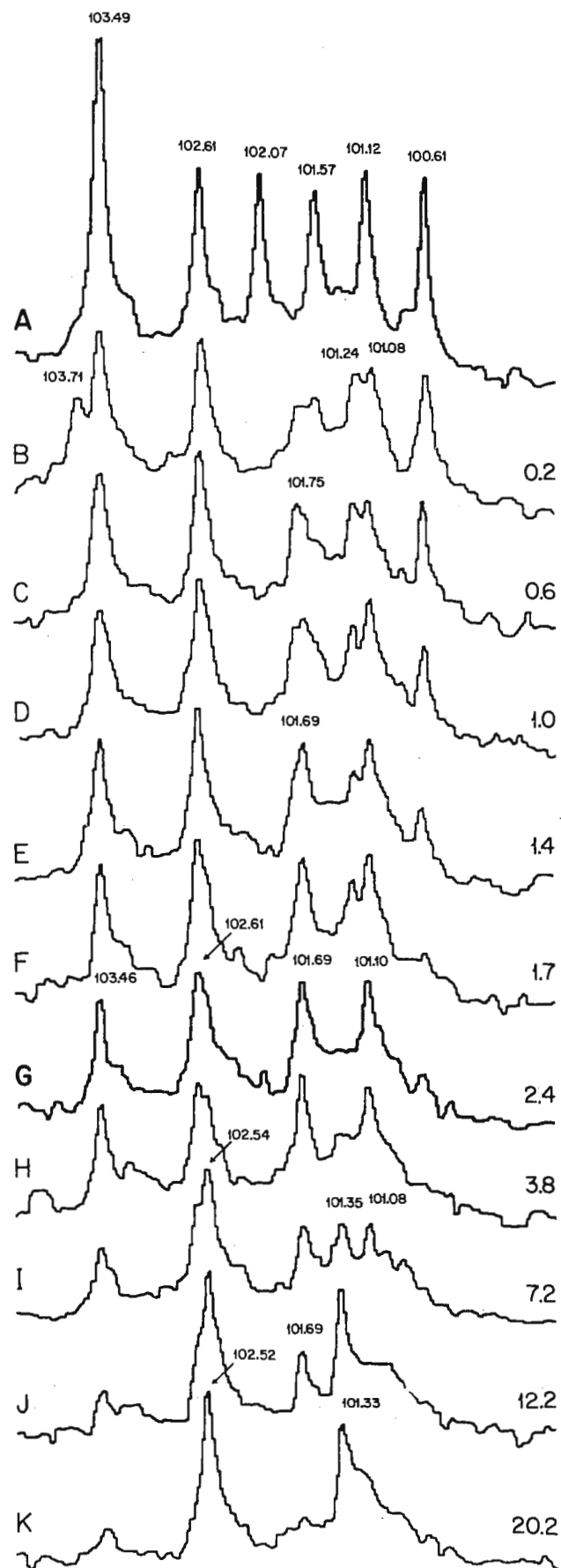
Adam Allerhand

Elisha Berman

Adam Allerhand

Elisha Berman

FIG. 1. Effect of α -mannosidase on the resonances of *O*-linked anomeric carbons of *Compound A*. Each spectrum was recorded at 40°C with the use of 2,048 accumulations and a recycle time of 0.66 s. Numbers above peaks are chemical shifts. A, 22 mM *Compound A* in H_2O , 50 mM sodium acetate, 1 mM zinc sulfate, pH 4.4. B-K, same as Spectrum A, but after addition of 100 units jack bean α -mannosidase. The number on the right of each spectrum indicates the interval (in hours) from the addition of α -mannosidase to the half-way point in the signal accumulation for that spectrum.



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

ROYAL SOCIETY OF CHEMISTRY

29th October 1980

30 Russell Square, London WC1B 5DT, U.K.
Telephone 01-580 3482

Dear Barry,

RESIDENTIAL SCHOOL ON NMR, NOTTINGHAM, SEPTEMBER 1981

The Royal Society of Chemistry is holding a Residential School on "NMR Spectroscopy - Principles and Modern Practice" at the University of Nottingham, England, in the period 7th-11th September 1981. The course is intended for those who are familiar with continuous-wave NMR but have little knowledge of Fourier transform techniques or of relaxation concepts. It should provide up-dating for industrial or academic research personnel, and deepening of knowledge for research students and suitably qualified technical staff. The lecturers will be W. Derbyshire (Nottingham Univ.), J. Feeney (National Institute for Medical Research), R. Freeman (Oxford Univ.), R.K. Harris (Univ. of East Anglia), B.E. Mann (Sheffield Univ.), K.J. Packer (Univ. of East Anglia) and D. Shaw (Oxford Research Systems), and the topics covered will range from Basic Principles and Relaxation Effects to Solid-State NMR and 2-D NMR. There will also be a series of seminars, mainly dealing with various applications aspects, and some practical demonstrations are also envisaged.

The co-organisers of the School are H. Booth (Nottingham Univ.), W. Derbyshire (Nottingham Univ.) and R.K. Harris (Univ. of East Anglia). TAMU NMR Newsletter readers and others who are interested in attending should ask for further information from Dr. A.D. Ashmore (Education Officer) at the address on this letterhead.

The last Residential School organised by the Chemical Society, as it was then, on this type of topic was held in 1976 at the University of East Anglia, and it attracted a range of participants from many countries. It is hoped that the same will be true for the 1981 School.

With best wishes

Yours sincerely,

Robin

R.K. Harris

**University of Houston**

Central Campus
Houston, Texas 77004

Department of Chemistry
713/749-2612

October 3, 1980

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

Dear Colleague:

We have a position available immediately for an experienced NMR specialist as our NMR Laboratory Manager. Responsibilities include maintenance, operation and training operators on our XL-100-Nicolet multinuclear and FT-80A instruments. Some knowledge of electronics is essential but a qualified electronics specialist will be available within the Department. The NMR Laboratory Manager will be expected to participate in planning for future expansion and improvements in the NMR facilities. Also, there will be opportunities for collaboration with faculty in NMR research areas. We will support and encourage the professional development of the successful applicant.

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R. A. Geanangel
Department of Chemistry
University of Houston Central Campus
Houston, Texas 77004

The NMR facilities are a vital component of many of the research programs here so we very much appreciate your help in locating a qualified individual to manage our laboratory.

Sincerely,

Russ Geanangel
Professor of Chemistry

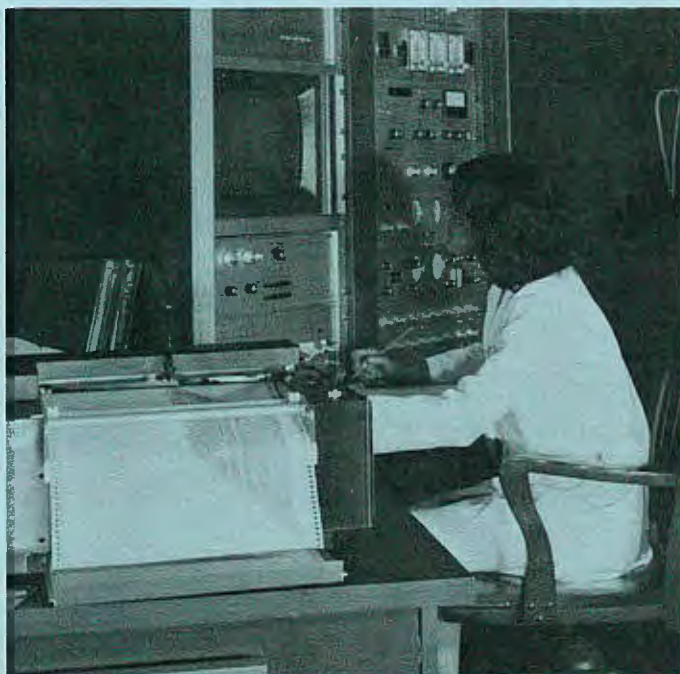
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