Texas A & M University N – M – R Newsletter

No. **233**

February 1978

σ

TAMU NMR NEWSLETTER - ADVERTISERS

Bruker Scientific, Inc.   - see p. 24
JEOL Analytical Instruments, Inc. - see p. (i) and outside back cover
GenRad   - see p. 19
Nicolet Instrument Corporation   - see p. 12
Varian Instrument Division   - see inside back cover
Wilmad Glass Co., Inc.   - see inside front cover

TAMU NMR NEWSLETTER - SPONSORS

Abbott Laboratories
Bruker Scientific, Inc.
JEOL Analytical Instruments, Inc.
Dr. R. Kosfeld, Abt. Kernres., Inst. f. Phys. Chem.,
  TH Aachen (Germany)
The Lilly Research Laboratories, Eli Lilly & Co.
The Monsanto Company
Nicolet Technology Corp., Palo Alto, CA
  (formerly Transform Technology, Inc.)
Unilever Research
Varian, Analytical Instrument Division

TAMU NMR NEWSLETTER - CONTRIBUTORS

The British Petroleum Co., Ltd. (England)
Eastman Kodak Company
E. I. DuPont DeNemours & Company
The Perkin-Elmer Company
Pfizer, Inc.
The Procter & Gamble Co., Miami Valley Labs
Shell Development Company
Union Carbide Corporation

DEADLINE DATES:	No. 234:	6 March 1978
	No. 235:	3 April 1978

All Newsletter Correspondence, Etc. Should Be Addressed To:

MERCK INSTITUTE

FOR THERAPEUTIC RESEARCH

BYRON H. ARISON, PH.D.
SENIOR INVESTIGATOR
DEPARTMENT OF BIOPHYSICS

TELEPHONE (201) 574 6746
(201) 574 5394

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

Dear Professor Shapiro:

Double Pulse Techniques As a Device For Purity Evaluation: ^{13}C Sensitivity of the SC-300

While double pulse experiments have been routinely used to suppress solvent signals they also can serve as a technique for purity evaluation particularly in the detection of small molecular weight contaminants in moderately large molecular weight substances. This application became evident during the course of studying an oligopeptide derivative (I) having a mw close to 1000. The spectrum (Figure 1) run in CD_3OD, also shows the presence of tetramethylsilane and residual amounts of dimethyl formamide and acetic acid. In addition, two multiplets at 3.57δ and 3.69δ were not easily rationalized in terms of the known amino acid composition and it was inferred that they probably represented an impurity. This view was supported by the observation that the line widths of the suspect signals were narrower than those of the peptide.

(I)
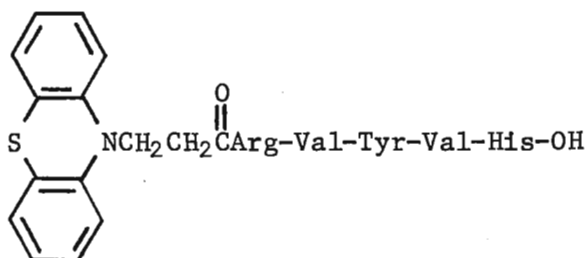
Figure 2 shows the spectrum obtained under conditions designed to minimize the residual solvent OH peak. The double pulse sequence also satisfied the requirements for suppressing the CD_2HOD, AcOH, DMF and TMS lines and interestingly, the 3.57δ and 3.69δ multiplets as well. The last finding provided compelling evidence that these unidentified resonances arose from an impurity since the T_1 values fell into the same class as those of the small molecular weight species and were well outside the range of those of the peptide.

Under the double pulse conditions, methyl ester and acetyl methyl protons in two oligopeptide derivatives were selectively reduced in relative area by about 50%. Since this intensity reduction is decidedly less than these protons experience in the unbound state, it appears that the partially relaxed spectra may also be used to determine whether small derivatizing agents are attached to a larger molecule.

The foregoing experiments were carried out on the Varian SC-300 which has been in continuous operation since November 1976. Although the system is equipped for carbon-13, phosphorus and deuterium, proton studies understandably have been our main preoccupation. Enough experience has been obtained on ^{13}C, however, to convince us that the sensitivity with the 5 mm probe is quite adequate for routine operation. The signal-to-noise ratio using the 90% ethyl benzene reference is approximately 160 to 1. What this means in terms of a real sample is illustrated in Figure 3 which shows the proton decoupled spectrum of a 16.5 mg specimen of methyl-α-D-mannoside obtained in under seven minutes (1000 transients; 0.4 second acquisition time; ca 55° flip angle). Consequently there is every reason to believe that except for cases involving long T_1's, 25-50 mgs of most medium molecular weight samples will provide satisfactory decoupled spectra in less than five minutes. It is worth mentioning that for this weight range the time requirements are comparable to those needed for proton spectra of equivalent S/N on a typical 60 MHz instrument.

Sincerely yours,

Byron H. Arison

Figure 1: ^1H Spectrum of (I)
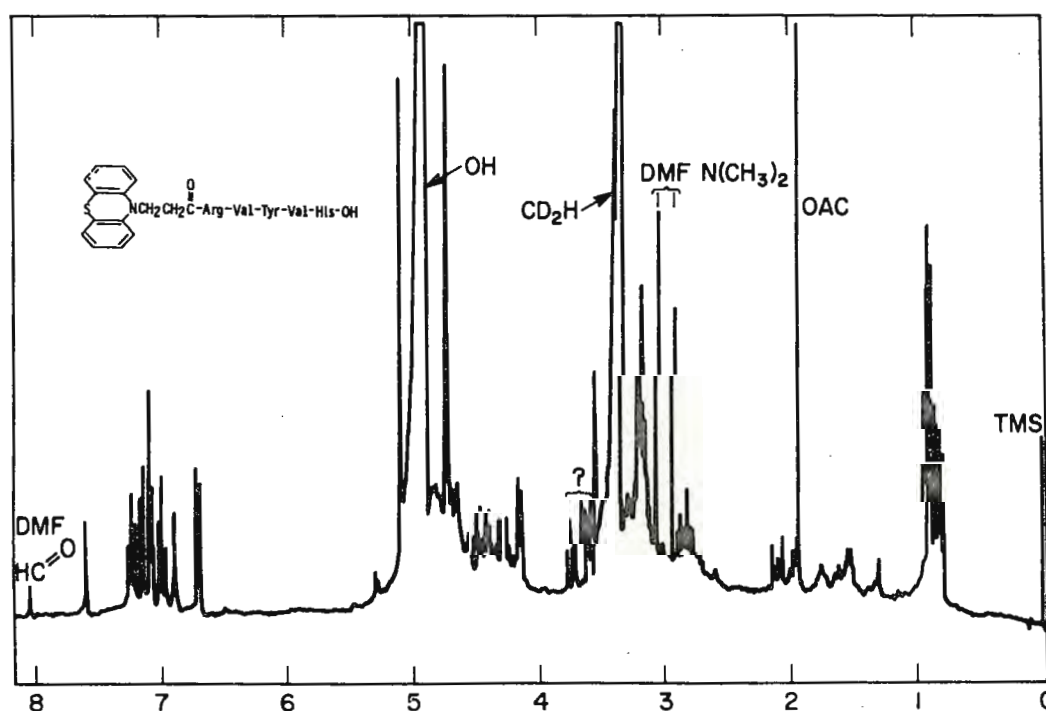
Figure 2: Double Pulse Spectrum of (I)
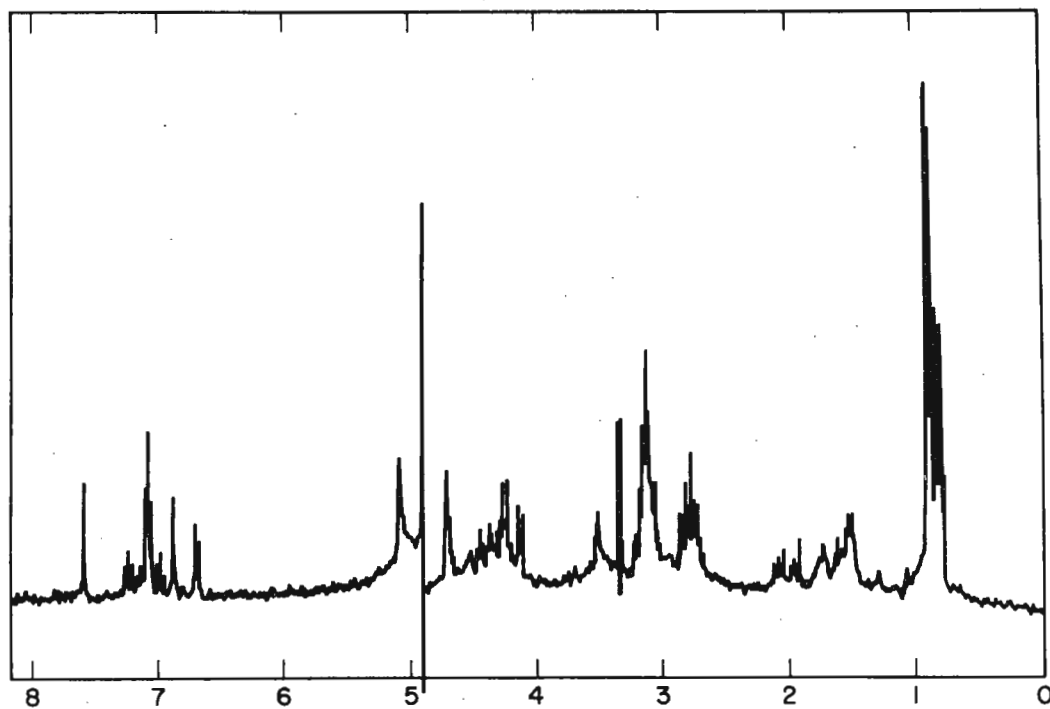
Figure 3: ^{13}C Spectrum, 16.5 mgs Methyl-α-D-mannoside

No.	PPM
1	101.7
2	73.3
3	71.3
4	70.7
5	67.5
6	67.3
7	61.7
8	55.4
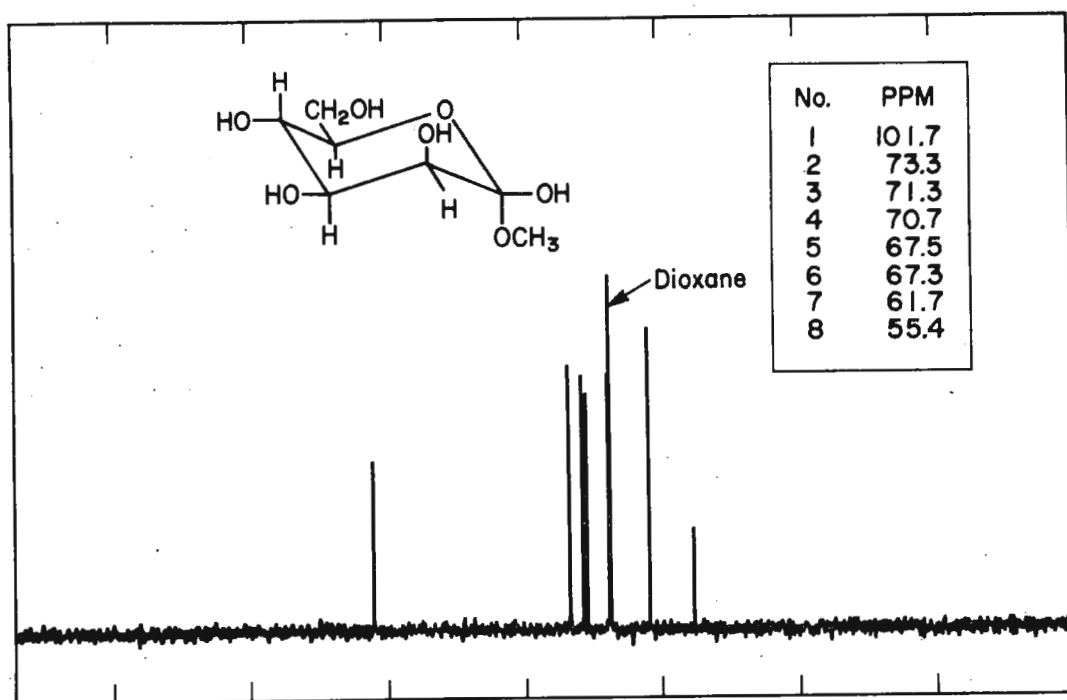
FACHBEREICH CHEMIE
DER PHILIPPS-UNIVERSITÄT

- Dr. Stefan Berger -

Fachbereich Chemie - Lahnberge · D-3550 Marburg 1

Professor B.L. Shapiro
Department of Chemistry
Texas A & M University

College Station, Texas 77843
USA

Lahnberge · Postfach 1929
D-3550 MARBURG 1
Telefon (0 64 21) 28 5520
Telex: 4 82 372

den 3-1-78

Dear Professor Shapiro,
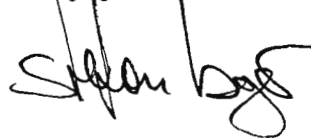
LIGHT for the XL-100

there are several reports dealing with the drilling of holes into
nmr probes to enable direct photochemistry during the nmr experiment.
As far as I am aware this has not been reported for the probes of
the XL-100 although the manufacturer has already provided excellent
access to the required place: the bore in the rear of the 4412 or
4415 probes meant for the external lock sample. All one has to do
is to drill a hole into the ceramic material inside the probe to let
the light through to the reciever coil.
For this purpose we sacrificed an old 4415 probe, dissasembled it
completely and drilled a hole into the ceramic cylinder as needed.
After reassembling we experienced some more leakage, but no signifi-
cant loss of resolution or sensitivity under normal operating condi-
tions. However, photochemistry with UV still did not work until we
realized that the outer glass tube of the 5 mm ^{1}H inserts is made of
normal glass and only the inner one is a quartz tube. The outer glass
tube can be removed and replaced by a quartz cylinder without damaging
the insert.
To guide the light from the lamp to the external lock hole we use a
75 cm long and 5 mm o.d. quartz rod available from Schott, W. Germany.
The system works perfectly for ^{1}H at variable temperature. For ^{13}C we
encounter some difficulties in effective irradiation since the re-
ciever coil is larger and blocks the light from the nmr tube. We hope,
however, to come around that problem.

Sincerely yours

Wellcome

The Wellcome Research Laboratories
The Wellcome Foundation Ltd

Langley Court
Berkenham
Kent BR3 3BS
Telephone 01-658 2211

telegrams and cables
WELLAB BECKENHAM
telex
WELLAB
BECKENHM 23937

BMNC/77/50 December 1977

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

Dear Professor Shapiro

Rapid-scan FT-n.m.r. on a Varian HA-100

As an initial contribution I think that it would be useful to set down
the progress that we have made in adapting our Varian HA-100 for the
acquisition of rapid-scan n.m.r. spectra.

The normal sweep oscillator network has been replaced by a Wavetek 111
sweep generator driven by a ramp from a Nicolet 535 signal averager.
Successive scans, taken from the unfiltered scope output are time-averaged
in the Nicolet 535 and transferred by rerouting the acquisition trigger
pulses to a DATAMAG n.m.r. data system controlling our adjacent Bruker
HFX90. This system, written around a PDP-11/20 with 1.2M word disc was
produced by Instem Limited, Stone, Staffordshire, England. When a rapid-
scan spectrum is to be processed through the DATAMAG system, its normal
pulse-FT operation is interrupted, all relevant information saved on disc,
and the manipulation of the HA-100 data is then performed. The correlated
spectrum is written back to the Nicolet which allows such operations as
digital smoothing, integration or convolution difference to be performed
prior to plotting on the HA-100 recorder, and as a result the interruption
of the Bruker operation need only be of the order of two minutes.

In the figure are shown results for a typical organic compound (i.e. one
within reach of my chair). The lowest spectrum (A) shows the aromatic proton
signals of m-nitroanisole, a single scan in 390 seconds. The centre trace
(B) is the result of averaging 26 scans of 15 seconds each into 4K channels.
The top spectrum (C) is the result of correlating the time-domain transform
of (B) with a theoretical lineshape function, core-filling to 16K and back
transforming.

Our principal use of this facility will almost certainly be in studying
interactions between small molecules and biomacromolecules.

Yours sincerely

Dr. J. C. Lindon
Department of Physical Chemistry
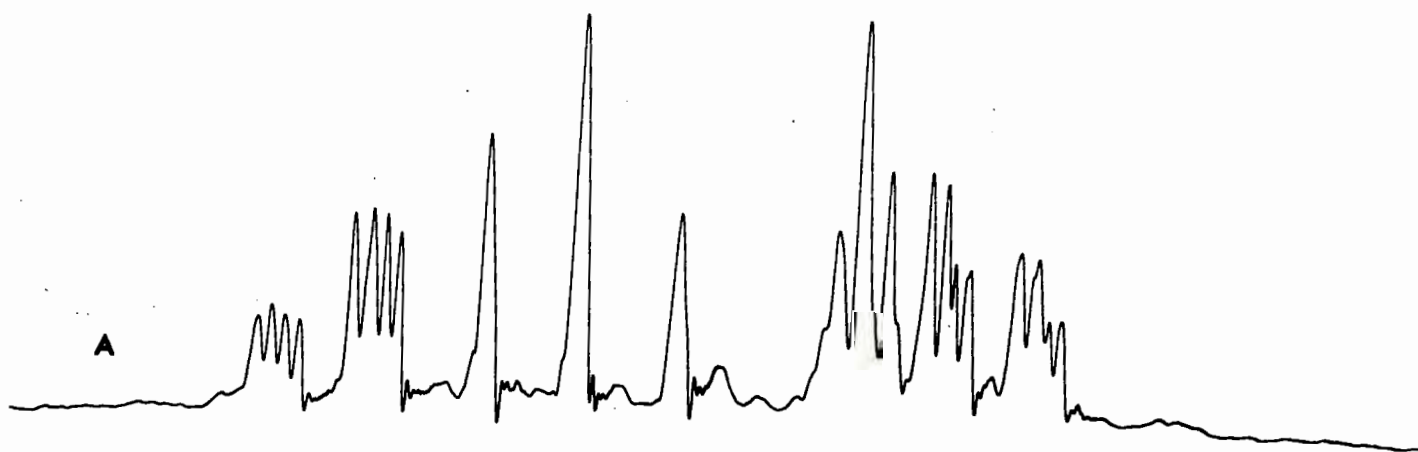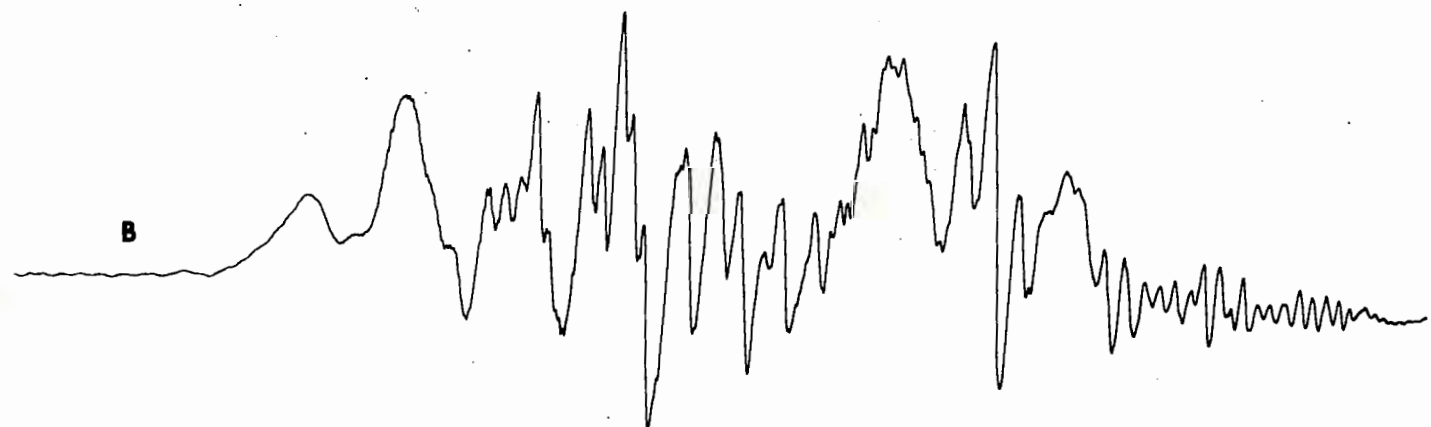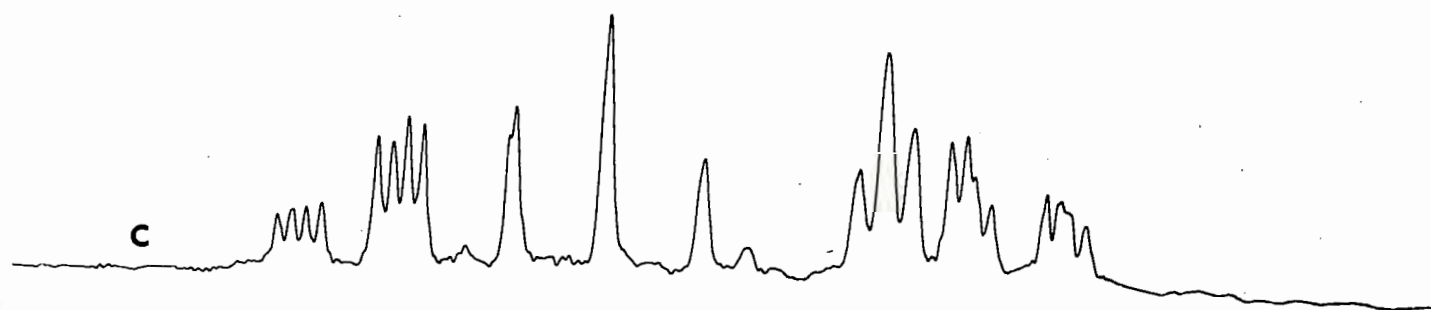
Koninklijke/Shell-Laboratorium, Amsterdam

Shell Research B.V.

Uw ref.:

Onze ref.:

Amsterdam, 19th December, 1977
Postadres: Postbus 3003
Tel. via telefoniste (020) 20 91 11
Tel. rechtstreeks (020)
Hr/Mw

Dear Barry,

^{15}N NMR of ammonia in the gas phase

We have recently begun an evaluation of ^{15}N NMR as a technique for investigating the nature of interactions between molecules and surfaces. Since the physisorbed state appears to be an intermediate one between gas and liquid, we started off with measurements on the gaseous state and measured the chemical shift, ^{15}N-^{1}H coupling constant, spin lattice relaxation time (T_1) and the nuclear Overhauser enhancement (NOE) for 90 % ^{15}N-enriched ammonia.

Measurements were carried out on a Bruker WH270 at 27.36 MHz using a 15-mm diameter probe. The gas sample, at one bar pressure, was restrained in a volume contained within the dimensions of the transmitter/receiver coil.

The chemical shift is 398.6 ppm upfield from nitromethane, in excellent agreement with the value reported by Litchman et al.[1] (398.9 ppm). The ^{15}N-^{1}H coupling was derived from the single resonance spectrum shown in fig. 1 as 61.8 Hz , also in good agreement with the value found in solution[2] (61.2 Hz).

T_1 was determined to be 0.30 s using the saturation recovery method described by Markley et al.[3] Figure 2 shows the return of magnetization as a function of time following the saturation pulse sequence. T_1 measurements using the inversion recovery technique were also made (T_1 = 0.24 s) but gave less reliable results due to inability of the pulse unit to produce a 180° pulse: it was necessary to use four successive pulses of 31 µs (i.e. 45°), which unfortunately led to a somewhat inhomogeneous H_1 field.

The NOE was derived from the "dynamic" sequence: .... decoupler off/fixed delay (10x T_1)/decoupler on/variable delay (t_i)/observe/decoupler off .... . The results are shown in fig. 3. No significant change of signal intensity occurs as a function of t_i, demonstrating that NOE is zero. This confirms the expected situation that there is no contribution to T_1 from a dipolar mechanism and that spin rotation relaxation is the only mechanism operative in gas-phase ammonia.

Yours sincerely,

KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM

A.D.H. Clague   J.P.C.M. van Dongen

1. W.H. Litchman, M. Alei Jr., and A.E. Florin:
   J.A.C.S., 91, 6574 (1969)
2. T. Axenrod: "NMR Spectra of Nuclei other than Protons",
   Wiley Interscience, New York, 1974, p. 84
3. J.L. Markley, W.L. Horsley, M.P. Klein:
   J. Chem. Phys. 55, 3604 (1971
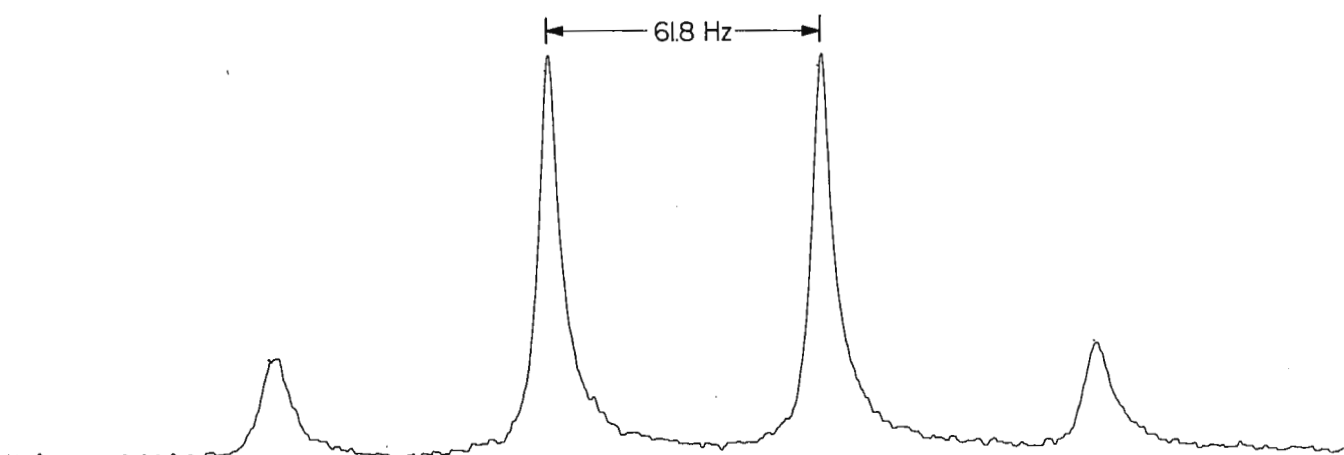
FIG. 1
27.36 MH ^{15}N SPECTRUM OF ^{15}NH$_3$ GAS (COUPLED)

| 0.01 | 0.05 | 0.10 | 0.15 | 0.20 | 0.25 | 0.30 | 0.40 | 0.50 | 0.70 | 1.00 | 1.50 | TIME, s |
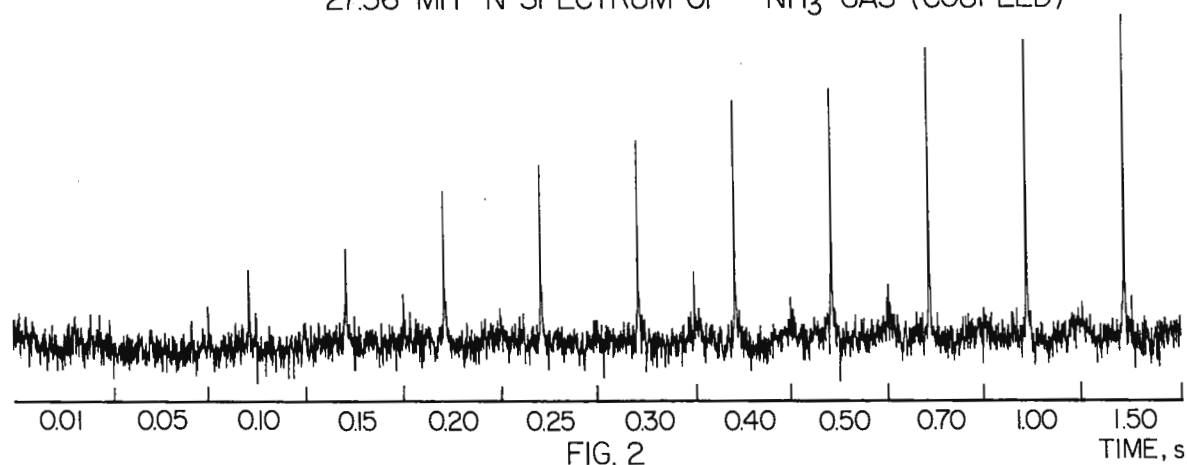
FIG. 2
SATURATION-RECOVERY T$_1$ DETERMINATION OF ^{15}NH$_3$ GAS AT 1 bar, 300 K

| .005 | .010 | .020 | .070 | .15 | .25 | .40 | .80 | 1.50 | 3.00 | TIME, s |
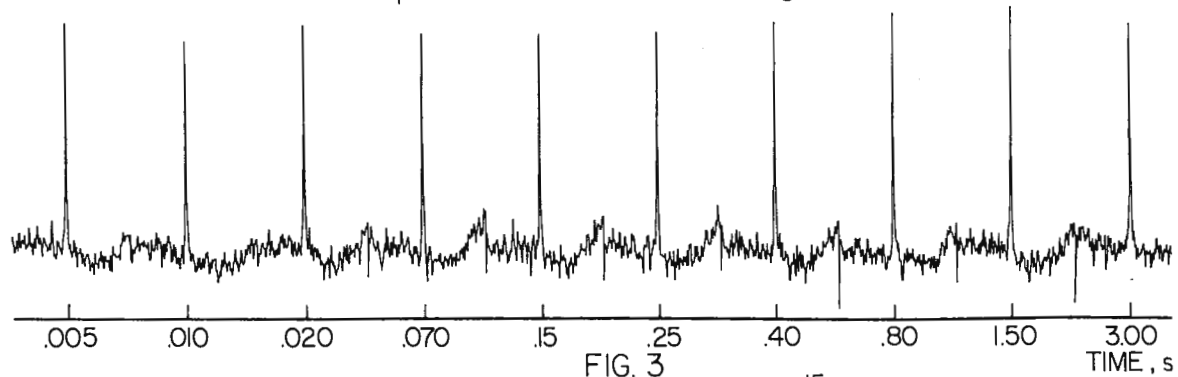
FIG. 3
DYNAMIC NOE DETERMINATION FOR ^{15}NH$_3$ GAS

UNIVERSITY OF WALES

University College of Swansea

Department of Chemistry

J. H. Purnell M.A. Sc.D.
Professor of Physical Chemistry and
Head of Department.
A. Pelter Ph.D.
Professor of Organic Chemistry.
J. H. Beynon Ph.D. D.Sc. F.R.S.
Royal Society Research Professor.

SINGLETON PARK SWANSEA SA2 8PP
UNITED KINGDOM
TEL SWANSEA (0792) 25678

27th January 1978.

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

Dear Professor Shapiro,

Combinatorics in N.M.R., part II[1]:
the Isotopic Isomers of the Estonian Silicon Chemical Shift
Standard

I wonder if other readers beside myself were intrigued by the high symmetry of the compound $Si_{16}O_{20}(CH_3)_{24}$ shown below, and which Lippmaa and co-workers report they use as a secondary ^{29}Si chemical shift standard for high-resolution solid-state N.M.R. How many silicon-isotopic isomers does it possess? Answering this question will give me an opportunity to expound Pólya's theorem.

The enumeration of isomers in chemistry was a problem which in the nineteenth century attracted the interest not only of chemists but of distinguished mathematicians; this work was crowned forty years ago by the work of the mathematician Pólya[3,4]. Reviews are available[5-7]. Pólya's Hauptsatz, though conceived in a chemical context, has proved to be of central importance in the pure mathematical discipline of Graph Theory[5]. It can obviously be applied to isotopic isomers[8]. Though Pólya's definitive presentation[3] may prove hard reading for non-mathematicians, I strongly recommend ref. 4, an exposition specifically aimed at chemists. A brief excerpt will illustrate its delightful style. "Es mag sein dass die vorangehende Herleitung der Formel (17) jedem Leser Mühe machen wird: dem Chemiker, weil er in der mathematischen, und dem Mathematiker, weil er in der chemischen Ausdrucksweise ungeübt ist. Jedoch ist die Formel (17) an und für sich volkommen anschaulich, usw." He certainly appreciated chemists' difficulties with mathematics, which were doubtless even greater at that period. Professor Pólya moved from Hungary to Switzerland and eventually California, where he now apparently flourishes in retirement, aged ninety. A few months ago, a distinguished Harvard chemist was telling me what a decisive influence Pólya's lectures at Stanford had had upon him.

In order to illustrate Pólya's approach, we first consider only the eight silicon atoms Nos. 1-8 at the corners of the cube. With them we associate a permutation group G_1, abstractly isomorphic to O_h, and formed by the action of

the elements of O_h on these atoms. Pólya's crucial concept is that of the cycle-index, in this case

$$Z(G_1;s) = \frac{1}{48}(s_1^8 + 8s_1^2s_3^2 + 13s_2^4 + 12s_4^2 + 8s_2s_6 + 6s_1^4s_2^2). \qquad (1)$$

The first term arises from the identity operation $\hat{E}$, which converts every atom into itself, constituting a cycle of order 1; there are eight of these. The second term arises from the triads $\hat{C}_3$. E.g. that though atoms 1 and 7 converts these two atoms into themselves - two cycles of order 1; it converts atom 2 into 4 into 5 into 2, and similarly with atoms 3, 6 and 8 - two cycles of order 3. The remaining terms follow obviously; the co-efficient 13 arises from the action of $3\hat{C}_2$, $6\hat{C}_2'$, $\hat{i}$ and $3\hat{\sigma}_h$.

Let us consider - since this is an N.M.R. newsletter - the number of magnetically distinct isotopic isomers, considering firstly the isotope ^{29}Si of spin $\frac{1}{2}$, and secondly the non-magnetic stable isotopes - thus 2 possibilities for each Si atom. We thus write $s_k = 2$, for all k, and substitute in (1), obtaining

$$Z(G_1;2) = 22$$

as our answer. If we wish to distinguish these more closely, we write

$$s_k = x^k + y^k,$$

and substitute into (1), obtaining:

$$Z(G_1; x+y) = \frac{1}{48}[(x+y)^8 + 8(x+y)^2(x^3+y^3)^2 + 13(x^2+y^2)^4 + 12(x^4+y^4)^2 +$$
$$+ 8(x^2+y^2)(x^6+y^6) + 6(x+y)^4(x^2+y^2)^2]$$
$$= x^8 + x^7y + 3x^6y^2 + 3x^5y^3 + 6x^4y^4 + 3x^3y^5 + 3x^2y^6 + xy^7 + y^8. \qquad (2)$$

The significance of this equation is that the co-efficient of x^jy^{8-j} is the number of distinct isotopic isomers containing j spin-$\frac{1}{2}$ silicon nuclei. The present problem is sufficiently simple that the reader can easily check for himself the correctness of these results.

We now return to the full problem with 16 silicon atoms. The action of the elements of O_h on these atoms forms a different permutation group, G_2, but still abstractly isomorphic to O_h. Because the relation of the eight additional atoms to the O_h operations (assuming an averaging of conformations) is the same as that of the original eight atoms, it is not difficult to see that the new cycle-index is obtained from (1) by replacing s_k by s_k^2. Thus

$$Z(G_2;s) = \frac{1}{48}(s_1^{16} + 8s_1^4s_3^4 + 13s_2^8 + 12s_4^4 + 8s_2^2s_6^2 + 6s_1^8s_2^4). \qquad (3)$$

The total number of magnetically distinct isotopic isomers is now

$$Z(G_2;2) = 1996.$$
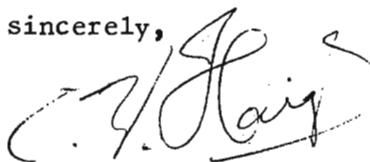
Furthermore, $Z(G_2; x+y) = x^{16} + 2x^{15}y + 10x^{14}y^2 + 24x^{13}y^3 + 73x^{12}y^4 +$
$$+ 136x^{11}y^5 + 246x^{10}y^6 + 318x^9y^7 + 376x^8y^8 + \text{etc.} \qquad (4)$$

(Obviously x^jy^{16-j} and $x^{16-j}y^j$ have the same co-efficient.) I leave to my experimental colleagues the task of elucidating the 1995 distinct ^{29}Si N.M.R. spectra thus shown to be theoretically possible!

Extension of the method to cases where more than two types of isotope per element require to be considered, and where the isotope-isomerism for further elements, e.g. ^{12}C, ^{13}C or ^{1}H, ^{2}H, is also of interest, involve no new principle and are straightforward. That the type of calculation described in this letter is not wholly academic is evidenced by the growing number of papers reporting spectra of quite large, and possibly symmetric, molecules in which the

proportion of, say, ^{13}C or ^{2}H is enriched well above the small natural abundance. For a very recent (but small) inorganic example, see ref. 9. And, finally returning to the subject of chemical shift standards, many readers will recall that CFCl$_3$ is nowadays discouraged as a standard for high resolution ^{19}F work precisely because of the fine structure arising from ^{35}Cl/^{37}Cl isomerism.

<div align="right">
Yours sincerely,

C. W. Haigh
</div>

P.S. May I draw the attention of interested readers to a new journal, whose initial pattern was not wholly dissimilar from that of this newsletter? It is 'MatCh, Informal Communications in Mathematical Chemistry', published and edited by Professor Dr. O. E. Polansky, Institut für Strahlenchemie, Max-Planck-Institut für Kohlenforschung, D 433 Mülheim a.d. Ruhr, Germany, from whom further details may be obtained. The predominant emphasis of the first issues was on chemical graph-theory.

References

1. For Part I, see C. W. Haigh, this Newsletter, 226-6 (July 1977).
2. E. Lippmaa, M. Alla, G. Engelhardt and T. Saluvere, this Newsletter, 227-3 (August 1977).
3. G. Pólya, Acta Math. <u>68</u>, 145 (1937).
4. G. Pólya, Z. für Kristallographie, <u>A93</u>, 415 (1936).
5. F. Harary and E. M. Palmer, 'Graphical Enumeration', Academic Press, New York, 1973, chap. 2.
6. A. T. Balaban, ed., 'Chemical Applications of Graph Theory', Academic Press, London, 1976, chaps. 1-5.
7. D. H. Rouvray, Chem. Soc. Rev., <u>3</u>, 355 (1974). [This contains an exhaustive bibliography.]
8. A. T. Balaban, in ref. 6, p. 64 (and refs. there cited).
9. O. Lutz and A. Nolle, this Newsletter, 228-9 (September 1977).

University of Waterloo

Waterloo, Ontario, Canada
N2L 3G1

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

Faculty of Science
Department of Chemistry
519/885-1211
December 14, 1977

Deuterium Splittings in Micellar Solutions

Dear Professor Shapiro:

Recently (Sept. 1977) TAMU Newsletter contained a letter entitled 'Deuterium Splittings in Micellar Solutions' in which the authors commented on the appearance of deuterium quadrupole splittings from perdeuterated benzene and cyclohexane when dissolved in micellar solutions of hexadecyltrimethylammonium bromide. We have been investigating the liquid crystalline properties of this and related systems for some time now.

These materials form lyotropic mesophases which provide extremely small D_2O deuterium splittings, usually less than 20 Hz, to be compared with about 400 Hz for similar phases prepared from decylsulfate or decylammonium for example. However when hydrocarbon chains were specifically deuterated the chain deuterium splittings were found to be similar to those observed for the decylsulfate and decylammonium phases. These results are typical for mesophases prepared from alkyl trimethylammonium or alkyl pyridinium systems and seem to indicate that water is very loosely associated with the headgroup and is essentially isotropic.

The above conclusion is exemplified by the accompanying figure. Here a mixed mesophase containing potassium dodecanoate (KC_{12}) and decyltrimethylammonium bromide (DTMABr) was investigated. All components of the mesophase were kept constant except that the molar ratio of one detergent to the other was varied. The results indicate that some type of water structure built around the carboxylate headgroups can no longer be supported after 30% of the potassium dodecanoate has been replaced. There follows a precipitous decline to small quadrupole splittings for D_2O as this structure is destroyed.

Please credit this letter to Prof. Reeves who handed me a pink piece of paper just before he left for Brazil.

Best wishes,

A. S. Tracey
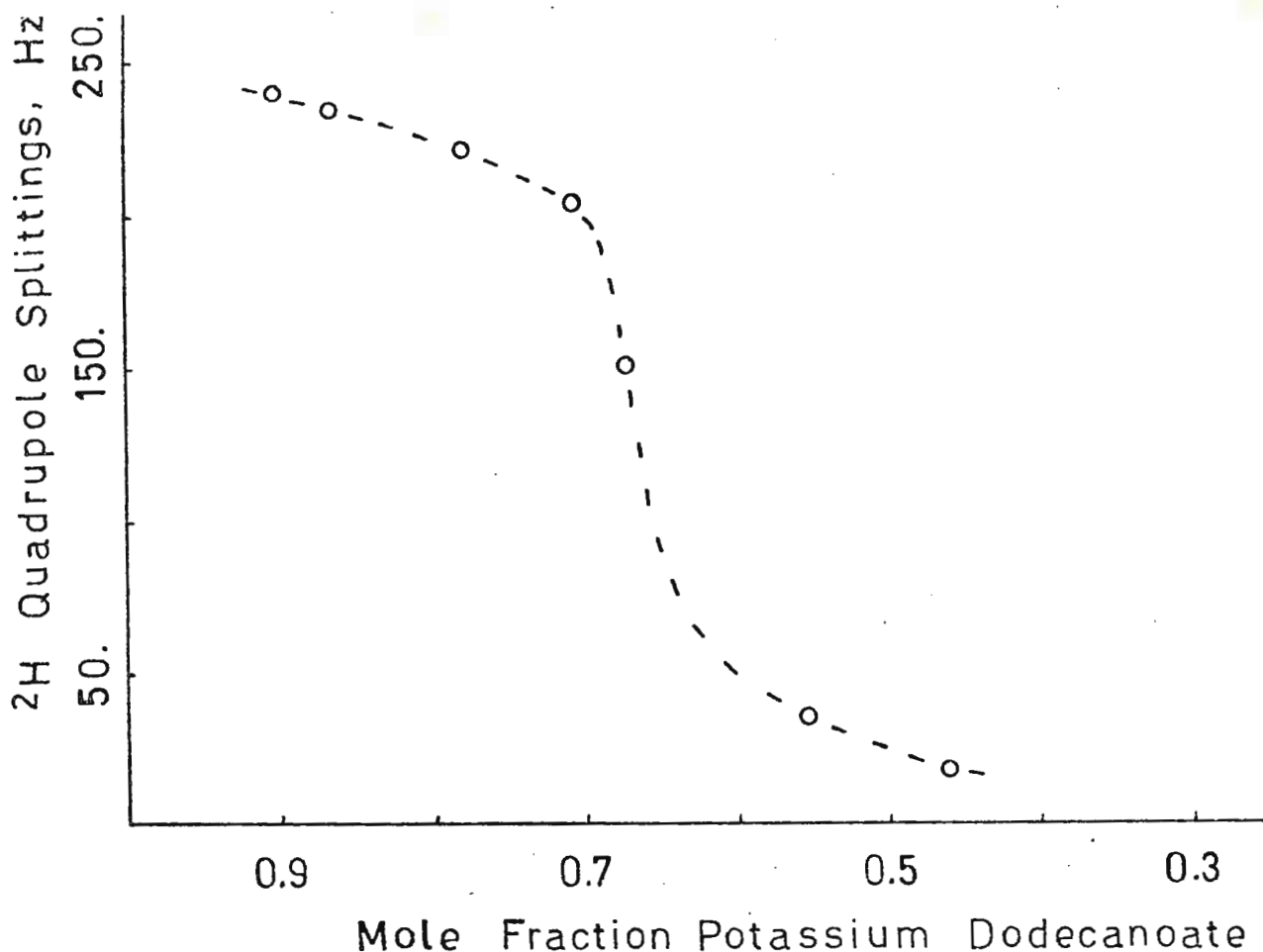
Effect of Exponentiation on Interpolation factor

```
.TY ETEST
        DO 10 L=2,12
        IMASK=2**(36.-L-2)-1
        TYPE 100, L,IMASK
100     FORMAT(I5,2X,O12)
10      CONTINUE
        END

.EX ETEST
LINK:   Loading
[LNKXCT ETEST Execution]
   2    040000000000
   3    020000000000
   4    010000000000
   5    004000000000
   6    002000000000
   7    000777777777
   8    000377777777
   9    000177777777
   10   000077777777
   11   000037777777
   12   000017777777

END OF EXECUTION
CPU TIME: 0.04   ELAPSED TIME: 24.42
EXIT
```

```
.TY ETEST
        DO 10 L=2,12
        IMASK=2**(36-L-2)-1
        TYPE 100, L,IMASK
100     FORMAT(I5,2X,O12)
10      CONTINUE
        END

.EX ETEST
FORTRAN: ETEST
MAIN.
LINK:   Loading
[LNKXCT ETEST Execution]
   2    037777777777
   3    017777777777
   4    007777777777
   5    003777777777
   6    001777777777
   7    000777777777
   8    000377777777
   9    000177777777
   10   000077777777
   11   000037777777
   12   000017777777

END OF EXECUTION
CPU TIME: 0.04   ELAPSED TIME: 25.33
EXIT
```

TUFTS UNIVERSITY

Department of Chemistry

January 10, 1978

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

"One Last Look for Sines"

Dear Barry:

    Having read Professor Kaiser's careful analysis of possible sine
look-up errors in small sine tables, we have carefully re-examined the
data and programs we used to base our conclusions of a minimum 128-
point sine table on.(TAMUNMR 215, 226 & J.Mag.Res., imminent) The
program was written in FORTRAN for our DEC-10 and generated the table
of the requisite length and then generated a mask word which was ANDed
with the number whose sine was to be determined in order to find the
distance between the two points in the table for interpolation. If
L is the $\log_2$ of the sine table length and the computer used has a
36-bit word length, then that mask is determined by

$$L = 2^{(36-L-2)} - 1$$

We found that the number returned from the exponentiation routine was
1 too large as shown in the attached program output if the number 36
was real, but correct if 36 was an integer. Thus, our mask became
zeroes in the cases where L<7, corresponding to table lengths of 64
and less. This happened in our case since we used the variable WRDLEN
for the word length 36. Careful examination of the machine code
generated by both the F40 and F10 compilers reveals that the call is
to a different exponentiation routine if the arguments are dominantly
integer, than if they are dominantly real. Thus, one of the system
routines appears to return numbers slightly too large. This occurs
with both compilers and regardless of whether the compiler is instructed
to "optimize" the code. This is disappointing since one might hope
that a power of two might be obtained by left shifting when all
numbers are clearly integers. Considering that one of our principle
interests has been errors caused by computer programs, this is an
interesting way of discovering one. We will publish a suitable correc-
tion to our forthcoming paper in J.Mag.Res., in which we have actually
found that sine tables as short as sixteen points produce errors too
small to detect in either peak position or intensity in a synthetic
high dynamic range spectrum.

Periodically yours,

James W. Cooper

Medford, Massachusetts 02155

almost

The ∧ Mile High PENIS Laboratory
Department of Chemistry

ᴄℱᴜ

1(303)491-6480
Colorado State University
Fort Collins, Colorado
80523

Titles: ^{113}Cd Spectra of Solids using ^{1}H Decoupling
and Cross Polarization; Symposium on the NMR
of Macromolecules

January 11, 1978

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

Dear Barry:

Dan Netzel of the Laramie Energy Research Center has asked me to
inform the newsletter readers that a symposium on the nmr of macro-
molecules (also a symposium on EPR) will be held as part of the 20th
Annual Rocky Mountain Conference on Analytical Chemistry in Denver,
August 7,8,9, 1978. Requests for information should be sent to:

Dr. Daniel A. Netzel, Chairman
Laramie Energy Research Center
P. O. Box 3395, University Station
Laramie, Wyoming 82071

During the past few months Gary Mennitt (here on sabbatical leave
from Brooklyn College) and Vic Bartuska have been observing ^{113}Cd
chemical shifts of solid complexes using ^{1}H decoupling and, in most
cases, cross polarization. We have been amazed at how small distortions
in the crystal from local symmetry (e.g., "tetrahedral" R_4NCdX_4 complexes)
give rise to such large chemical shift anisotropies. To date our work
has been mainly concerned with observing powder patterns, but we are
now moving into some single-crystal and magic-angle spinning work. (Vic
has been busy trying to remove the magic from magic-angle spinning).

Best regards.

Sincerely,

Gary E. Maciel
Professor

The University of Manitoba

Department of Chemistry
Winnipeg, Manitoba
Canada R3T 2N2

UM

January 9, 1978.

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

Dear Prof. Shapiro:

Short Title: The Vanishing ^{2}H Lock And Bang Your Head Against The Disk.

Recently, two problems have plagued our Bruker WH-90-DS spectrometer.
The first concerns the external ^{2}H-lock on our mid-range probe. The
capillary containing a $CuSO_4.D_2O$ solution had a pinhole, and eventually
the D_2O evaporated. Since the coils are glued to the tube, one has either
to wait for BRUKER to replace the sample block or to build one's own.

The capillary can be made from a 3.0 mm O.D. tube which is heat sealed
at both ends after being filled with a concentrated solution of $CuSO_4.D_2O$.
Cooling the tube in liquid nitrogen simplifies the second seal. The coils
can be wound with 0.004 in. enamel-coated copper wire. A disposable pipet
with the indented bulb end removed serves as a convenient winding tube.
Two thin ($\sim$ 1 mm in width) strips of masking tape arranged crosswise over
the end of the pipet and along the length of the tube facilitate the removal
of the finished coils. Two loops of 15 turns each are wound, separated
by about 2 mm, with 7 cm of lead wire remaining from each coil. The tape
is cut and used to secure the coils for removal. The excess wire between
the coils should be evenly distributed between them, having about 2 mm of
wire joining the coils. The coils are elongated to fit lengthwise against
the capillary, placed on opposite sides in a Helmholtz configuration, and
secured with tape. The unit is replaced in the aluminum block and reconnected
to the probe. The procedure for tuning the circut at the ^{2}H frequency is
similar to that used for tuning the observe-channel on the multinuclear
probe, using a suitable scope (e.g. a Tektronix 475). A 50 Ω load must be
attached to the reflectance box.

The second problem involved our Diablo disk drive. The symptoms were similar
to those described by Dr. J. M. Williams in TAMUNN-266. The problem would

January 9, 1978,
Prof. B. L. Shapiro.

start with a switching on and off of the relay and "ready" light. Subsequent
to this abnormal behavior, we experienced difficulty in loading from, or
storing to, disk. Our drive experienced three head crashes and two trips
to Boston before the problem was identified by Tom Barton from Diablo.

In the disk pack the actual platter is secured to the spindle by a pressure
plate held down by four screws. Even slight jolts to the disk pack can cause
the platter to shift somewhat. You can check to see if this has happened as
follows. Remove the top skin from the drive and loosen the four spring loaded
screws on the back of the drive located behind the interface connector terminals,
(refer to Diablo series 30 disk drive maintenance manual page 2-3, figure 2.5)
Raise the electronics assembly (page 2-3 figure 2-4). Insert a new or trouble-
some disk in the drive and switch the drive to run. As the disk starts to
move, observe the platter from the top and side. There should be no (or very
little) up and down, or in and out motion when viewed from the side or top.

Other problems can arise from dust. All new disks have a little dust on them
and can be cleaned as follows. If the platter spins true, let it reach speed
and use the disk exercises software supplied with the computer. The disk
diagnostic package for the Nicolet 1180 is ideal for this. Test #4 will write
random numbers, block by block, starting at track $\emptyset$ across the entire disk.
Run this test with the cover off. When the heads stop, hit "return" on the TTY
to end the test and switch the drive to load. Remove the disk pack and place
a Kimwipe dampened with isopropanol between the heads. Manually close the heads
onto the Kimwipe (refer to page 5-9 figure 5-8 view A, pulling bale "D" out of the
solenoid will manually load the heads on the Kimwipe). Pull the Kimwipe through
the heads a couple of times. Then buff the heads gently with a dry Kimwipe to
remove the residual film (this is important, failure to do this will result in a
head crash). Test #3 of the Nicolet package reads and writes random numbers from
block to block. This test should be allowed to run for about 24 hrs. to see if
the disk is good. The heads should be cleaned again after the test is finished.
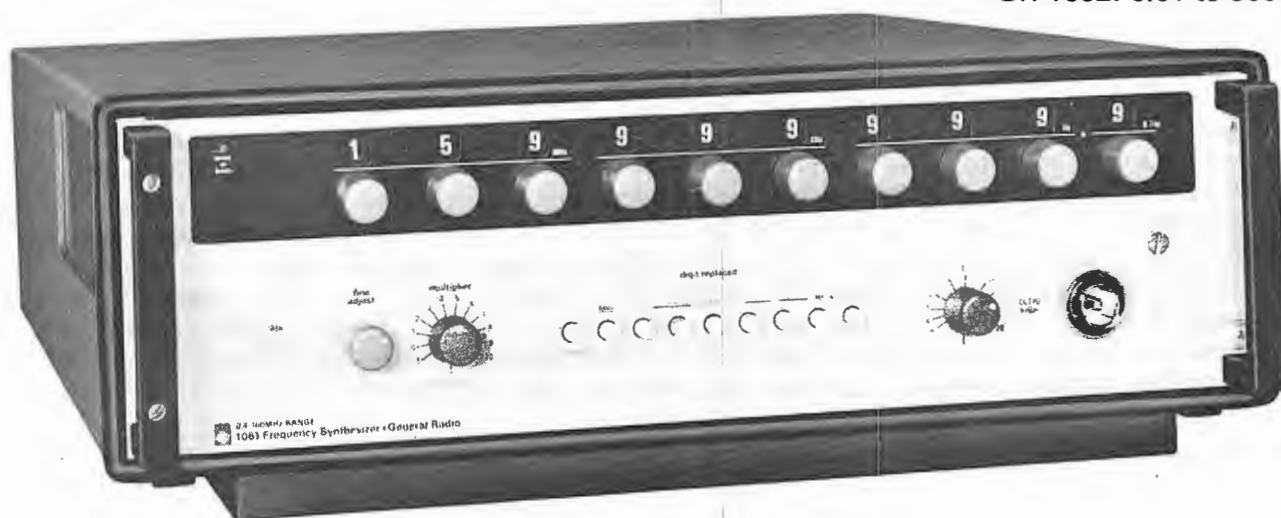
Sincerely,

Walter P. Niemczura.

WPN/ud

P.S. Please credit this contribution to Ted Schaefer's account. Thanks.

Frequency Synthesizers for NMR...

Koninklijke/Shell-Laboratorium, Amsterdam

Shell Research B.V.

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

Uw ref.:

238

Onze ref.:   AG

Amsterdam, January 30th, 1978
Postadres: Postbus 3003
Tel. via telefoniste (020) 20 91 11
Tel. rechtstreeks (020)
    Hr/Mw

Subject: Position vacant for an NMR spectroscopist

Dear Barry,

A position is vacant in the NMR group of our Analytical Department
for a physical-chemist with graduate or postdoctoral experience in
high resolution solid-state NMR spectroscopy.

The work will entail participation in a research and development
programme on the application of solid-state NMR for analytical pur-
poses as well as the measurement and interpretation of ^{1}H and ^{13}C
NMR spectra for a wide range of liquid or soluble materials, including
polymers, exploratory chemicals and oil products.

Candidates are requested to write with curriculum vitae to Dr. G. Dallinga
at the above address.

Yours sincerely,
KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM

(Dr. A.D.H. Clague)

University of Melbourne

SCHOOL OF CHEMISTRY

Parkville, Victoria 3052

24th January, 1978.

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

Dear Professor Shapiro,

SENSITIVITY MEASUREMENTS AND PERFORMANCE OF FX100

We have recently taken delivery of an FX100 spectrometer, the first part of a special order from JEOL for a high sensitivity, multinuclear instrument with triple irradiation facilities and foreground/background data system. Installation of the basic spectrometer (^{1}H, ^{13}C, ^{19}F) is now complete and we are pleased with its performance.

The FX100 exceeds the specification figures by a substantial margin. For example, for ^{13}C, the resolution of proton decoupled benzene (50% in acetone-d$_6$, 100 Hz spectral width, 8K data points, zero time constant exponential multiplier) is 0.09 Hz. The sensitivity obtained under JEOL's standard conditions (90% ethyl benzene, 5000 Hz, 8K data points) but with zero time constant has been recorded as 400:1. We were thus interested in the letter of Zens and Grant (227-19) where they obtained a S/N figure of 274:1 for coupled dioxane (80%) in a 22 mm tube.

There are a number of operating and processing factors which can seriously affect S/N ratios but which are generally not specified when instrument performance is being reported. Our spectra of ethyl benzene show the o and m aryl carbon signals with S/N of 400:1 but each line consists essentially of only one point! Secondly with any protonated carbon the S/N may be enhanced by residual NOE if the decoupler has not been turned off for five times T_1 before measurement. Thirdly, the obvious one, an exponential multiplier changes the S/N as shown for dioxane in the Figure. The spectrum of Zens and Grant appears to have had some exponential multiplier applied, since the splitting due to $^2J_{CH}$ is not apparent.

Our spectra of dioxane show S/N ratios of 44 (JEOL EX=0), 65 (EX=7*) and 81 (EX=14*). All other things being equal, a 22 mm probe should be a factor of 4.84 ($22^2/10^2$) more sensitive than a 10 mm one. This factor brings these figures to 213, 315 and 392 respectively.
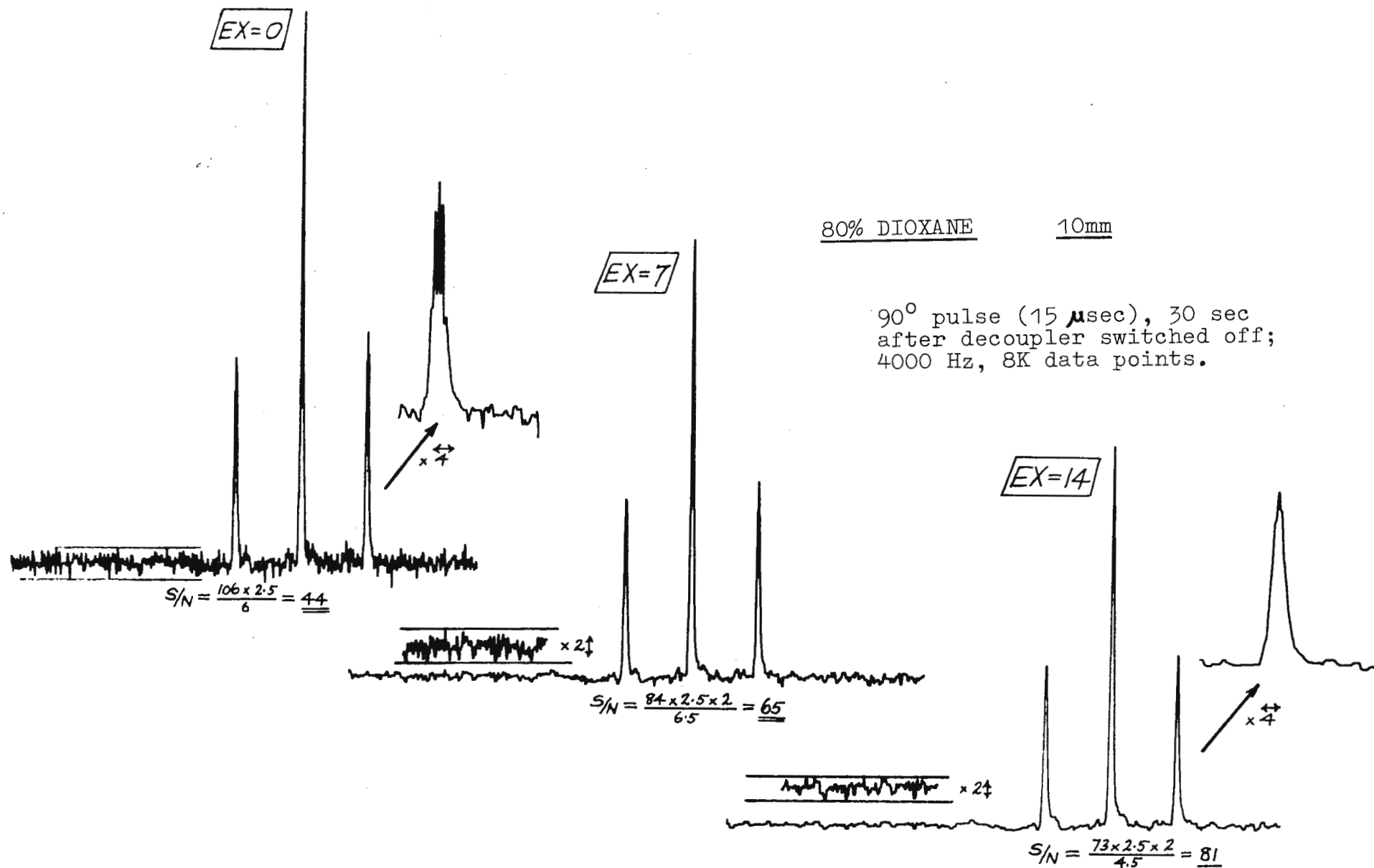
Would it not be better if S/N ratios quoted by manufacturers and users were based on an agreed time constant in the exponential multiplier,for example, zero?

Yours sincerely,

R. A. Craig.
R. A. Craig.

D. P. Kelly.
D. P. Kelly.

*These correspond to line broadenings of 0.54 and 1.08 Hz respectively.

EX=0

EX=7

EX=14

80% DIOXANE   10mm

90° pulse (15 μsec), 30 sec
after decoupler switched off;
4000 Hz, 8K data points.

$S/N = \dfrac{106 \times 2.5}{6} = \underline{\underline{44}}$

$\times 4$

$\times 2\updownarrow$

$S/N = \dfrac{84 \times 2.5 \times 2}{6.5} = \underline{\underline{65}}$

$\times 2\updownarrow$

$\times 4$

$S/N = \dfrac{73 \times 2.5 \times 2}{4.5} = \underline{\underline{81}}$

NATIONAL CHEMICAL RESEARCH LABORATORY

OF THE SOUTH AFRICAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

AIR MAIL

Telephone 74-6011 Telegrams **NAVORSCHEM**

P. O. Box 395

OUR FILE 600/6-Pach.   YOUR FILE   **PRETORIA**

Prof. B.L. Shapiro
Department of Chemistry
Texas A & M University
COLLEGE STATION
Texas 77843

18 JAN 1976

Dear Prof. Shapiro

"RESIDUAL SPLITTINGS IN OFF-RESONANCE DECOUPLED NMR SPECTRA" - ERRATUM

I hope the following "erratum" will qualify as a regular contribution
to your NMR Newsletter.

Dr Klaus Roth from the "Freie Universität in Berlin" has pointed out to
me that formula [3] in my communication[1] on "Residual Splittings in Off-
Resonance Decoupled NMR Spectra" is incorrect and should read

$$\Delta\nu = J_R[(\gamma H_2)^2 + \tfrac{1}{4}(J_0^2 - J_R^2)]^{\frac{1}{2}} / (J_0^2 - J_R^2)^{\frac{1}{2}} \quad \dots\dots\dots\dots\dots\dots \text{[3]}$$

The necessary condition for the simplification to the final formula [4],
which correlates the decoupler offset $\Delta\nu$ with the residual splitting J_R at
a particular decoupling power γH_2,

$$\Delta\nu = \gamma H_2 \, J_R/(J_0^2 - J_R^2)^{\frac{1}{2}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{[4]}$$

should therefore be replaced by $\gamma H_2 \gg \tfrac{1}{2} (J_0^2 - J_R^2)^{\frac{1}{2}}$.

In fact, it is easily seen that the original restricting condition
$(\gamma H_2 \gg \tfrac{1}{2}|J_0 - J_R|)$ and the corrected expression $\gamma H_2 \gg \tfrac{1}{2} (J_0^2 - J_R^2)^{\frac{1}{2}}$ can be
reduced to the simpler and better defined condition $\gamma H_2 \gg \tfrac{1}{2}|J_0|$ since
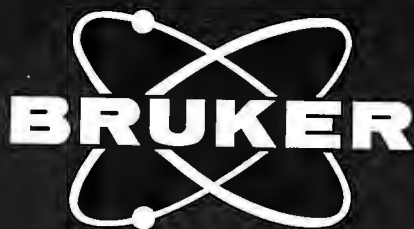$0 < |J_R| < |J_0|$.

Fortunately, the error does neither affect the final formula [4] nor any
of the conclusions drawn in the communication.

Yours sincerely

K. Pachler
HEAD: PHYSICAL CHEMISTRY DIVISION

Reference:
(1)   K.G.R. Pachler, J. Magn. Resonance 7, 442 (1972).

Department of Energy
Laramie Energy Research Center
P.O. Box 3395, University Station
Laramie, Wyoming 82071

February 1, 1978

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

Dear Dr. Shapiro:

<u>Carbon-13 Chemical Shift Assignment for a Pheromone of Pharaoh's Ant,</u>

Compound <u>1a</u> has been identified as a pheromone of pharaoh's ant, <u>Monomorium pharaonis</u>[1]. We have synthesized 1a (2,3) (shown below) and several analogs bearing methyl groups at the 3, 5, and/or 7 positions. In each case the substituent geometry is that of <u>1a</u>, ie, each may be regarded as an "all-cis" structure as is <u>1a</u>. ^{1}H NMR data and infrared data (4) permitted us to assign <u>trans</u>-fusion of the two rings. Compounds not bearing alkyl groups on both C-3 and C-5 existed in chair form; compounds such as <u>1a</u> were best regarded in boat structure. ^{13}C NMR assignments were easily made based on various standard techniques. In particular, butyl carbon resonances for <u>1a</u> were based upon spin-lattice relaxation data. The segmental motion of the butyl carbons gave substantial increases in the chain carbon relaxation times as compared to the relaxation times of the ring methylene carbons. A strong δ-syn-axial effect involving the C-5 methyl and the butylmethylene carbons of <u>1a</u> was noted which was also observed in the methyl groups of the 3,5-dimethyl analog.

Incidental to this work was an attempt to assign ^{13}C NMR resonances to the compounds which are diastereomers of 1a. These compounds had been previously synthesized (2,3) and laboriously purified. The ^{1}H NMR and infrared data suggested pronounced differences in conformation, but because of difficulty in synthesis analogs were not available. Our assignments of ^{13}C resonances for 1a and its isomers are given in Table 1. This set of assignments appears to be consistent with the ^{1}H NMR and infrared data. Compounds 1d, however, produced a ring methylene carbon signal at 19.8 ppm. This was quite high compared to our other signals. Shown below are our compounds 1a-d in the conformations we believe they retain.

1a	1b	1c	1d
Trans-Fusion	Trans-Fusion	Cis-Fusion	Trans-Fusion
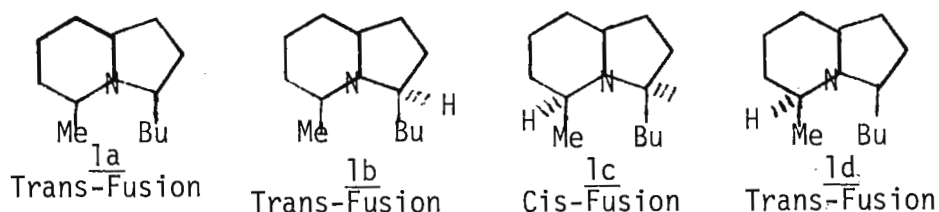
Ref:

1. F. J. Ritter, I. E. M. Rotgano, E. Talman, P. E. J. Verwiel, and F. Stein, Experientia 29, 530 (1973).

2. J. E. Oliver and P. E. Sonnet, J.Org.Chem., 39, 2662 (1974).

3. P. E. Sonnet and J. E. Oliver, J.Heterocycl.Chem., 12, 289 (1975).

4. E. Talman, F. J. Ritter and P. E. J. Verwiel, Pac. Inst. Symp. Mass. Spec., Biochemistry and Medicine, Milan, 1973.

Sincerely,

P. Sonnet

D. Netzel

Enclosure:
As stated

^{13}C NMR Shifts[a] for 3-butyl-5-methyloctahylroindolizines

No.	Compound[b]	C-1	C-2	C-3	Ring Carbons C-5	C-6	C-7	C-8	C-9	5-CH$_3$	α-CH$_2$	Butyl Carbons β-CH$_2$	γ-CH$_2$	δ-CH$_3$
1a	(5Z,9Z)-3-butyl-5-methyl X	31.8	29.7	61.8	59.7	36.4	25.3	30.9	67.6	22.9	39.8	28.7	23.2	14.3
1b	(5E,9E)-3-butyl-5-methyl X	33.0	26.8	58.6	51.8	35.2	24.9	30.6	58.9	20.9	25.2	29.6	23.3	14.3
1c	(5Z,9E)-3-butyl-5-methyl X	26.6	19.6	55.0	48.4	36.4	27.6	29.1	59.4	20.6	29.1	28.9	23.5	14.4
1d	(5E,9Z)-3-butyl-5-methyl X	33.2	32.0	55.4	47.2	33.1	19.8	30.1	58.7	7.4	28.44	28.36	23.5	14.3

a. PPM from TMS

b. Z and E refer to the cis and trans hydrogen relative to the alkyl on C-3.

c. X = octahydroindolizines

Department of Chemistry

The Florida State University
Tallahassee, Florida 32306

January 19, 1978

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

<u>Postdoctoral Positions Available</u>

Dear Barry:

Leo Mandelkern and I have several postdoctoral positions available starting this spring or summer. In each case the successful candidate will utilize all of our major nmr instrumentation (including a Bruker HX-270 and our SEMINOLE 35kGauss multi-nuclei spectrometer as well as an FT Bruker HFX-90).

We have sufficient funding to fill three positions:

1. <u>Physical or organic chemist with computer programming experience</u> (salary, $\sim$ \$10K; to work with GCL). Two responsibilities: (a) to set up the software package for our new Data General Eclipse S-130 computer, which will be interfaced to the SEMINOLE and a microcomputer network; (b) to continue experimental and/or theoretical work in variable frequency ^{13}C relaxation studies of alkyl chain dynamics (see Levy, et al, JACS, <u>99</u>, 5492, and JACS, <u>100</u>, Jan. issue, in press).

2. <u>Physical, polymer or organic chemist</u> to work on ^{13}C nmr studies of synthetic high polymers in solution and bulk liquid states (see Macromolecules, <u>10</u>, 557; also D.E. Axelson and L. Mandelkern, J. Poly. Sci., <u>13</u>, in press). (Joint position, with Leo Mandelkern (primarily) and G.C. Levy, salary $\sim$ \$10K.)

3. <u>A physical chemist or chemical physicist with high power rf experience</u> to help develop high resolution solids FT nmr capabilities for the SEMINOLE spectrometer and apply that methodology to solid bulk polymer studies (joint position, salary $\sim$ \$12K).

Anyone interested in one or more of these positions should write to me and also arrange to have two letters of recommendation forwarded directly. Starting dates are not critical, except perhaps for position 2 (early start desired). Each position is for one year, with renewal negotiable provided funding remains available.

Yours sincerely,

George C. Levy
Professor

GCL:dt

UNIVERSITY OF CALIFORNIA, SAN FRANCISCO

SCHOOL OF PHARMACY
DEPARTMENT OF PHARMACEUTICAL CHEMISTRY   SAN FRANCISCO, CALIFORNIA 94143

December 29, 1977

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

       <u>Rotating Frame Spin-Lattice Relaxation in the Presence of an</u>
       <u>Off-resonance rf Field. Studies of Slow Motion on a</u>
       <u>Commercial FT Instrument.</u>

Dear Barry:

We have been developing an off-resonance $T_{1\rho}$ technique which appears to be more easily performed on a Fourier transform NMR instrument than either T_2 experiments or the more usual on-resonance $T_{1\rho}$ experiments. Information concerning motions with correlation times longer than the inverse Larmor frequency can be obtained without recourse to T_1 measurements. We have illustrated the $T_{1\rho}^{off}$ method for dipole-dipole relaxation of protons due to other protons (1) and of carbon-13 caused by protons (2). Rotational correlation times were readily determined for the viscous liquid glycerol (1) and for several proteins in aqueous solution (2,3). We have also extended the technique to examine scalar relaxation of the second kind, specifically observing ^{31}P in PBr_3. The parameter of interest for the $T_{1\rho}$ experiment is the ratio R of the ^{31}P resonance intensity in the presence and absence of an rf field applied off-resonance. The Figure shows the experimental ratio for three different rf field strengths as a function of the frequency off-resonance and the excellent fit of the theoretical curves to the data. The curves were calculated using a bromine relaxation time of 0.10 μs in excellent agreement with the published T_1 of bromine in PBr_3 (4). Although the extraction of motional information does not require an explicit relaxation time determination, it is possible to calculate an on-resonance $T_{1\rho}$ of 0.13 sec from our data in reasonable agreement with the published value of 0.17 sec (5).

                Yours truly,

                Tom

                Thomas L. James
                Assistant Professor of Chemistry
                and Pharmaceutical Chemistry

                Gerald B. Matson
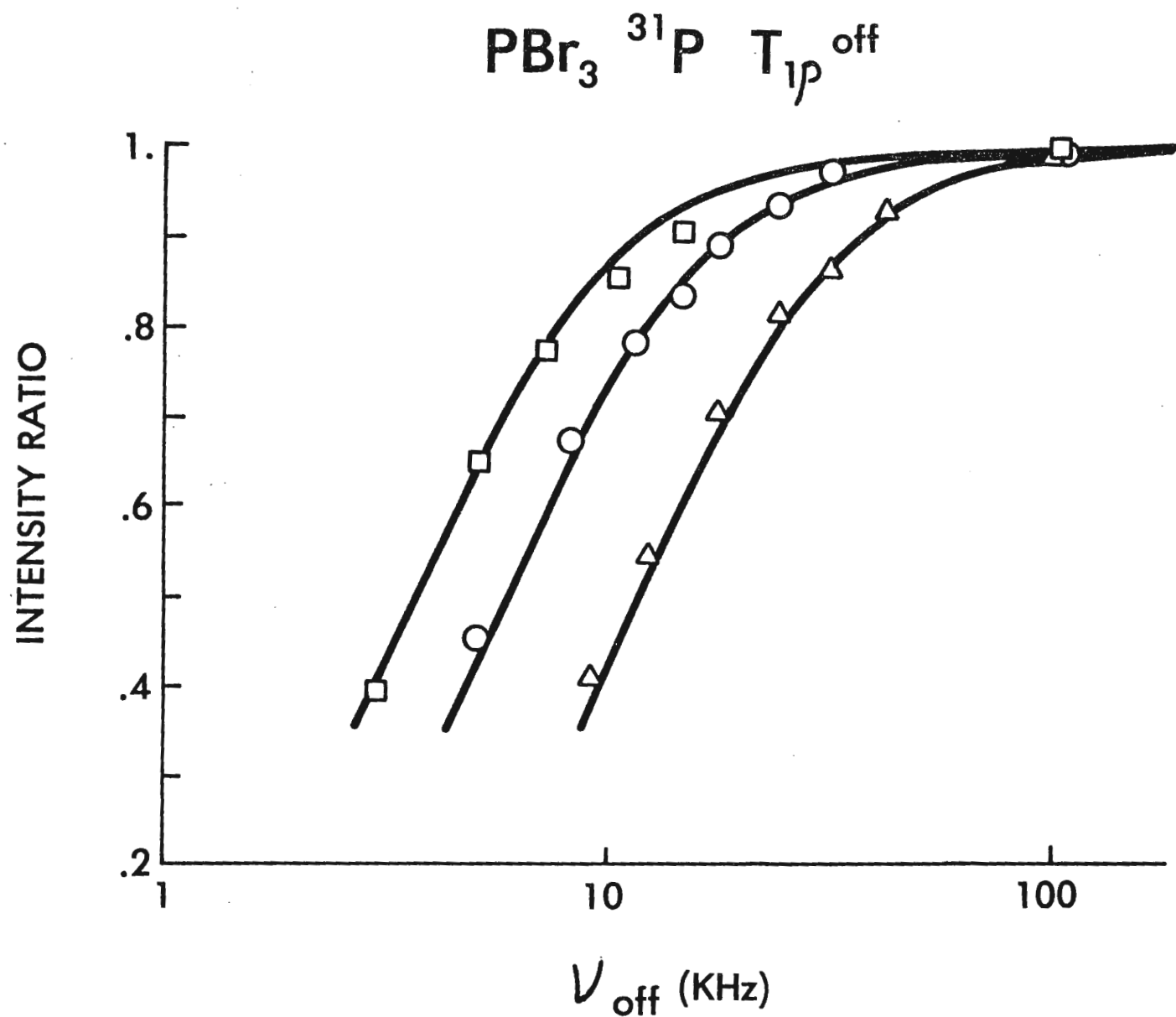   Assistant Research Spectroscopist

TLJ/GBM:gfc

$$PBr_3 \ {}^{31}P \ T_{1\rho}{}^{off}$$

Figure 5. 40.5 MHz ^{31}P spectra of PBr$_3$ at 32^{0}C in the presence of an rf field H$_1$ of strength 0.983 gauss (△), 0.492 gauss (○), and 0.308 gauss (□) as a function of the off-resonance frequency ν_{off} for the rf field.

(1) James, T.L., Matson, G.B., Kuntz, I.D., Fisher, R.W., and Buttlaire, D.H., J. Magn. Res., in press.

(2) James, T.L., Matson, G.B., and Kuntz, I.D., J. Amer. Chem. Soc., in press.

(3) James, T.L., Matthews, R., and Matson, G.B., submitted.

(4) Rhodes, M., Aknes, D.W., and Strange, J.H., Mol. Physics, 15, 541 (1968).

(5) Leipert, T.K., Noggle, J.H., Freeman, W.J., and Dalrymple, D.L., J. Magn. Reson., 19, 208 (1975).

UNIVERSITY OF UMEÅ
Department of Organic Chemistry
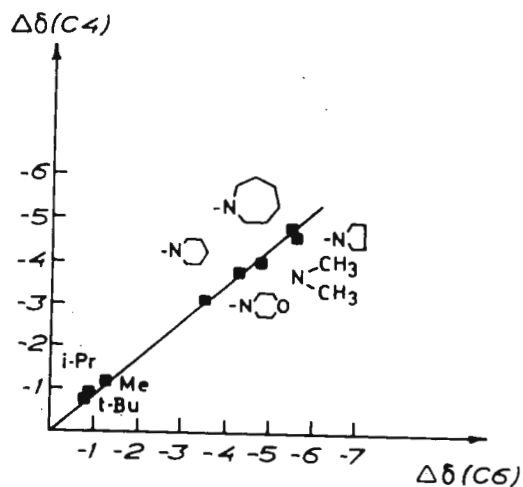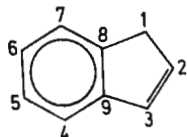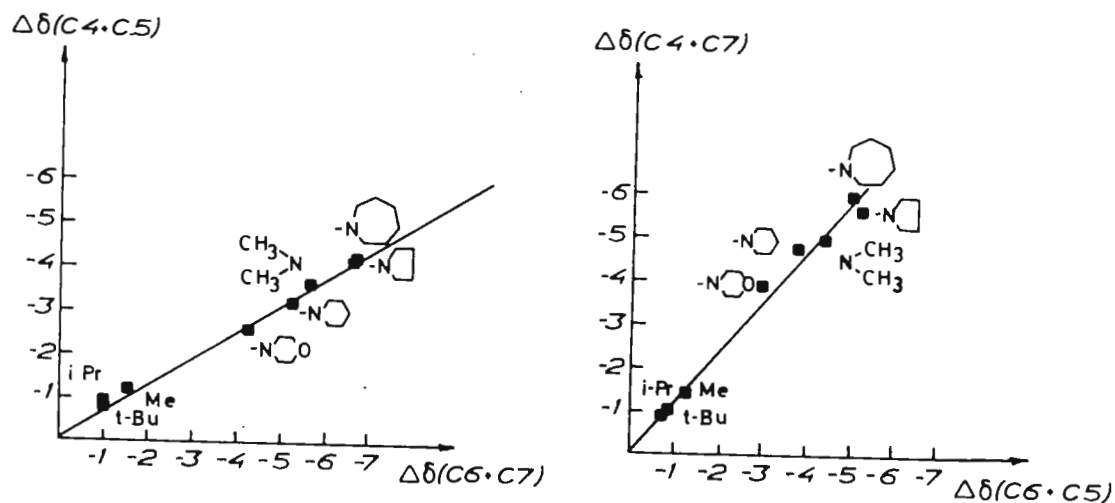
January 27th 1978.

Professor Bernard L. Shapiro

Texas A & M University

Department of Chemistry

College Station TX 77843

Alkyl Group Hyperconjugation as Probed by CMR.

Dear Barry,

Our interest in planar carbanions as characterized by ^{13}C NMR, and the problem how to interpret the observed alkyl group effects, prompted us to look into the substituent effects of the parent carbon acids. We found the 2-substituted indenes to be ideal for these purposes, partly due to their rigidity and planarity, but mainly due to circumstance, that the C5 - C6 chemical shift differential of symmetry reasons should be a reliable probe of through-bond π-effects. For the alkyl groups we noticed an alternating pattern very similar to the trend observed for analogs having a cycloamino substituent in the 2-position. Most interestingly the interaction was most significant for methyl, an observation which supports the classical view of hyperconjugation. Any through-space effect can be excluded to account for this observation. Another evidence in favor of a σ-π overlap is the fact, that introduction of methyl groups in the remaining positions of the five-membered ring did not affect the C5 - C6 shift differential. The similarity in alkyl and cycloamino group effects is illustrated on the following page by simple variable-by-variable plots

Kindest regards

/ Ulf Edlund /

# University of Illinois at Urbana-Champaign

January 5, 1978

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

Dear Professor Shapiro:

### SST Probe; More SEFT; ^{2}H NMR and Neutron Diffraction; Postdoc Available

I would like to show Newsletter readers some recent results we have obtained in high-field ^{13}C and ^{2}H NMR.

First, we have built a sideways-spinning tube (SST) probe for our 3.52T widebore supercon spectrometer. We use 20 mm tubes, sample size is about 6.5 mls, and sensitivity on the standard dioxane test on our prototype probe is 230:1--about the same as commercial systems using up to twice this sample size. Our advantage is of course due to use of solenoid rather than Helmholtz coil geometry. Using the SST-probe we have looked at T_2 relaxation behavior of methine and nonprotonated aromatic carbons in proteins, using spin-echo FT methods. The following normal and spin-echo Fourier transform ^{13}C NMR spectra

Spin-echo FT
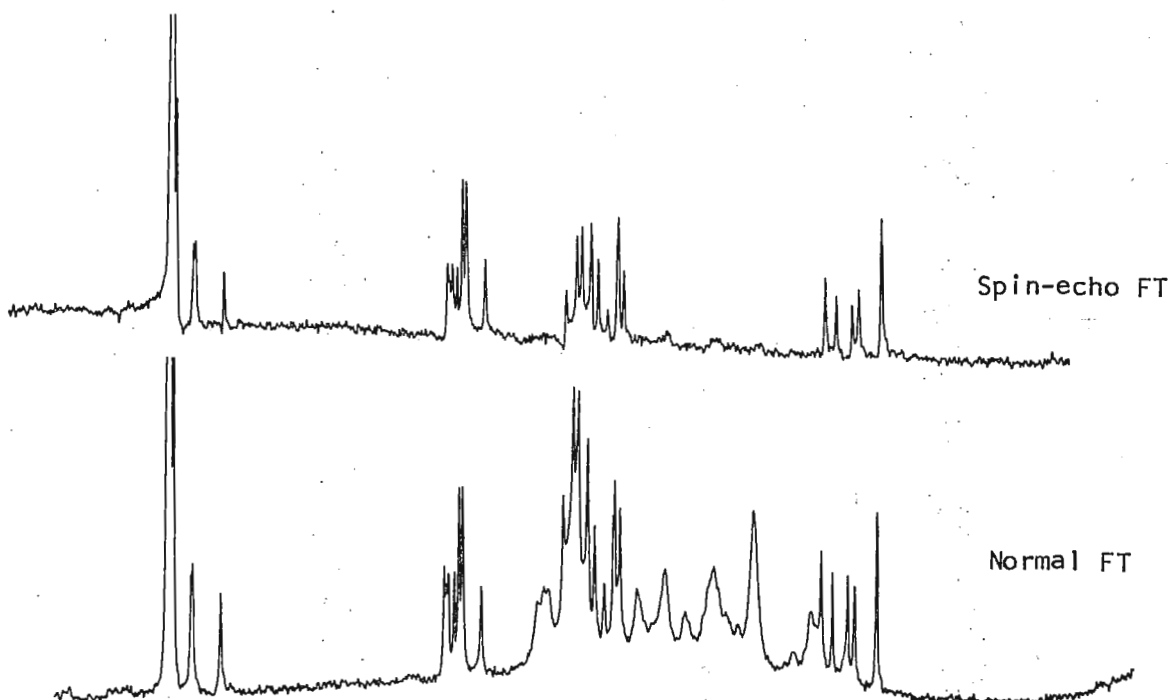
Normal FT

of lysozyme (12,000 scans) were taken under conditions of <u>full</u> proton de-coupling: the top spectrum is a SEFT spectrum with τ = 40 msec, the bottom a normal FT spectrum (τ = 0). The SEFT spectrum only contains contribu-tions from nonprotonated carbons--the method is thus an alternative to weak-decoupling/convolution difference schemes, but does away with the base-line manipulation stage.

Second, I would like to note some combined NMR and neutron diffraction results we have obtained on specifically ^{2}H-labelled phospholipids, of the following general structure:
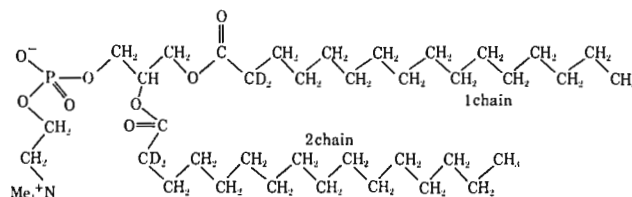
We first reported ^{2}H NMR of labelled model membrane systems in TAMUN some time ago (<u>159</u>, 6). We have now made a large range of these compounds, and have obtained ^{2}H NMR data on our homebuilt 5.4T spectrometer, together with ~1.5 Å neutron Fourier (difference) profiles.

Deuterium FT NMR

$\Delta\nu_Q$ = 33.4 kHz

(25mgs/10 mins)

Neutrons

d = 33.5 Å (!)
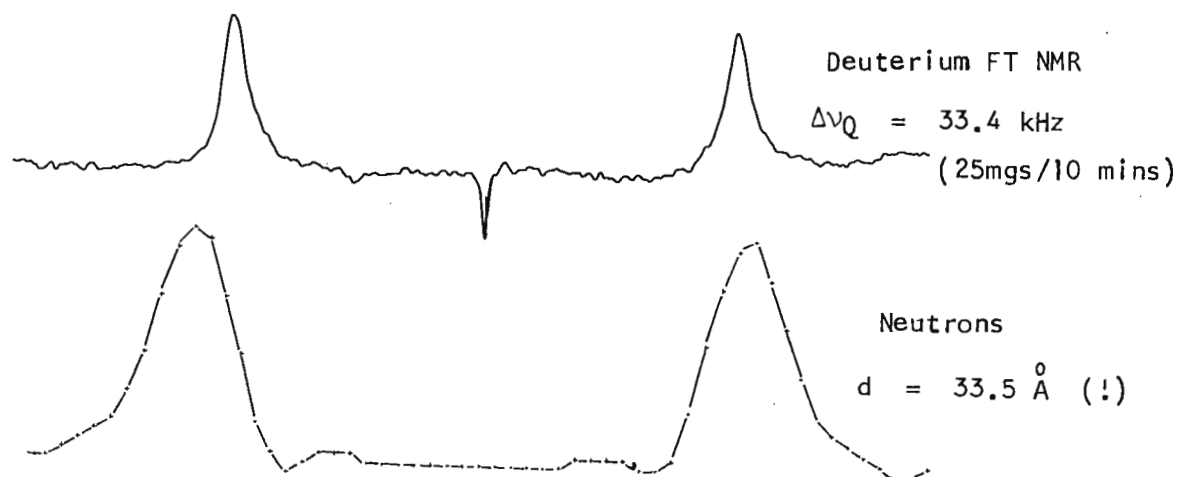
The latter data gives the precise spatial disposition of the ^{2}H nucleus, and we have used this information to check out a variety of mathematical treatments of the NMR data which in theory may give the same results.

We have obtained excellent agreement between the NMR calculations (for a lecithin-cholesterol membrane system) and the neutron experiments, as shown in the following table:

Method	Chain length ($\overset{\circ}{A}$)	Membrane thickness ($\overset{\circ}{A}$)
NMR (no chain tilt)	11.4_2	30.9
NMR ($13°$ chain tilt)	11.8_6	31.9
Neutron diffraction	11.9_5	33.5

I shall have a postdoc position available for the Fall for work in the ^{13}C, ^{2}H and/or neutron diffraction area (the latter to be done in collaboration with David Worcester at A.E.R.E., Harwell and I.L.L., Grenoble), and would be pleased to hear from any interested parties.

Yours sincerely,

Eric Oldfield
Assistant Professor of Chemistry

EO:nw

the University of Alabama in Birmingham / UNIVERSITY STATION/BIRMINGHAM. ALABAMA 35294

the Medical Center / SCHOOL OF MEDICINE / COMPREHENSIVE CANCER CENTER

January 4, 1978

<u>Bruker HX-90 Phantom Free Induction Decay</u>

Dear Barry,

We encountered a serious problem recently with our spectrometer which manifested itself in the form of freak FID's such as the one shown above for ^{1}HOD. The problem may have been with us for some time in a less noticeable form and therefore we thought that other Bruker users might be interested in our findings.

We attacked the problem by checking the receiver section of the spectrometer, and we discovered that the 2.05 MHz IF-reference frequency was jumping occasionally by thousands of hertz. Further checks indicated that the $[30 \text{ MHz} + \Delta f_1/3]$ signal in the LO-PROTONEN section was fluctuating in the same manner. Tracing the signal further, we found that the $[10 \text{ MHz} + \Delta f_1/9]$ signal was the source of the problem. When we changed the ppm switch from $+\Delta f$ to $-\Delta f$, the problem disappeared. We then exchanged the 10.000 MHz Quartz Oscillator cards in the f_1 and f_2 channels of the crystal oven and the instability was transferred from the f_1 channel to the f_2 channel. After replacing the transistors and diodes on the faulty oscillator PC board, the problem was alleviated.

We suggest that users monitor the <u>short term</u> stability of signals derived from the LO-PROTONEN section as an occasional precautionary measure. The performance of these circuits may not be taken for granted, and one may not be able to rely on obvious aberrations in performance as a clue that something is wrong.

Yours truly,

Jerry L. Dallas
NMR Core Facility
Comprehensive Cancer Center

JLD/cd

P.S. Please credit this contribution to Dr. Robert E. Lenkinski

the University of Alabama in Birmingham / UNIVERSITY STATION/BIRMINGHAM. ALABAMA 35294

the Medical Center / SCHOOL OF MEDICINE / COMPREHENSIVE CANCER CENTER

JOHN R. DURANT, M.D., DIRECTOR

January 25, 1978

(205) 934-5077

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

Dear Dr. Shapiro:

We are recruiting a Manager for the NMR Core Facility of the Compre-
hensive Cancer Center. The facility now consists of a Bruker HX-90 spec-
trometer (Nicolet 1085 data system) modified for multinuclear operation by
Dr. Dan Traficante of MIT and also equipped with about eight probes for
specific nuclei. We are presently in the process of reaching a final
decision on the purchase of a superconducting spectrometer system(s), which
will also be managed by this individual (i.e. purchase funds already avail-
able). Managerial duties include spectrometer maintenance, development of
facilities and techniques for biomedical research (electronics technician
available), and interaction with various users of this facility. The
qualifications in order of importance are: 1) expertise in nmr spec-
trometer electronics and operation, 2) general applications of nmr spec-
troscopy, and 3) biomedical applications of nmr. The candidate could hold
a B.S., M.S. or Ph.D. Salary and status are negotiable. This person will
be responsible for day to day operation of the Cancer Center NMR Core
Facility. While, as Director, I have ultimate responsibility for this
Facility, it is my policy to give the manager a maximum degree of freedom
and responsibility. Some of the work will be on a service basis; the
majority will involve collaboration; independent research in the general
areas of interest of the Cancer Center is encouraged. We are not looking
specifically for a faculty level person. In fact, we would probably prefer
a more junior level appointment. However, we wish to leave open the possi-
bility of a faculty appointment to a person of exceptional experience
and/or promise.

Please have suitable candidates write to me or telephone
(205-934-5696). Thank you for your cooperation.

Sincerely yours,

Jerry D. Glickson
Director, NMR Core Facility
Associate Professor of
Biochemistry

JDG/cd

STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305

STANFORD MAGNETIC RESONANCE LABORATORY

Professor Oleg Jardetzky

(415) 497-6153
(415) 497-4062

January 30, 1978

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

RE: TAMU NMR Newsletter

Dear Barry:

With the forthcoming departure of our Operations Manager, Dr. W. W. Conover
for a position at Nicolet, an opening is created on our staff for an individual with
a high degree of skill in the design, construction and maintenance of electronic
equipment related to NMR. The primary duties of this individual will be the mainten-
ance and continual upgrading of the existing HXS-360 facility, training and consul-
tation with users and development of new applications of magnetic resonance and
related technology. Should the applied-for funding be approved, he will be respons-
ible for the construction of a 600 MHz instrument. Depending on his background
and interests, he can additionally have substantial freedom in the choice of new
instrumental or methodological developments or collaboration on current biophysical
problems. We are interested in a highly talented, highly competent and highly
motivated individual. The overriding considerations are ability and productivity,
but the requirement for a Ph.D. in an exact science or a graduate degree in engineer-
ing would be waived only in the most exceptional circumstances. The appointment
is at the level of Research Associate and salary is negotiable, depending on the
candidate's qualifications and years of applicable experience.

I will very much appreciate your recommending any potential candidate(s) and
bringing this opportunity to his attention. Stanford University is an equal opportunity/
affirmative action employer.

Yours sincerely,

Oleg Jardetzky

OJ/aw

THE UNIVERSITY OF ROCHESTER
COLLEGE OF ARTS AND SCIENCE
RIVER STATION
ROCHESTER, NEW YORK 14627

DEPARTMENT OF CHEMISTRY

January 20, 1978

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

Dear Barry:

I will have two postdoctoral positions available in my lab-
oratory in the next few months. The starting dates are flexible
(anytime during the next six to eight months) as I am primarily
interested in the quality of the applicants. The main thrust of
our research program is the spectroscopic study of drug:nucleic
acid complexes using both oligonucleotides and polymers. I am
particularly interested in persons with nucleic acid experience
and/or a background in spectroscopy, although top-notch candidates
in all areas will be considered for this biophysical postdoctoral
position. We make extensive use of proton FT nmr, circular dichroism,
flourescence, and absorption spectroscopies in our studies which
are designed to investigate the geometry, thermodynamics and
sequence preferences that are associated with the intercalation
of drugs into nucleic acids. A recent article in Nature (269,
627 (1977)) illustrates one of our recent contributions to this
area and provides references to some of our earlier work.

If you know of any candidates for these positions I would
appreciate it if you would inform them of these openings or forward
their name and address to me and I will contact them directly.
Interested applicants should forward a curriculum vitae, copies of
their transcript(s) and arrange to have three letters of recommen-
dation sent on their behalf.

Sincerely yours,

Tom

Thomas R. Krugh
Associate Professor

TRK:lcb