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NMR
NEWSLETTER

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September, 1982

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DEADLINE DATES: No. 289   4 October 1982
                              No. 290   1 November 1982

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

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

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

4000 Düsseldorf, den 27.7.82
Universitätsstr. 1/26.42.U1.32
Telefon 0211 - 311-2288/2287
Telex 8 587 348 uni d

to
Prof. Dr. B. Shapiro
Department of Chemistry
Texas A & M University
College Station
TX 77 8 43 USA

Dear Professor Shapiro!

In collaboration with Dr. Martin Feigel[*] we started our interests
for applications of 2DNMR in organo phosphorus chemistry.
We looked into L-Menthyl-dichlorophosphine, having the (1R, 3R, 4S)-
configuration for the menthyl skeleton. A 40% v/v solution in
toluene-d_8 yielded the following 360 MHz ^{1}H NMR data.: Table 1.
Conventional ^{1}H-SR and ^{1}H- ^{1}H -DR confirmed the spin assignment
given in Table 2. 90,52 MHz ^{13}C NMR results for a 60% v/v solution
in toluene-d_8 are listed in Table 3.

Yours sincerely

G. Tossing   *G.Hägele*

[*]Martin Feigel   Gudrun Tossing   Gerhard Hägele
present address:
University of
California,
Los Angeles
Dept. Chemistry   Wolfgang Kückelhaus

N.B.: Fig. 1 was obtained using KUEPLO, a program which
      predicts molecular geometry and allows for intra-
      molecular and overall rotations. KUEPLO-parameters
      were fed into E. Keller's SCHAKAL plotting routines.

Keywords: 2DNMR of L-Menthyldichlorophosphine
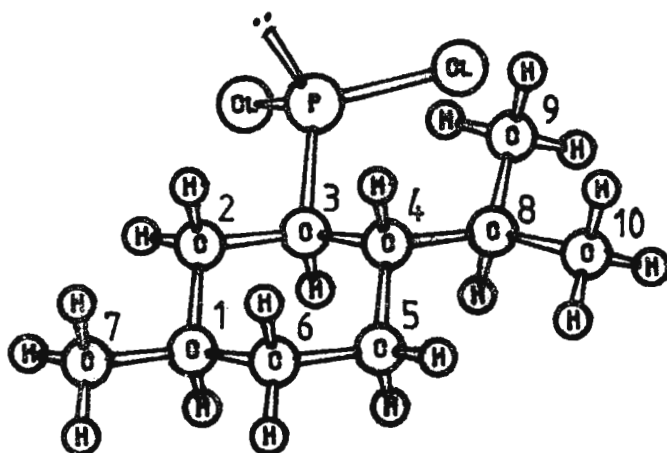
C_i	δ_C ppm	J_{PC_i} Hz
C_3	49.416	53.2
C_4	44.417	8.9
C_6	34.651	
C_2	32.812	
C_1	32.366	
C_8	28.237	24.4
C_5	24.015	6.1
CH_3-7	22.362	
CH_3-10	21.232	
CH_3-9	15.508	2.4

Table 3

Nr.	H_i	δ_H ppm
1	H_{2eq}	2.259
2	H_8	2.216
3	H_{3ax}	1.783
4	H_{6eq}	1.673
5	H_{5eq}	1.650
6	H_{4ax}	1.416
7	H_{1ax}	1.279
8	H_{2ax}	1.181
9	H_{5ax}	0.998
10	H_{6ax}	0.835
11	CH_3-7	0.911
12	CH_3-9	0.873
13	CH_3-10	0.798

Table 1

$H_i H_k$	$J_{H_i H_k}$ Hz
$H_{2ax}H_{2eq}$	(−) 11.9
$H_{5ax}H_{5eq}$	(−) 11.5
$H_{3ax}H_{4ax}$	11.3
$H_{4ax}H_{5ax}$	11.5
$H_{4ax}H_{5eq}$	3.2
$H_{4ax}H_8$	3.2
$H_{1ax}CH_7$-7	6.3
$H_8 CH_3$-9	6.7
$H_8 CH_3$-10	6.8
PH_{3ax}	(−) 26.8
PH_{2ax}	4.8
PH_{2eq}	2.0
PH_{4ax}	3.3
PH_8	4.1
PCH_3-9	1.7

Table 2

Institut für Organische Chemie I
der Universität Düsseldorf

4000 Düsseldorf, den 11.8.1982
Universitätsstraße 1
Fernsprecher 311-2298/99

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

^{13}C NMR of a dynamic silatropic lactam-lactim equilibrium

Dear Professor Shapiro:

It is well known that silylated amides may carry the silyl group either at the nitrogen or at the oxygen atom. When both isomers simultaneously occur, dynamic NMR spectra are observed due to the migratory aptitude of the silyl group[1]. In the case of silylated lactams, the position of the silatropic lactam-lactim equilibrium might be used as an indicator[2] for the corresponding prototropic equilibrium which usually is far on the lactam side. Silylated saturated lactams have been shown in numerous studies to exist in the N-silyl form. By the recent use of ^{15}N NMR[3], also reported in this Newsletter (277, 1), the same conclusion was reached. However, in a short note Russian workers[4] claimed the presence of the lactim tautomer in equilibrium with the predominating lactam form in the case of trimethylsilylated 2-piperidinone on the basis of ^{1}H(^{29}Si) INDOR spectra.

In view of the important implications by such a finding, I studied the trimethylsilylated 6-methyl-2-piperidinone which should further destabilize the lactam form on steric reasons. The temperature dependent ^{13}C NMR spectra shown in the figure indeed confirm the presence of a dynamic equilibrium.
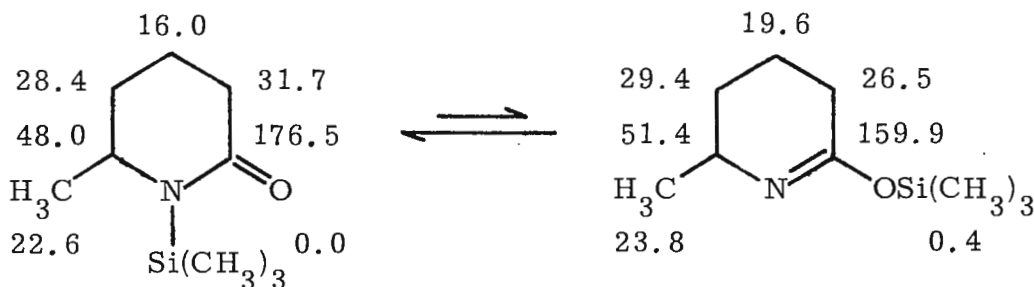
Assignment of the resonances in the slow exchange spectrum is easily accomplished by examination of the different broadening and coalescence behavior of the various pairs of carbon resonances. The position of the equilibrium is strongly temperature dependent as indicated by the shifts of the averaged but still broad resonances of C-4 and C-6 at 70°C. As a consequence, some resonances of the minor lactim isomer are still visible as broad humps at ambient temperature.

Sincerely yours,

1) J. F. Klebe, Acc. Chem. Res. 3, 299 (1970).

2) A. Steigel and R. Fey, Chem. Ber. 113, 3910 (1980); A. Steigel, Chem. Ber. 113, 3915 (1980).

3) P. R. Srinivasan, S. P. Gupta, and S. Y. Chen, J. Magn. Res. 46, 163 (1982).

4) A. I. Albanov, M. F. Larin, V. A. Pestunovich, M. G. Voronkov, E. P. Kramarova, and Y. I. Baukov, Zh. Obshch. Khim. 51, 488 (1981); Chem. Abstr. 94, 207997 (1981).
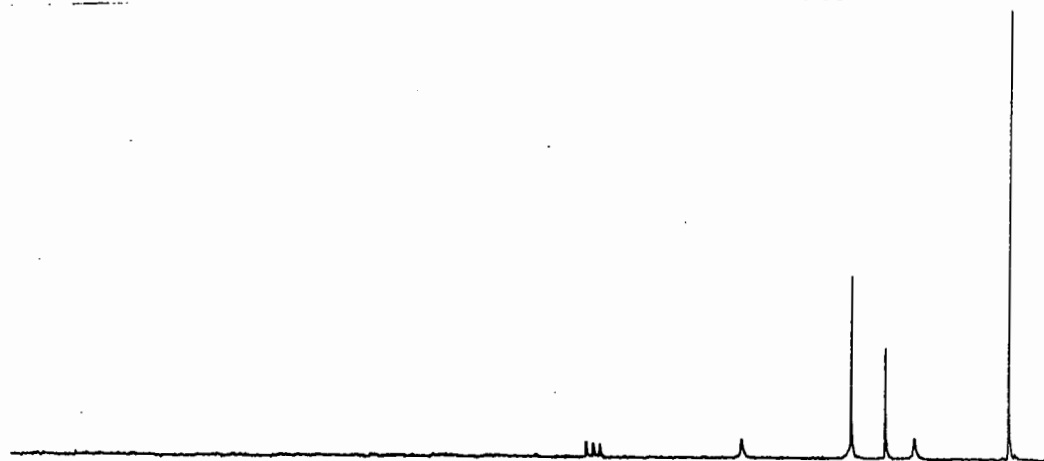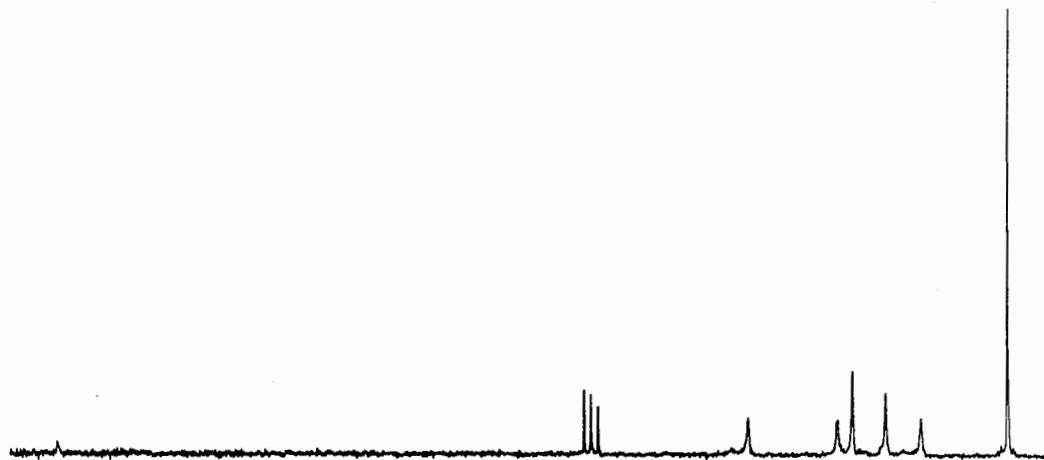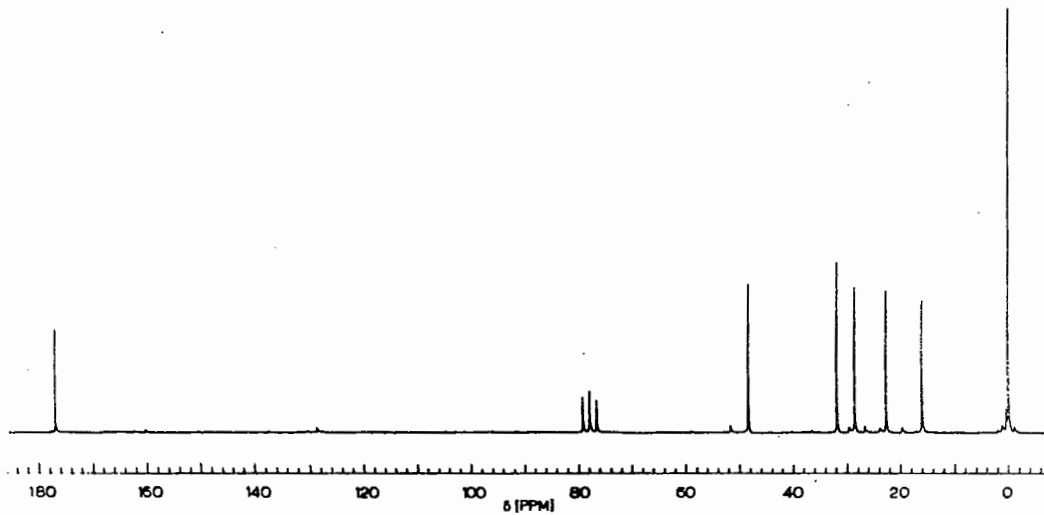
GRACE

August 6, 1982

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

Subject: NMR Determination of Primary and
Secondary Alcohols After Acetylation
with Trifluoroacetic Anhydride

Dear Barry:

We've recently found that acetylation with trifluoroacetic anhydride increases the chemical shift difference between $R-CH_2-O$ and $R-\underset{\underset{R'}{|}}{CH}-O$ protons of primary and secondary alcohols to a large enough extent to allow quantitative analysis of mixtures by simple proton NMR. There are references in the literature to the use of trifluoroacetic anhydride acetylation coupled with fluorine-19 NMR. One example is: T. Groom, J. S. Babiec, Jr. and B. G. VanLeuwen, J. Cell. Plastics 10(1), 43-5 (1974). We have found no reference to the use of this reagent followed by analysis using proton NMR.

As an example, comparing the appropriate shifts in 1-hexanol and 2-hexanol with those of the acetylation products:

	Chemical Shift, ppm	
1-hexanol (RCH_2OH)	3.65	
acetylation product		4.38
2-hexanol $R\underset{\underset{Me}{|}}{CH}-OH$	3.80	
acetylation product		5.13

The accompanying figure shows the 4-6 ppm region of a proton NMR spectrum of the acetylation product of a blend

Dr. B. L. Shapiro   August 6,1982

containing 50 mol percent 1-hexanol and 50 mol percent 2-hexanol.

Finally, to illustrate the quantitative significance of this separation, we prepared several blends of 1-hexanol and 2-hexanol, performed the acetylations (using 2-3 times as much anhydride as alcohol, by weight, allowing to react at room temperature for three hours), and obtained proton NMR spectra. Mole percents 1-hexanol blended and found are shown below.
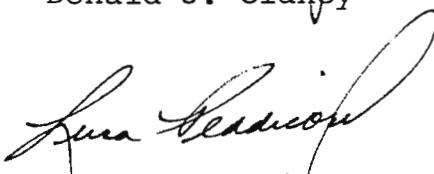
	Blended	Found
Mole % 1-Hexanol	89.4	87.1
	66.0	64.0
	50.6	50.0
	25.4	26.7
	13.2	14.7

Best wishes from WRC.

Sincerely,

Donald J. Clancy

DJC:al
82-75

LBP:al
82-67

Lura B. Peddicord
Analytical Research Dept.

1.2   1.4

1-HEXANOL + 2-HEXANOL

50:50 MOLE % BLEND
AFTER ACETYLATION WITH
TRIFLUOROACETIC ANHYDRIDE
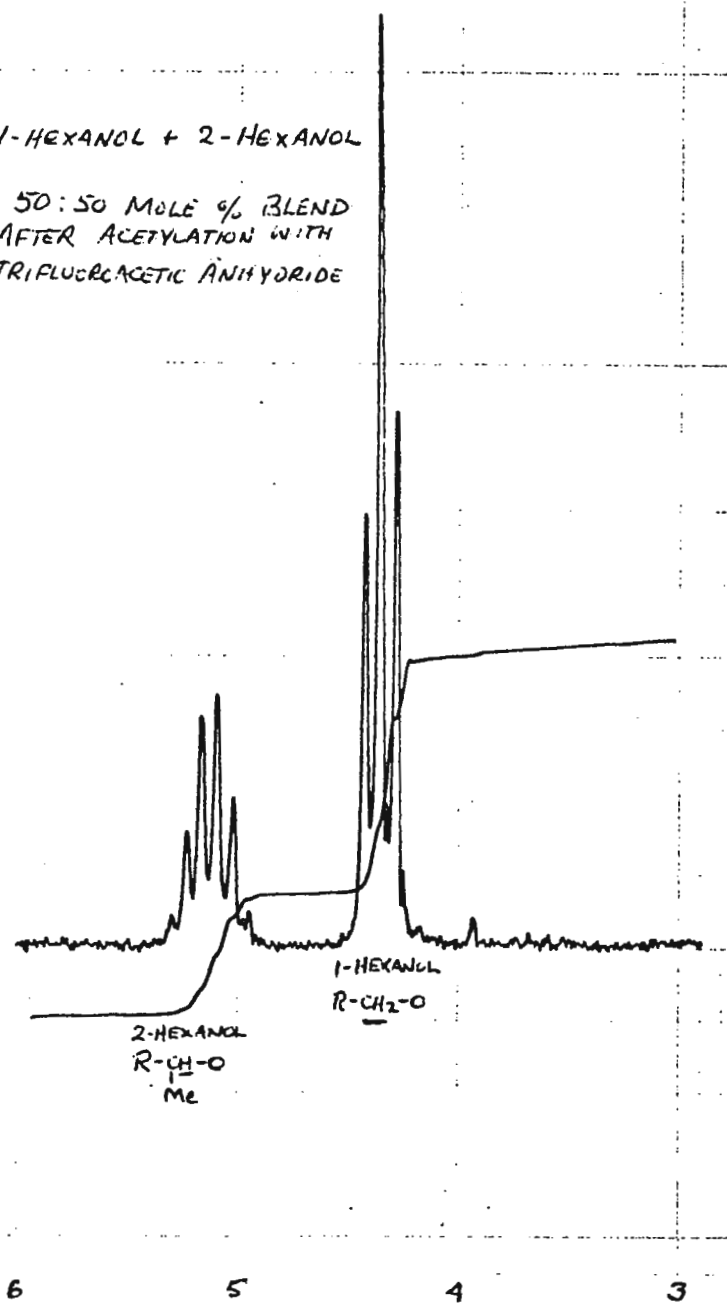
1-HEXANOL
$R-CH_2-O$

2-HEXANOL
$R-CH-O$
|
Me

6   5   4   3

PHILIP MORRIS
U.S.A.

August 2, 1982

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

Dear Barry:

During a routine structural assignment of a series of diastereomeric β-hydroxy esters of the following type.

$$R = CH_3, CH_2CH_2CH_3,$$
$$CH(CH_3)_2$$

$$R' = CH_3, CH_2CH_3$$
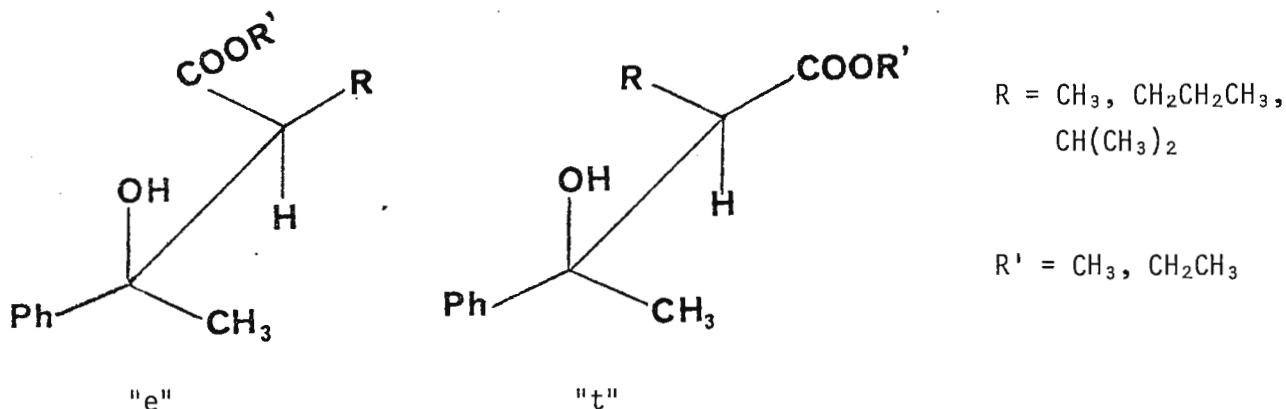
we came upon a rare four bond coupling transmitted through σ-bonds between a hydroxyl proton and the protons of a geminal methyl group. In weakly hydrogen bonding solvents such as $CDCl_3$ which allow intramolecular hydrogen bonding between the hydroxyl proton and ester carbonyl, we found $^4J(OH,CH_3) = 1.0$ Hz in the "e" isomer, while the "t" isomer exhibits $^4J = 0.3$ Hz. A value of $^4J(OH,CH_3)$ as large as 1 Hz occurs very infrequently since the "W" configuration of bonds required for maximal coupling is seldom achieved. Only the "e" isomers can form a "W" configuration between the hydroxyl proton and one of the methyl protons, thus the appearance of $^4J(OH,CH_3) = 1$ Hz is diagnostic or the "e" isomers in this series of compounds. The trick of adding molecular sieves directly to the NMR tube containing the sample was found to be highly effective in removing residual water in order to sharpen the hydroxyl proton resonance. Details will appear soon in J. Org. Chem.

Sincerely,

Jan

Jan B. Wooten, Ph.D.
Research Scientist

JBW/bpp

UNION CARBIDE

UNION CARBIDE CORPORATION
P. O. BOX 8361, SOUTH CHARLESTON, W. VA. 25303
RESEARCH AND DEVELOPMENT DEPARTMENT
Technical Center

August 11, 1982

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

MAS of Air Sensitive and/or Corrosive Materials

Dear Dr. Shapiro:

High resolution NMR of solids is experimentally more difficult than for liquids because of the need to rotate the sample at high speeds. This difficulty is greater if the sample is air sensitive and/or corrosive towards the rotor material. We would like to report that it is possible to avoid this problem by first sealing off the sample in a glass ampule. As an example, the MASS ^{31}P-spectrum of phosphorus pentoxide shown below was run using a glass ampule in an Andrew-type rotor machined from Delrin.

In our experience two key factors contribute to stable spinning 1) the ampule should be pretapered to a smaller (coaxial) diameter and 2) the ampule should be spun inverted. The design we use is shown below.

Ampule:

9 MM OD

10 MM

15 MM

- WIDE MOUTH TO ASSIST FILLING AND/OR ATTACHMENT TO A VACUUM LINE
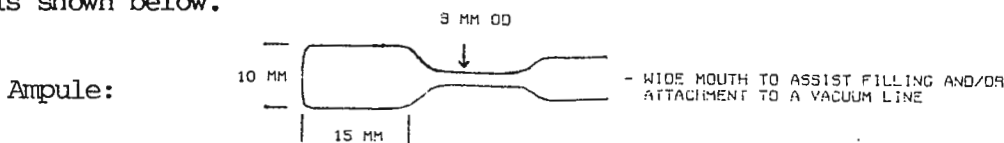
The narrow taper enables hot-flame, quick-sealing of the ampule in a way that avoids undue sample heating. Spinning the sample with the tip down puts the seal, which is never perfectly symmetrical, nearer the center-of-mass of the rotor and also reduces the overall rotor-sample height. Both contribute to greater stability at high speeds. Long tips and fairly assymmetrical seals can be tolerated with this configuration. To maintain the best filling factor we drill a hole in the cone of the rotor to accommodate the tip.

Rotor with

Ampule
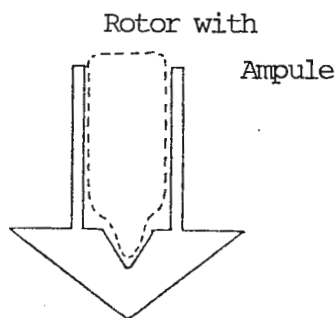
Sincerely,

Bill

W. H. Dawson

PHOSPHORUS PENTOXIDE

P_4O_{10}

81 MHz ^{31}P SPECTRUM

MASS = 3700 Hz

400   200   0   -200   -400   PPM

UNIVERSITY OF UPPSALA
THE INSTITUTE OF PHYSICAL CHEMISTRY   Uppsala 18.8 1982
UPPSALA. SWEDEN

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

"Peak heights in spin-echo and pulsed-gradient spin-echo
measurements."

Dear Professor Shapiro,

It was pointed out several years ago by the Volds (J. Amer.
Chem. Soc., $\underline{96}$ 4043 (1974)) that homonuclear scalar
couplings give rise to transverse relaxation paths which
cause T_2 to become considerably shorter than T_1, even in
the absence of slow processes. Naïvely this can be thought
of as destructive interference between J-modulation components.
Normally, this will not cause any particular problems and
most practising NMR spectroscopists are probably unaware of
those effects. However, in pulsed-gradient spin-echo
experiments, which are becoming increasingy popular, this may
lead to considerable artifacts in evaluated self-diffusion
coefficients in multicomponent systems if one assumes that
echo amplitudes are directly related to the number of nuclei
in individual components. This will apply in the FT version
as well as in the unresolved PGSE technique.
   When fitting experimental peak heights to an equation of
the form

$$A_i = C_1 \cdot \exp\left(-\gamma^2 G^2 \delta^2 D_1 \left(\Delta - \tfrac{1}{3}\delta\right)\right) + C_2 \cdot \exp\left(-\gamma^2 G^2 \delta^2 D_2 \left(\Delta - \tfrac{1}{3}\delta\right)\right)$$

in a two-component system one must allow both C_1 and C_2 to
be adjustable parameters. They are not directly related to
the actual concentrations of species 1 and 2 and need not
even have the same sign.
   I hope that this will keep my subscription running.

Yours sincerely

Peter Stilbs

Peter Stilbs

BP

BP RESEARCH CENTRE

SUNBURY-ON-THAMES

MIDDLESEX

ENGLAND
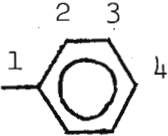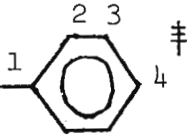
^{15}N AND ^{13}C CHEMICAL SHIFTS OF ISOCYANURATES

In the synthesis of flexible polyurethane foams, urethanes, allophanates, ureas, biurets, isocyanurates, uretidinediones and carbodiimides are formed as intermediates or final products, their concentrations being both formulation and catalysis dependent (1).

These flexible materials, although crosslinked, give well resolved ^{15}N and ^{13}C spectra when obtained at elevated temperatures (80-130°C in DMSO solution). IR and Raman spectroscopic identification of some of the above mentioned functional groups is possible but uncertainty exists as to the assignment and presence of isocyanurate structures (A) :

(A)
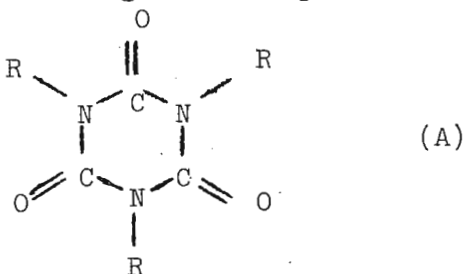
We have obtained ^{15}N and ^{13}C data on some model compounds and these allowed us to positively identify structures (A) in flexible polyurethane foams. The tabulated data was obtained on a Jeol FX-270 system in DMSO-d$_6$ solutions (5-10 per cent weight/weight).

R in (A)	$\delta\ ^{15}N$	$\delta\ ^{13}C$‡				
		C=O	C_1	C_2	C_3	C_4
$\overset{1}{-CH_2}-\overset{2}{CH}=\overset{3}{CH_2}$	-235.8^+	148.31	44.38	131.75	117.15	
$\overset{1}{-CH_2}-\overset{2}{CH_2}-OH$	-240.4^+	149.07	44.25	57.56		
phenyl (1, 2, 3, 4)	-225.6^+	148.83	134.34	(128.07)	(128.20)	127.91
$-CH_3$ ‡	-287.5	161.00	27.19			
phenyl (1, 2, 3, 4) ‡	-273.2	159.21	133.48	(128.62)	(130.03)	125.23

+ ^{15}N Chemical shifts (in ppm, relative to internal CD_3NO_2 at 5.00).

‡ ^{13}C Chemical shifts (in ppm, relative to internal DMSO-d_6 at 39.6).

( ) Assignments could be reversed.

‡ Ref 2.

1. Polyurethanes : Chemistry and Technology Part I and II. J.H. Saunders and K.C. Frish, Interscience Pub NY 1964.

2. Kricheldorf, H.R., and Hull, W.E., Makromol Chem, 1981, 182, 1177.

J.D. Pownall   *J. Pownall*

H. Pyszora   *H. Pyune*

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

Dear Professor Shapiro:

We have recently acquired a Bruker ER 200 D Electron Spin Resonance Spectrometer with a Bruker ER/150 Electron-Nuclear Double Resonance Accessory (ENDOR) to upgrade the ESR capability at our laboratory. Several figures are provided showing temperature dependent proton ENDOR spectra of the widely studied Coppinger's radical (galvinoxyl). The galvinoxyl radical (Fig. 1) is a two-ringed structure with three types of protons. There is a single methylenyl proton, 4 ring protons, and 36 tertiary butyl protons.

Fig. 2a shows the ESR spectrum of galvinoxyl (dissolved in paraffin oil) at room temperature. The t-butyl proton couplings are not resolved, but the room temperature ENDOR spectrum (Fig. 2b) does show a resolved hyperfine coupling from the t-butyl protons (centered about ν_H).

Below room temperature the ESR spectral information is poor (as indicated in Fig. 3a) but the ENDOR spectrum is most informative, showing resolved hyperfine couplings from several inequivalent protons. (The inequivalence is due to restricted motion of the ring structures of the parent molecule.) Upon cooling to an even lower temperature (as shown in Fig. 4) the inequivalence of the proton hyperfine couplings appears more resolved. Under proper conditions ENDOR is a technique with significantly higher resolution than ESR.

Sincerely,

M. D. Pace
Polymeric Materials Branch
Chemistry Division

W. B. Moniz
Polymeric Materials Branch
Chemistry Division

$(CH_3)_3C$ $\quad$ H(5) $\quad$ H(2) $\quad$ $C(CH_3)_3$

H(1)

O $\quad$ $=C$ $\quad$ $O\cdot$

$(CH_3)_3C$ $\quad$ H(4) $\quad$ H(3) $\quad$ $C(CH_3)_3$
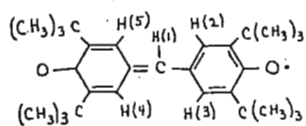
methylenyl proton = H(1)

ring protons = H(2-5)

t-butyl protons = H(6-41) (not numbered)

FIG. 1 Galvinoxyl molecule

1G

$A^{H(2-5)}$

$A^{H(1)}$
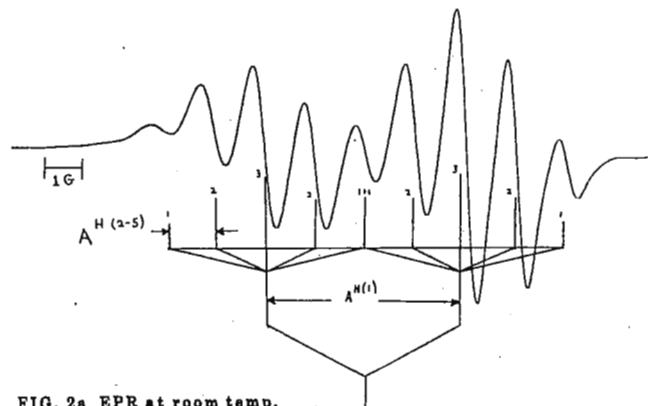
FIG. 2a EPR at room temp.

ν_H

$A^{H(6-41)}$

$A^{H(2-5)}$
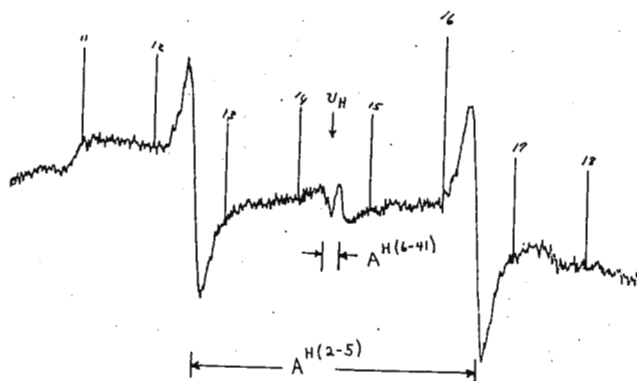
FIG. 2b Proton ENDOR at room temp.

1G
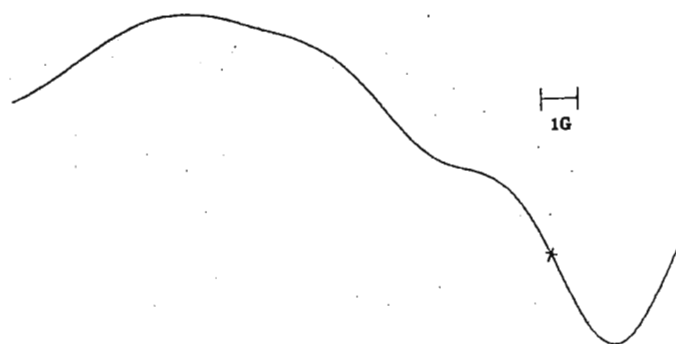
FIG. 3a EPR spectrum at -60°C

11 12 13 14 ν_H 16 17 18 19

15

$A^{H(6-41)}$

$A^{H(2-5)}$
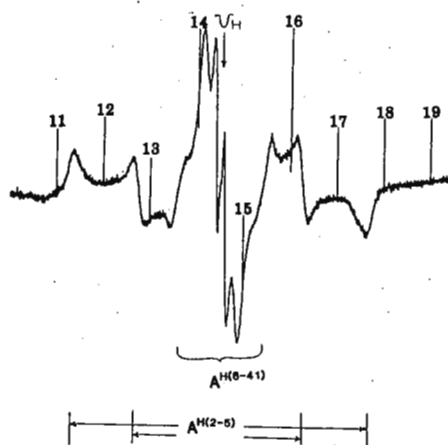
FIG. 3b Proton ENDOR at -60°C

11 12 13 14 ν_H 16 17 18

15

$A^{H(6-41)}$

$A^{H(2-5)}$
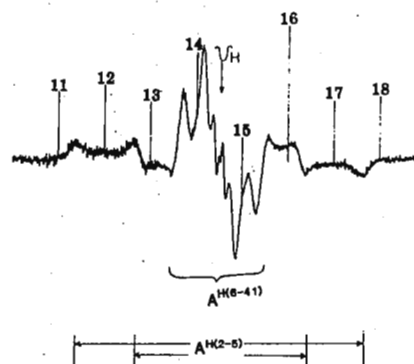
FIG. 4 Proton ENDOR at -100°C

Wageningen

Department of Molecular Physics

Your reference	
Your letter of	
Our reference	82/1097 dJ/jbw
Date	August 18, 1982
Enclosures	

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

Subject Suppression of artifacts in spinning sideband free MAS spectra

Dear Dr. Shapiro,

The appearance of spinning sidebands in MAS spectra at high fields
is a problem, since resonances can be obscured. Dixon (JMR 44, 220
(1981) and 45, 173 (1981)) proposed a pulse sequence to get phase
altered spinning sideband spectra. His method uses four 180° pulses
with different delays and data acquisition starts after two rotor
revolutions. Our method (de Jager, TAMU Newsletter 277 (1981), Datema,
7th Ampère Summerschool Portoroz (1982) and Hemminga, to be published)
uses one 180° pulse after one half rotor revolution and data acqui-
sition starts after one rotor revolution. This results in a spectrum
with inverted first order sidebands. A linear combination of this
spectrum and a normal spectrum results in a cancellation of first order
sidebands.

Both methods suffer from the following weaknesses: 1. r.f. pulses are
not delta functions. 2. pulse angle misset. 3. r.f. field inhomogeneity.
4. acquisition delay. In a four pulse sequence these effects cumulate.
It will be clear that our method gives better results, because it uses
a *single* 180° pulse and a *short* acquisition delay.

In order to get a clear idea about these problems, we have been in-
vestigating the effect of 180° pulses on the centerband and spinning
sidebands in the ^{1}H NMR spectrum of a 5 mm TMS sample on our Bruker
CXP 300 at low speed spinning in small linear and quadratic field gra-
dients. To study the effect of r.f. field inhomogeneity, a sample is
used that extends the r.f. coil. The intensity and phase distortions
on the spectrum are shown in fig. 1. A summation over a four step pulse
sequence with special phase shifts, shown below, eliminates these
distortions (fig. 2).

$$90^{\circ}_{x} - t - 180^{\circ}_{x} - t - \text{acqu.} - 5T_1$$

$$x \qquad -x \qquad "$$
$$-x \qquad y \qquad "$$
$$-x \qquad -y \qquad "$$

This sequence is also used for the suppression of artifacts in 2D-J
spectroscopy (Bodenhausen JMR 27, 511 (1977)).

In order to cycle out errors in the quadrature detection system, the whole four step sequence can be repeated four times, incrementing all phases of pulses and receiver each time by 90°, giving a total of 16 steps. The Dixon four pulse method would require 1024 (!) steps to get the same compensation effect.

Please credit this contribution to prof.dr. T.J. Schaafsma.

Sincerely,

P.A. de Jager
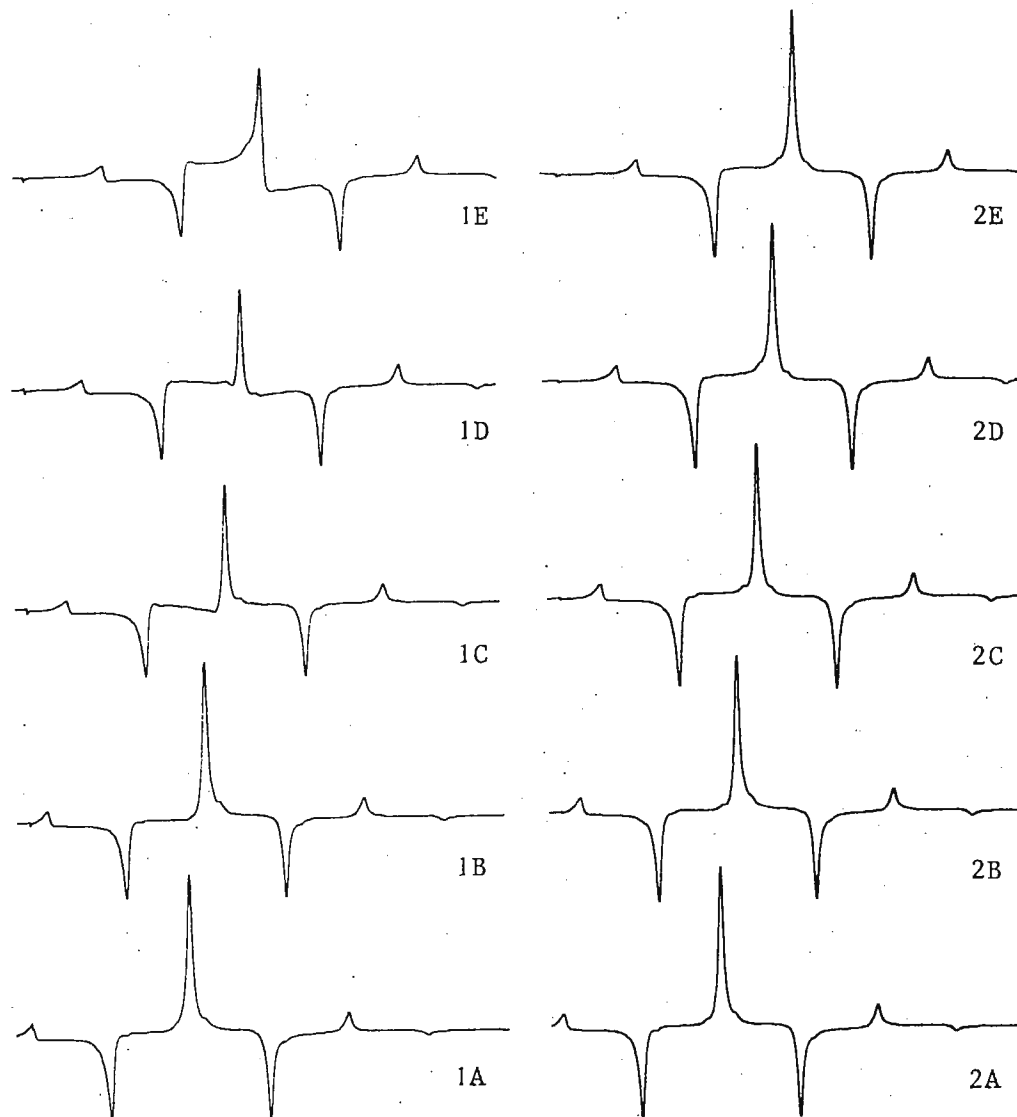
Fig.1 300 MHz ^{1}H NMR spectra of the TMS resonance of a 5 mm sample spinning at 18 Hz in the presence of a linear field gradient in the X direction. The sample extends the r.f. coil. Pulse sequence:
$90^o_x - t - 180^o_{\underline{x}} - t - $ acqu.

t = 31.3 ms ≃ 0.57 rotor revolutions. Line broadening: 1 Hz, 90° pulse: 9 μs, 180° pulse: 18 μs. 1 scan. Centerband offset is 36 Hz (A) and is increased in steps of 4.5 Hz (B - E). All spectra are plotted with the same phase correction. For all spectra the vertical scale is the same.

Fig. 2 Artifacts suppressed with the four step sequence. Same conditions as Fig. 1.

University of East Anglia

School of Chemical Sciences
University of East Anglia
Norwich. NR4 7TJ, ENGLAND

Telephone Norwich (0603) 56161
Telegrams UEANOR NORWICH

5th August 1982

Dear Barry,

MAR sideband intensities for J-split doublets in solids

Recently, in studies on organophosphorus compounds, we have observed indirect (scalar) spin-spin coupling between ^{31}P and ^{13}C nuclei in ^{13}C solid-state high-resolution NMR spectra. The spectra were recorded under conditions of magic-angle rotation (MAR) and high-power proton decoupling, using standard cross polarization and non-quaternary suppression (NQS) pulse sequences (the latter in order to differentiate carbon types). When relatively slow rates of rotation were used, the experiments provided unusual spectral appearances not previously reported in the literature. The spectra show two peaks due to simple (P,C) scalar coupling (averaged by MAR to one-third of the tensor trace) but with different intensity patterns of the spinning sidebands.

An example is given as Fig. 1A which illustrates the high-resolution MAR NQS spectrum of dimethyl diphenylphosphonium iodide, $[Me_2Ph_2P]^+I^-$. Peaks labelled (1) and (2) may be attributed to the quaternary carbons, with the respective spinning sidebands assigned as ssb_1 and ssb_2. The doublet at lower frequency (3) is a residual signal due to the carbons of the relative mobile methyl group. The separation of peaks (1) and (2) is 91.6 Hz, which is comparable to the solution state splitting of 88.9 Hz. At slower spinning speeds the number of spinning sidebands increases and the differences with respect to the two peaks are more clearly seen, as in Fig. 1B.

The differing intensity distribution among the sidebands for peaks (1) and (2) may be explained theoretically by the combined effects of (P,C) dipolar coupling, ^{13}C shielding anisotropy, and (P,C) indirect spin-spin coupling. We anticipate that static powder patterns based on peaks (1) and (2) (arising from molecules with differing ^{31}P spin components) would show very different widths because in one case the shielding anisotropy adds to the spread of frequencies produced by the dipolar interaction, whereas in the other case the two interactions partially compensate. The line narrowing produced by MAR allows one to observe the phenomenon clearly.

The slow-spinning NQS MAR NMR spectra enable the parameters affecting individual powder-pattern subspectra to be determined by moment analysis techniques. As a consequence, we are able to derive values for all three shielding tensor components, together with the (P,C) dipolar coupling constant (possibly incorporating some anisotropy in (P,C) indirect coupling), together with some information on the geometric relation between the two tensors. The scalar coupling acts as a convenient marker to separate the two subspectra, and the known sign of $^1J_{PC}$ helps in the interpretation. Full details of this work are being prepared for publication.
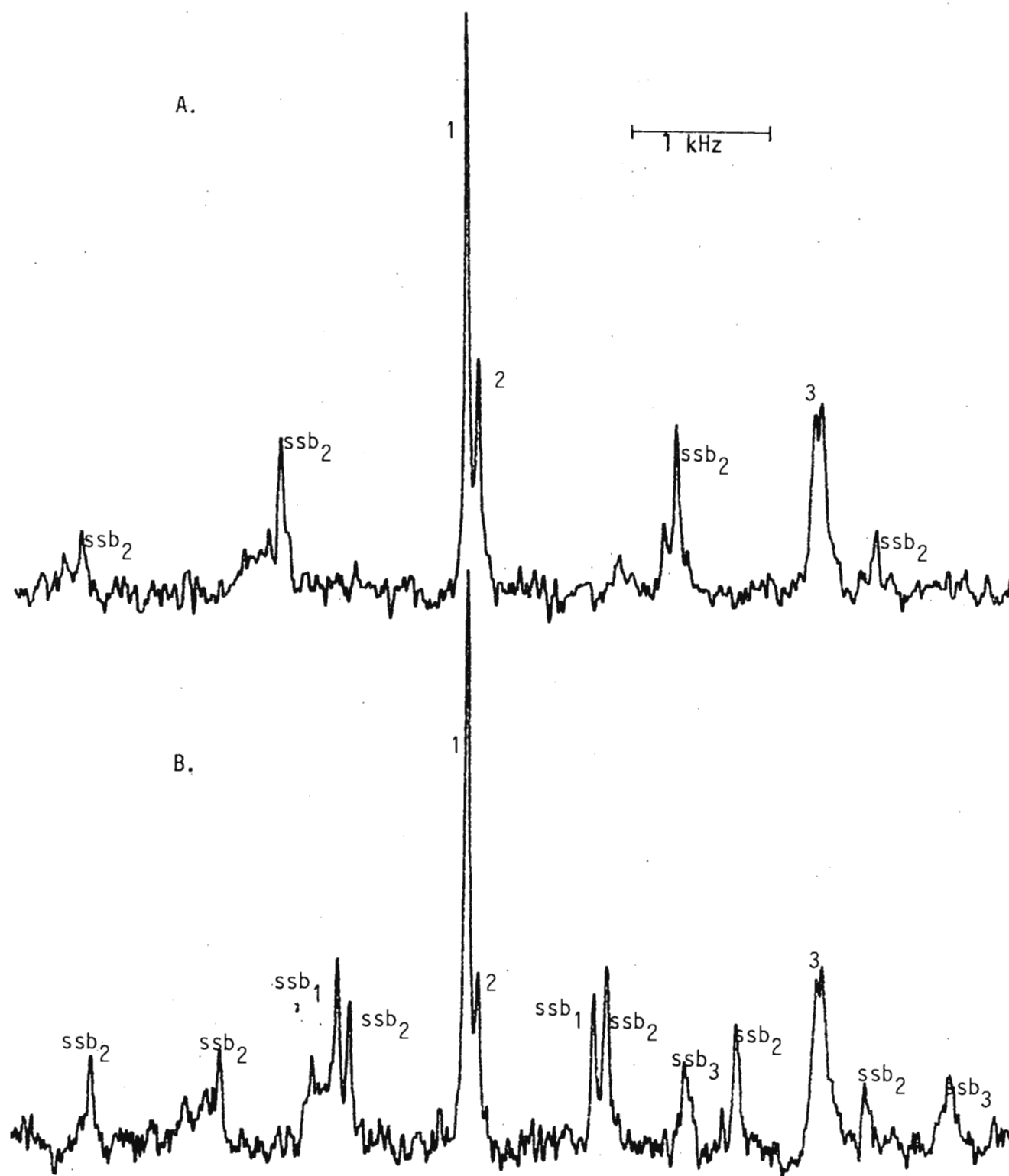
Fig. 1: NQS MAR ^{13}C NMR spectrum of dimethyldiphenyl-
phosphonium iodide. Frequency 22.63 MHz (C-13)
with 5 ms contact pulses.
A. Spinning speed 1.46 kHz, 2500 transients
B. Spinning speed 0.95 kHz, 5000 transients

We hope this reinstates RKH's "subscription" to TAMUNMR (if
the usual rules of inertia have broken down so that we've already been
de-registered - TAMUNMR takes so long to arrive that we cannot be sure
whether or not you've applied the cut-off yet!).

Best wishes

Robin   *Ken**   *Ann*

ROBIN K. HARRIS   KEN J. PACKER   ANN M. THAYER

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

* Forged by RKH as Ken is on
holiday (and hence cannot be
held responsible for any errors
in the letter).

FIG. 1
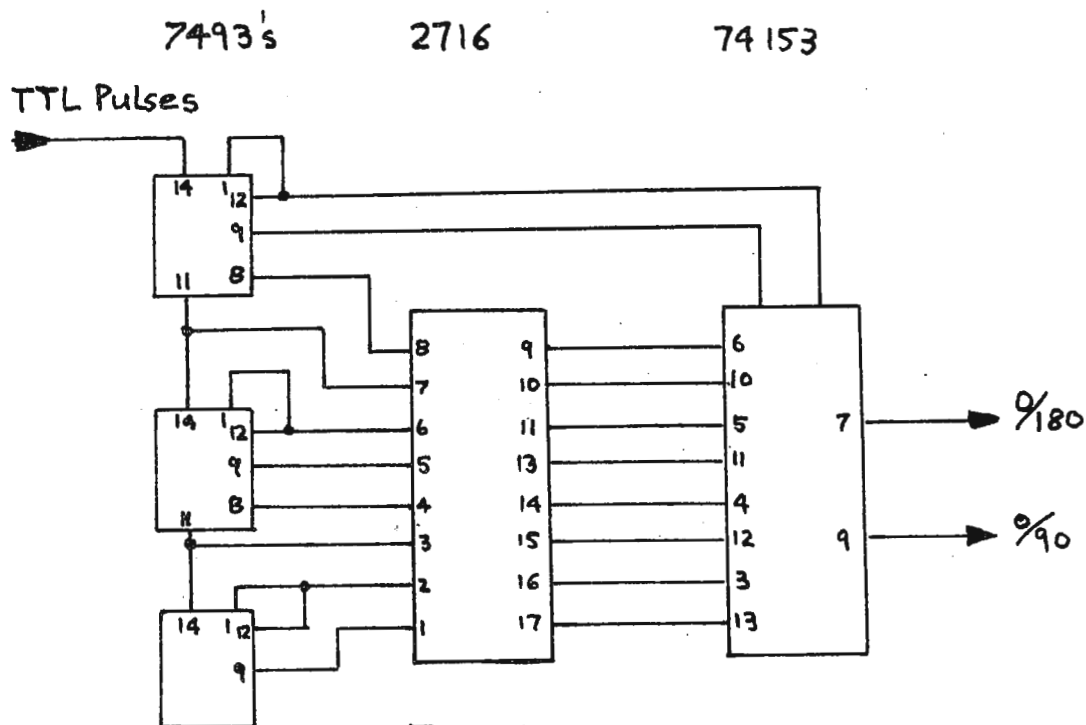
DEPARTMENT OF HEALTH & HUMAN SERVICES

Public Health Service
Building 2, Room B2-02

National Institutes of Health
Bethesda, Maryland 20205

August 23, 1982

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

Dear Barry:

<u>Another Hardware MLEV</u>[1]

Having seen the need to free our 293's from the software version, we have implemented the circuit in Fig. 1. The MLEV sequence is programmed into the ROM (2716) for any desired length on any Eprom programmer. Each complex inversion occupies one word (8 bits) of memory, which is being read in 2-bit steps by the multiplexer 74153.

Shown is MLEV 256, and in our case an R = 14, an $\overline{R}$ = BE in hexadecimal since we have an inverter following (Mod/CW gate). Otherwise, R = EB and $\overline{R}$ = 41. For a quadriphase signal a 74155 can be added to the output. The circuit is fed with pulses at intervals of X (R/4). Our first version uses a programmable divider running off the master clock, but this appears to be overkill since the value is not critical. A stable free running oscillator does fine on the others.

We have added the circuit to the world's one and only NIC 270 and should have it on our NIC 500 and NIC 360 by the time you read this. It can be treated like another source of modulation on the decoupler and gated on and off by the computer.

Please credit this to Ted Becker's account.

Sincerely yours,

Rolf G. Tschudin
Laboratory of Chemical Physics
National Institute of Arthritis,
 Diabetes, and Digestive and
 Kidney Diseases

[1] M. H. Levitt, R. Freeman and T. A. Freukiel, J. Magn. Reson. <u>47</u>, 328 (1982).

College of Arts and Science

UNIVERSITY OF MISSOURI-COLUMBIA

Department of Chemistry

123 Chemistry Building
Columbia, Missouri 65211
Telephone (314) 882-2439

August 18, 1982

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

Dear Professor Shapiro:

1. Another New Pulse Sequence for Polarization Transfer

NMR polarization transfer in liquids can be accomplished by a new pulse sequence:

^{1}H: $\pi/2$ (y) - τ - π(y) - τ - $\pi/2$(x) - τ - $\pi/2$ ($\pm$y) -

^{13}C $\pi/2$(x) π(x) - acquire or evolve

which significantly differs from the others, since the last $\pi/2(\pm y)$ pulse turns protons back into the xy plane of the rotating frame*. If the phase of this pulse is changed for 180°, only signals at $^{13}CH_2$ spins are reversed. Doublets and quartets are observed (fig. 1) if both spectra are added, while subtraction leaves only "triplets" as opposite peaks at frequencies $\gamma_i \pm J$.
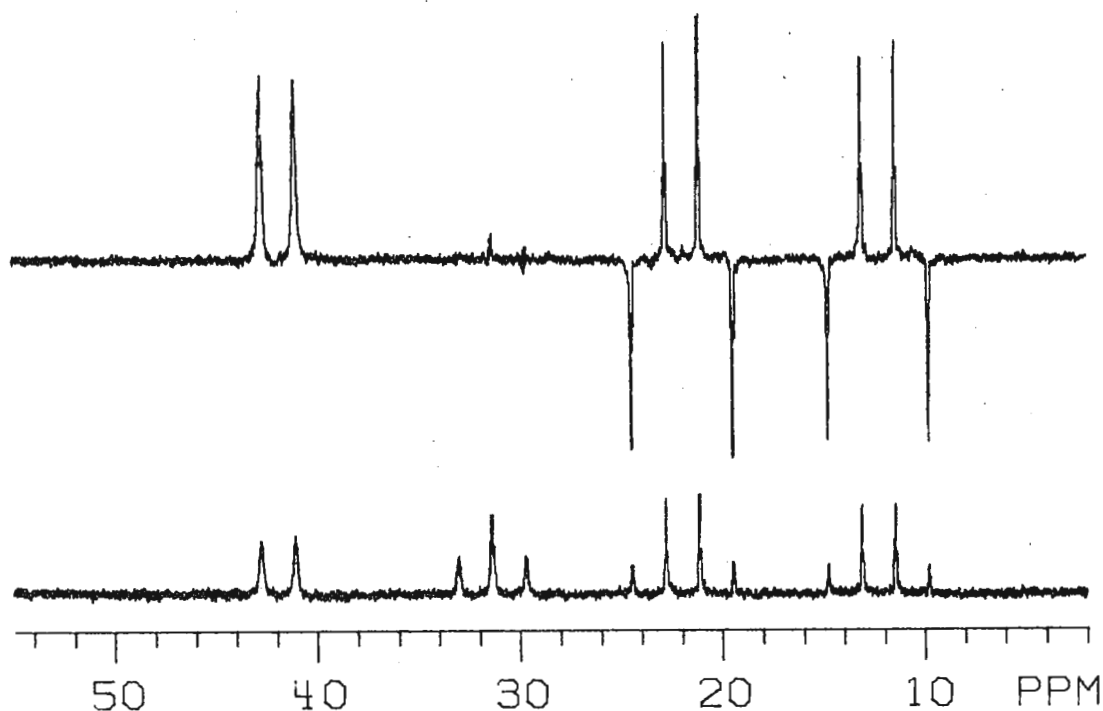
* and several new effects are observed

Professor B.L. Shapiro

2.   On the Use of Long Range Couplings in INEPT
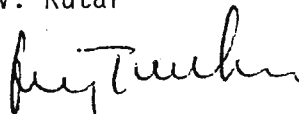
We want to echo the letter by Brevard and Schimpf (April 1982) on the use of
long range couplings for polarization transfer. We have been measuring
$^1J(^{77}Se-^{13}C)$ from ^{77}Se satellites (3.8%) of ^{13}C spectra for compounds with a
C = Se double bond. The carbon is, of course, non protonated. Using decoupled
INEPT and long range coupling of ~4.5Hz, we were able to observe clearly the
^{77}Se satellites in 3 hours from very dilute samples. From the normal spectrum
the main peak was barely observed in about an hour. If an appropriate long range
coupling constant is used, the enhancement of S/N, by polarization transfer
over NOE is usually larger for nonprotonated carbon than protonated carbon,
taking both the enhancement factor and repetition rate into consideration.

Finally, we have a Brüker HX-90 spectrometer (equipped with a Nicolet 1080
computer, 5mm proton, 10 and 13mm ^{13}C probes, variable temperature accessories)
for sale. Anyone interested in the whole system or any part of it should
contact Tuck Wong at 314-882-7725 or 882-3291.

Sincerely yours,

V. Rutar

Tuck C. Wong

UNIVERSITY OF SOUTH CAROLINA

COLUMBIA, S. C. 29208

SOUTH CAROLINA MAGNETIC
RESONANCE LABORATORY

(803) 777-7341

August 23, 1982

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

RE: Cadmium-113 NMR Shielding Tensors

Dear Barry,

Thank you for the less than subtle yellow(?) reminder. We have
been performing some single crystal ^{113}Cd nmr experiments on a variety
of compounds. These results will be summarized in two papers we plan
to submit to JACS in a few months. Those of your readers who are
interested can drop us a line requesting the preprints when available.
I have enclosed some of our results on $Cd(NO_3)_2 \cdot 4H_2O$ and $CdCa(OAc)_4 \cdot 6H_2O$.

We have also been doing some FORTRAN programming on our Aspect
2000A. The programs are not completely finished as yet but we will have
static powder and MAS simulation programs running within a month or
so. Anyone interested can send me a blank "Bruker-type" floppy and I
will provide a FORTRAN source file and a position independent load module.

Warmest Regards,

Paul D. Ellis
Professor of Chemistry and
Facility Director

:tb
Enclsoure

TABLE 3.6   Principal elements of the ^{113}Cd shielding tensor and the direction cosines relating the PAS and the crystallographic unit cell for CdCa(OAc)$_4$·6H$_2$O.

TENSOR ELEMENT (ppm)[a]	DIRECTION COSINES			ANGLES (Degree)		
	a	b	c	a	b	c
σ_{11} -74.6	-.0115	.9998	.0139	90.6	1.04	89.2
σ_{22} -73.0	.9999	.0116	-.0017	.667	89.30	90.1
σ_{33} 101	.0019	-.0139	-.9999	89.9	90.8	179

[a] All shifts are reported relative to solid Cd(ClO$_4$)$_2$.

TABLE 3.8   The principal elements of the ^{113}Cd shielding tensor and the corresponding direction cosines for Cd(NO$_3$)$_2$·4H$_2$O. Direction cosines relate the tensor PAS and the orthorhomic unit cell.

TENSOR ELEMENT (ppm)[a]	DIRECTION COSINES			ANGLES (degree)		
	a	b	c	a	b	c
σ_{11} -174.4	.0561	.0036	.9984	86.8	89.8	3.2
σ_{22} -154.3	- 8552	.5162	.0462	149	58.9	87.3
σ_{33} 22.2	.5152	.8564	-.0320	59.0	31.1	91.8

[a] All shifts are reported relative to solid Cd(ClO .) .

DEPARTMENT OF CHEMISTRY
TEL. (403) 432-3254
TELEX 037-2979

THE UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA, CANADA
T6G 2G2

August 23, 1982

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

^{13}C Homonuclear Decoupling on the Bruker WH-400

Dear Barry:

^{13}C NMR spectra of compounds synthesized from ^{13}C dilabelled acetate display easily recognizable $^1J_{CC}$ couplings. The observation of equal J_{CC} pairs of which one resonance has been unambiguously assigned can confirm the assignment of the other resonance. Often, however, because of the similarity in carbon types, the magnitudes of J_{CC} will not be very different. To circumvent this problem we have incorporated ^{13}C homonuclear decoupling hardware into our Bruker WH-400.

Shown in Figure A is a portion of the ^{1}H decoupled ^{13}C spectrum of 11-0-acetylcyathatriol derived biologically from [1,2 - ^{13}C$_2$] acetate (structure is shown in the inset with bold lines indicating positions of dilabel incorporation). The numerous J_{CC} splittings are clearly evident in the spectrum. In Figures B and C, carbon 12 and 9 are irradiated, respectively, with collapse of carbon 15 and 17 as expected. There is a loss of S/N of about a factor of 3 in the homonuclear irradiated case, however, all of the coupled pairs may be identified with a series of irradiations.

A PTS 160 Frequency Synthesizer was used to generate the irradiation frequency, which was gated by the SPF$_2$ line of the Aspect 2000 Computer. The gated output was fed into a Bruker B-SV3 BX unit for tripling and amplification. The r.f. was coupled into the probe via a Narda Microline Directional Coupler (Model No. 4001B-10). The ^{13}C receiver preamp was attached to the "coupled output port"; the probe to the "terminated port" and the ^{13}C decoupler to the "output". The "input port" was terminated at 50Ω. This configuration provided the best isolation between the preamp and the decoupler and best coupling between the probe and the preamp and decoupler. The Bruker directional coupler did not work as well as the Narda. The Bruker ^{1}H decoupler was also modified to hold the BB status line on no matter what command was entered via the software.
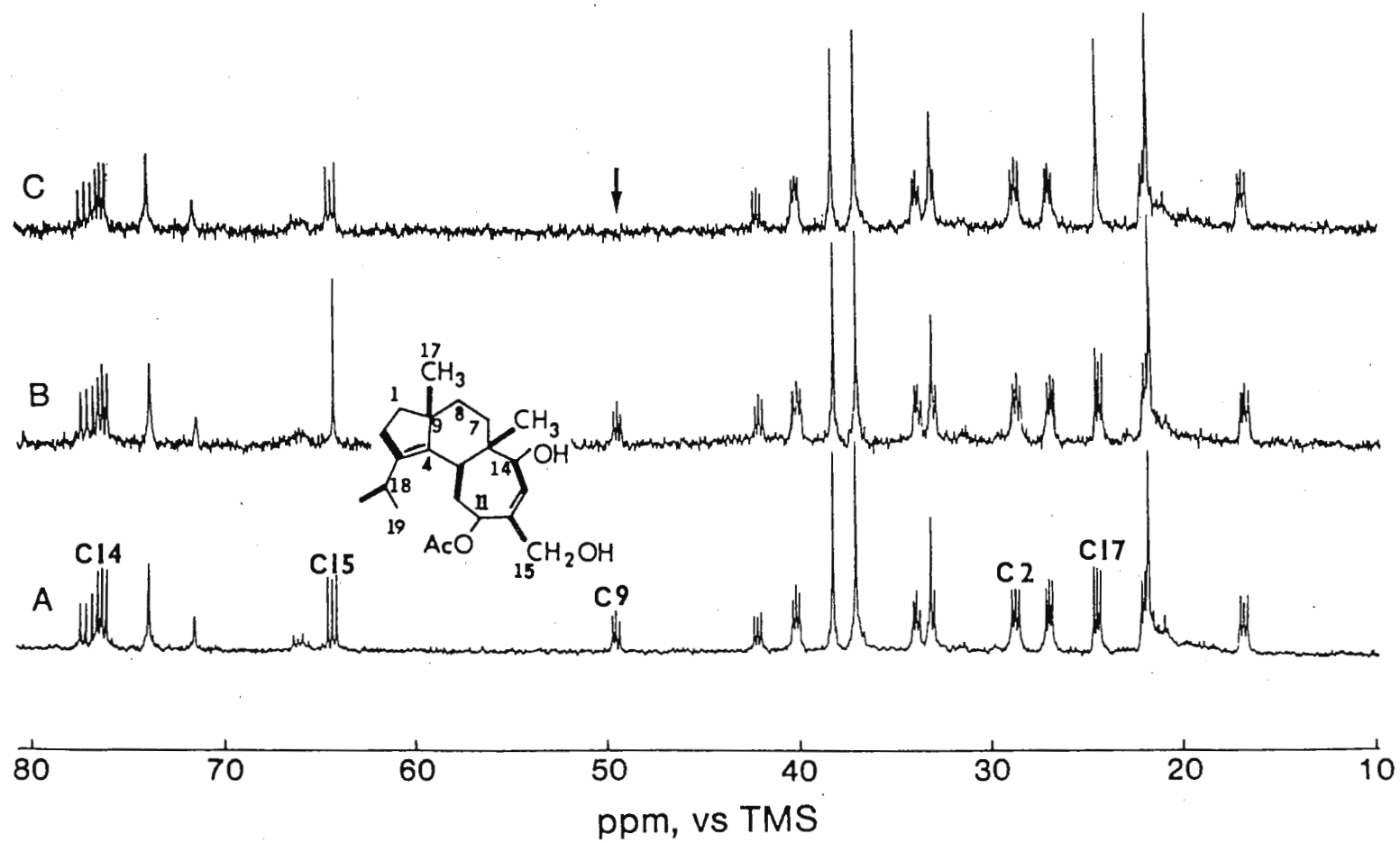
Sincerely,

Tom Nakashima

Tom Nakashima

TN:sjm

ppm, vs TMS

UNIVERSITY OF MINNESOTA   Department of Chemistry
TWIN CITIES   Kolthoff and Smith Halls
                          207 Pleasant Street S.E.
                          Minneapolis, Minnesota 55455

August 27, 1982

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

Dear Barry,

In our continuing efforts to understand nuclear relaxation, we believe we have stumbled upon an interesting example of the dominance of scalar relaxation of the second kind. In the accompanying figure, A is the proton decoupled ^{15}N NMR spectrum of $[Co(^{15}NH_3)_6]^{3+}$ ion in D_2O recorded at 7.05T. The eight line spectrum arises from the spin-spin coupling of the six equivalent ^{15}N nuclei (I = 1/2) to the central ^{59}Co (I = 7/2), with $J_{59Co-15N}$ = 62 Hz. Deconvolution of this spectrum using the NMCCAP routine on our NIC-1280 shows that all the lines are of equal intensity as expected, but the six inner lines are broader than the outermost set by a factor of ~2, the actual line-widths being 38 ± 2 Hz and 18.7 ± 1 Hz, respectively. The individual components of the deconvoluted spectrum are plotted in C.

$-800 \quad -1000 \quad -1200 \quad -1400 \quad -1600 \quad Hz$
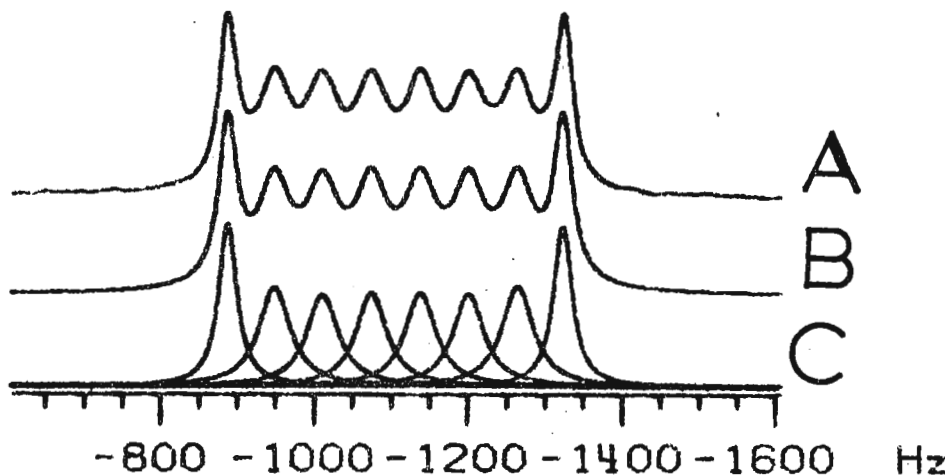
We expect that the ^{15}N linewidths are dominated by scalar relaxation of the second kind so that the correlation time for the ^{15}N broadening is the reciprocal of the ^{59}Co relaxation rate. That the outermost lines, arising from the +7/2 and -7/2 states of the cobalt manifold, are half as wide as the inner six lines is consistent with the cobalt transition rate being half as large for the ±7/2 states (Δm_I = only + or -1) compared with the remaining states (Δm_I = both + and -1).

Best regards,

J. H. Russell   V. P. Chacko   R. G. Bryant

JHR/VPC/RGB:db

AM 400

BRUKER AM 400 WIDE BORE

setting new landmarks in performance

BRUKER
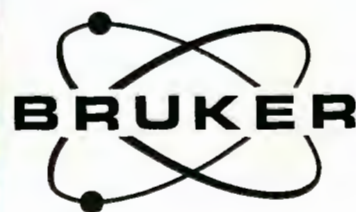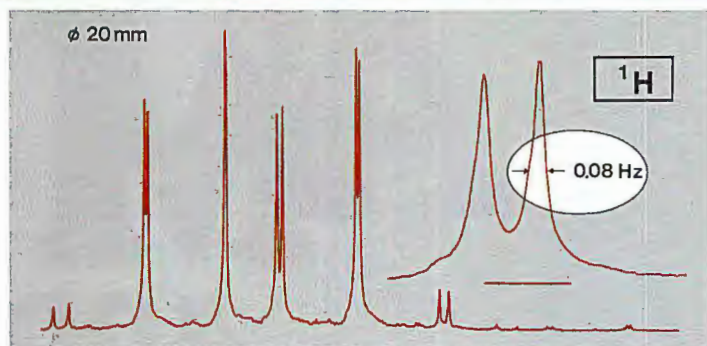
TOP RESOLUTION

Standard resolution test with a mixture of 15% o-dichlorobenzene in deuterated acetone. A 20 mm sample was measured using the decoupling coil of the multinuclear probehead.
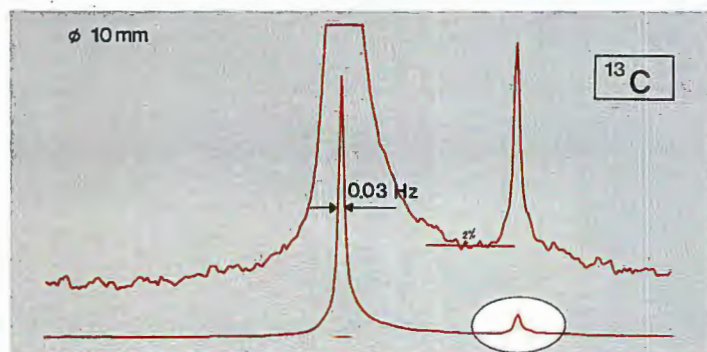
Spectrum of CS_2 shows a perfect separation of the isotope peak. It demonstrates excellent line shape and resolution (0.03 Hz).

TOP SENSITIVITY
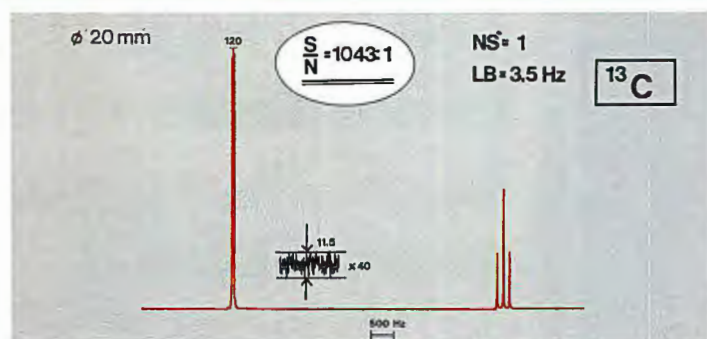
A solution of 60% deuterobenzene in dioxane (ASTM test) leads to a signal to noise ratio of more than 1000:1 for single pulse experiments.
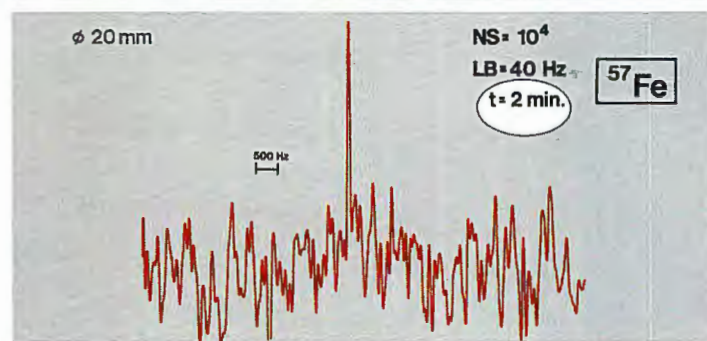
High sensitivity is obtained also with a special 20 mm broad band probe for low γ nuclei. The spectrum shows the ^{57}Fe signal of 1m ferrocene in deuterobenzene measured in 2 min.

AM 400 – you will see the difference!

HERCULES

August 6, 1982

Professor Bernard L. Shapiro
Department of Chemistry
Texas A & M University
College Station, Texas 77873

Dear Barry:

^{13}C Assignments in Hydroxylic Compounds from Isotope Effects

Deuterium isotope effects on ^{13}C-NMR spectra are well-known in the art and are often used for signal assignments. Thus, e.g., Barrelli et al., Org. Magn. Resonance, 19, 102 (1982), recently used synthetic deuteration at carbon-1 of the ethanol moiety of 2-(2-methoxyethoxy)ethanol.

For hydroxylic compounds, we have been routinely using partial deuteration of the hydroxyl group(s). This is easily achieved in situ by the addition of the appropriate amount of D2O to a DMSO solution of the compound of interest. Because in such solutions the hydroxyl-hydrogen exchange is usually slow on the NMR time scale, the upfield deuterium isotope effect results in splittings of the α- and β-carbons by ca. 0.12 and 0.04 ppm, respectively. As an example, the splitting of these carbons in 2-(2-ethoxyethoxy)ethanol are shown in the figure. Spectra were recorded at 90.70 MHz.

Please credit this contribution to Walter Freeman's account.

With kindest regards.

Sincerely,

Jacques

Jacques Reuben
Analytical Division

^{13}C - NMR PEAKS OF C-1 AND C-2 OF
CH₃CH₂OCH₂CH₂OCH₂CH₂OH
WITHOUT (A) AND WITH (B) ADDED D2O

-OCH₂CH₂OD

6710.50 6707.10   5612.00 5601.51

B

OCH₂CH₂OH

A

74.0 PPM   61.8 61.6 PPM

JR·amt

3rd August, 1982

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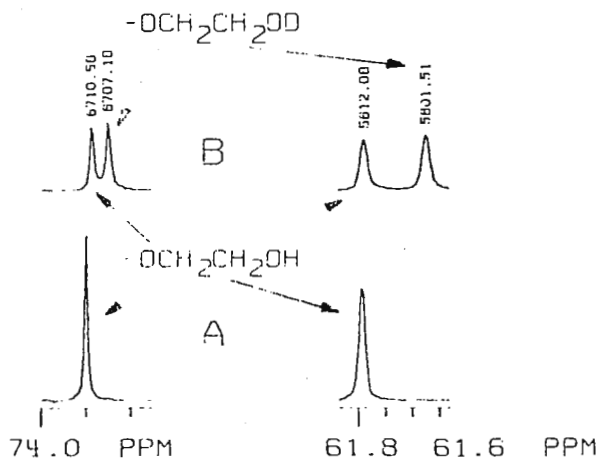Texas A & M University,
College Station, Texas 77843,
U.S.A.

Dear Professor Shapiro,

Multi-nuclear NMR of trans $PtCl(SiPh_3)(PMe_2Ph)_2$

It has been about a year since our Bruker WP80SY arrived during which time it has barely stopped pulsing. Our WM360 which has just arrived is operating very satisfactorily and making great demands on our time with high field proton work.

However we have recently carried out some multi-nuclear NMR on the complex trans $PtCl(SiPh_3)(PMe_2Ph)_2$ prepared, but not completely separated, from cis $PtCl_2(PMe_2Ph)_2$. The ^{31}P, ^{195}Pt, ^{29}Si obtained in $CDCl_3$ are shown in the figure. The ^{31}P and ^{29}Si spectra were obtained on the WP80SY at 32.43 and 15.92 MHz, the ^{195}Pt spectrum was recorded on the WM360, since it turned up at an appropriate time, at 77.13MHz.

The ^{31}P signal of trans $PtCl(SiPh_3)(PMe_2Ph)_2$ appears at $\delta_P = -144.3$ ppm relative to TMP, the ^{195}Pt satellites give $J(PPt) = 2795$Hz. The cis starting material comes at $\delta_P = -156.2$ ppm with $J(PPt) = 3545$Hz, the low field ^{195}Pt satellite is just resolved from that of the trans product.

In the ^{195}Pt spectrum trans $PtCl(SiPh_3)(PMe_2Ph)_2$ has $\delta_{Pt} = -2918.4$ppm relative to Na_2PtCl_4, the triplet separation yields $J(PtP) = 2799$Hz. Use of a little more line broadening(and perhaps imagination)just shows the ^{29}Si satellites for the centre line of the triplet(shown in the inset expansion, each division is 500Hz), these lead to the approximate value of $J(PtSi) = 1421$Hz. The cis complex has $\delta_{Pt} = -2763$Hz and $J(PtP) = 3542$Hz.

The ^{29}Si spectrum was obtained overnight with $Cr(AcAc)_3$ added. The Si-P coupling of course produces the triplet structure and the ^{195}Pt satellites are clearly visible(with a little zero filling). We obtain $\delta_{Si} = -11.4$ppm relative to TMS, $J(SiPt) = 1432$Hz and $J(SiP) = 10.8$(average). The peak at -18 ppm is due to $HSiPh_3$. Although this spectrum is adequate we hope to do better with other Si studies on the WM360 with which we can carry out INEPT experiments not possible on our WP80SY since this is equipped with the older Bruker 3 clock pulser board and cannot produce short enough proton decoupler pulses as possible with the newer Bruker pulse programmer. We shall be occupying ourselves with these newly acquired delights as soon as time permits.

Yours sincerely,

Michael D. Rowe

J. Vinaixa

^{31}P

−100   −200

^{195}Pt

−2750   −2850   −2950

^{29}Si

40   0   −40
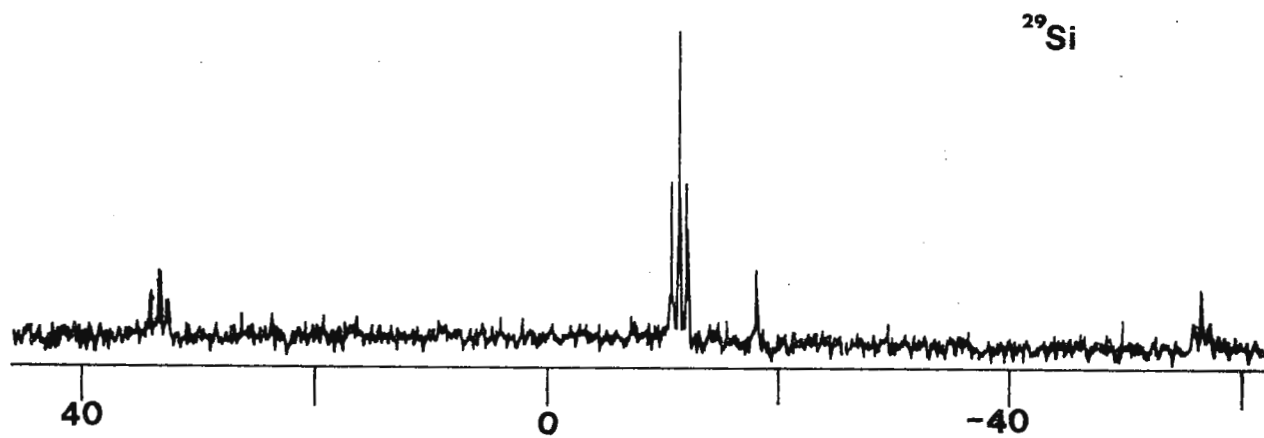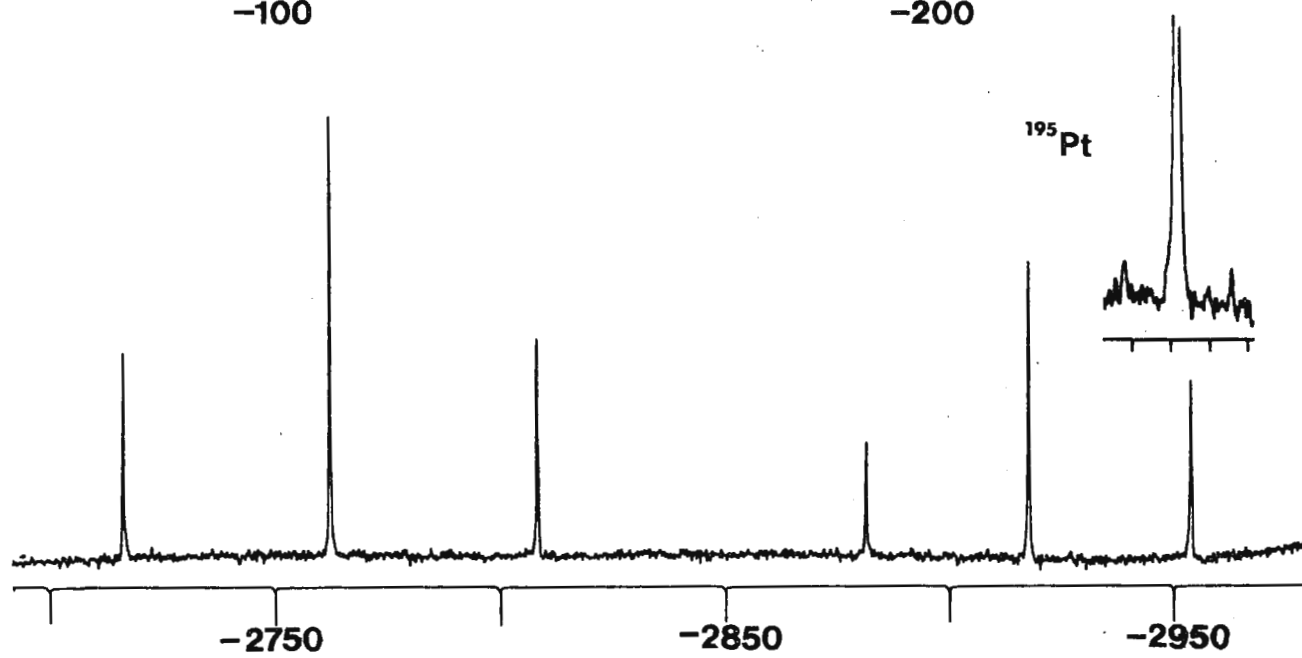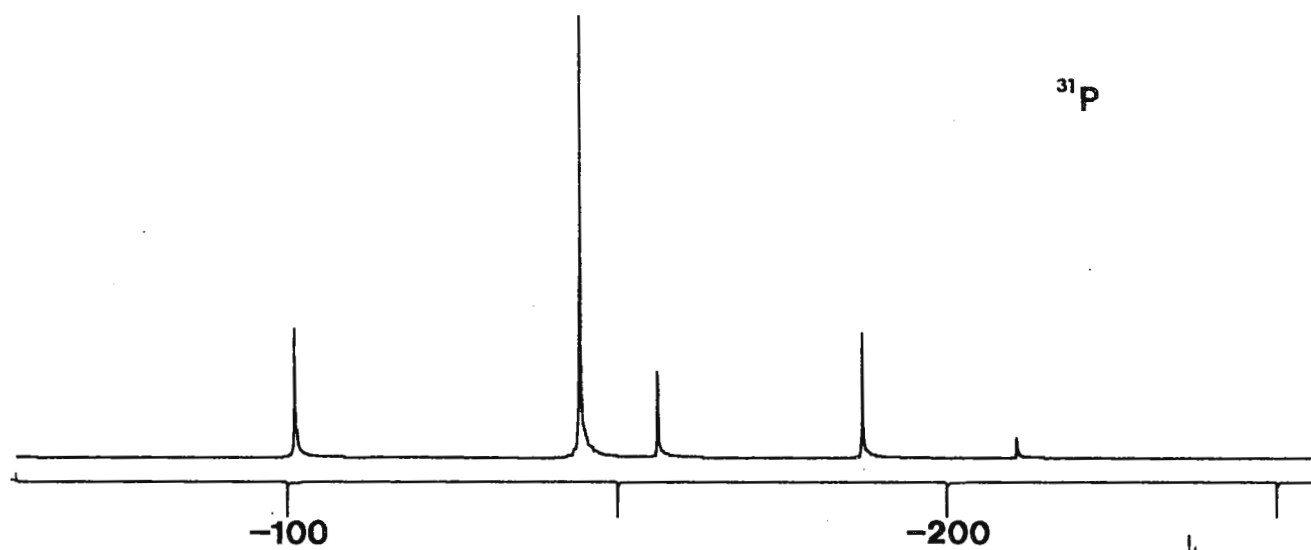
United States
Department of
Agriculture

Science and
Education
Administration

Agricultural Research
Northeastern Region
Eastern Regional
Research Center

600 East Mermaid Lane
Philadelphia
Pennsylvania
19118

August 20, 1982

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

Subject: Detection of Structural Asymmetry by ^{13}C CP-MAS NMR Spectroscopy

Dear Professor Shapiro:

We suggest that ^{13}C CP-MAS NMR is an excellent technique for establishing the crystalline and/or chemical state of carbohydrates. In recent reports, we have established that a single phase crystalline reducing sugar may contain multiple isomeric structures[1]. Conversely, a crystalline reducing sugar having multiple phases or nonequivalent sites in a unit cell can be mistaken as a mixture of isomers, when in fact only one anomeric form is present[1a].

α,α-Trehalose $\cdot$ $2H_2O$ is a symmetrical, nonreducing disaccharide incapable of undergoing mutarotation. For this reason, it is an excellent candidate for studying physically induced changes in crystalline transitions by CP-MAS NMR. As can be seen from the structure of α,α-trehalose $\cdot$ $2H_2O$ in Fig. 1, the two water molecules are unsymmetrically disposed within the molecular framework[2]. This gives rise to the nonequivalence of the C-6 and C-6$'$ (Fig.2) resonances at δ 61.7 and δ 63.2, respectively. These shifts are analogous to those reported earlier for the C-6 resonance of α-$\underline{D}$-glucose H_2O (δ 61.8) and anhydrous α-$\underline{D}$-glucose (δ 64.5).[3] Nonequivalence, corresponding to the water induced asymmetry at C-2 and C-2$'$ is probably responsible for the other two shifts at δ 68.5 and δ 71.4.

Upon heating to 98°α,α-trehalose $\cdot$ $2H_2O$ loses its water of hydration as well as its crystallinity[4] and exhibits the broadened spectrum in Figure 2. Further heating of the sample to 140° gives rise to a new anhydrous crystalline form (2c). which appears to contain either two nonsymmetry-related sites per unit cell or conformationally nonequivalent rings[5], ($^4C_1$ vs. $^1C_4$) per molecule. Azeotropic distillation of water from a pyridine[6] solution containing the crystalline dihydrate gives rise to crystals that have the identical spectrum of the 140° generated anhydrous form. Conversely, recrystallization of the crystalline anhydrous material from 50% aqueous ethanol regenerates the crystalline dihydrate.

A single crystal X-ray study to determine the nature of the observed solid state asymmetry of the 140° generated material is in progress.

Sincerely,

Philip E. Pfeffer

Kevin B. Hicks

1. (a) P. E. Pfeffer, K. B. Hicks, and W. L. Earl, Carbohydr. Res. (in press, 1982).
   (b) G. A. Jeffrey, R. A. Wood, P. E. Pfeffer, and K. B. Hicks, submitted to
        J. Am. Chem. Soc.
2. G. M. Brown, D. C. Rohrer, B. Berking, C. A. Beevers, R. O. Gould, and
    R. Simpson, Acta Cryst., Vol. B28, Part II, 3145 (1972).
3. P. E. Pfeffer and K. B. Hicks, Texas A & M Newsletter No. 278, 31 (1981).
4. H. J. Reisener, H. R. Goldschmid, G. A. Ledingham, and A. S. Perlin,
    Can. J. of Biochem. and Physiol., 40, 1248 (1962).
5. C. A. McDowell, A. Naito, J. R. Scheffer, and Y-F Wong, Tetrahedron Lett. 22,
    4779 (1981).
6. G. Birch, J. Chem. Soc., part C, 3489 (1965).

α,α-TREHALOSE DIHYDRATE
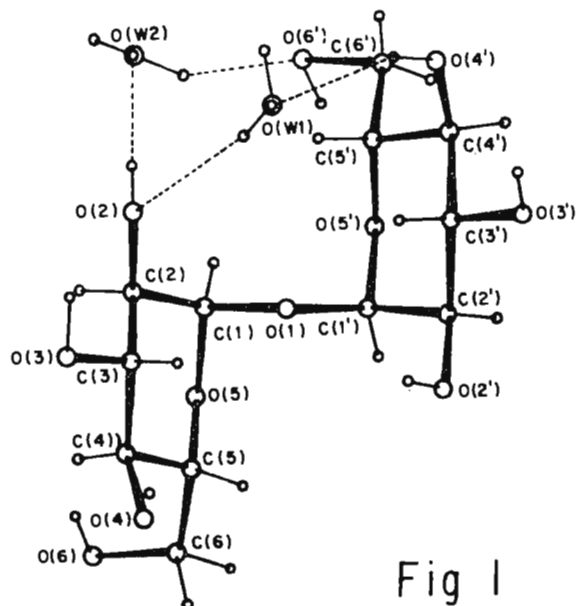
Fig 1

Legend for figure:

^{13}C CP-MAS spectra of (a) α,α-trehalose · $2H_2O$; (b) the same sample, after being heated at 98° for 4 hours; (c) after additional heating of sample in (b) for 4 hours at 140°. An identical spectrum was obtained as shown in (c) when the α,α-trehalose was obtained by dehydration in pyridine. Spectra were obtained at 15 MHz with 1K transients, a 10 G decoupling field, contact time of 3 msec, 2K data points zero filled to 8K, and a displayed frequency of 2 KHz.

α,α-TREHALOSE

Fig 2

C

B

140°

Crystalline
Anhydrous

Pyridine

98°

A

Crystalline
Dihydrate

110 100 90 80 70 60 PPM
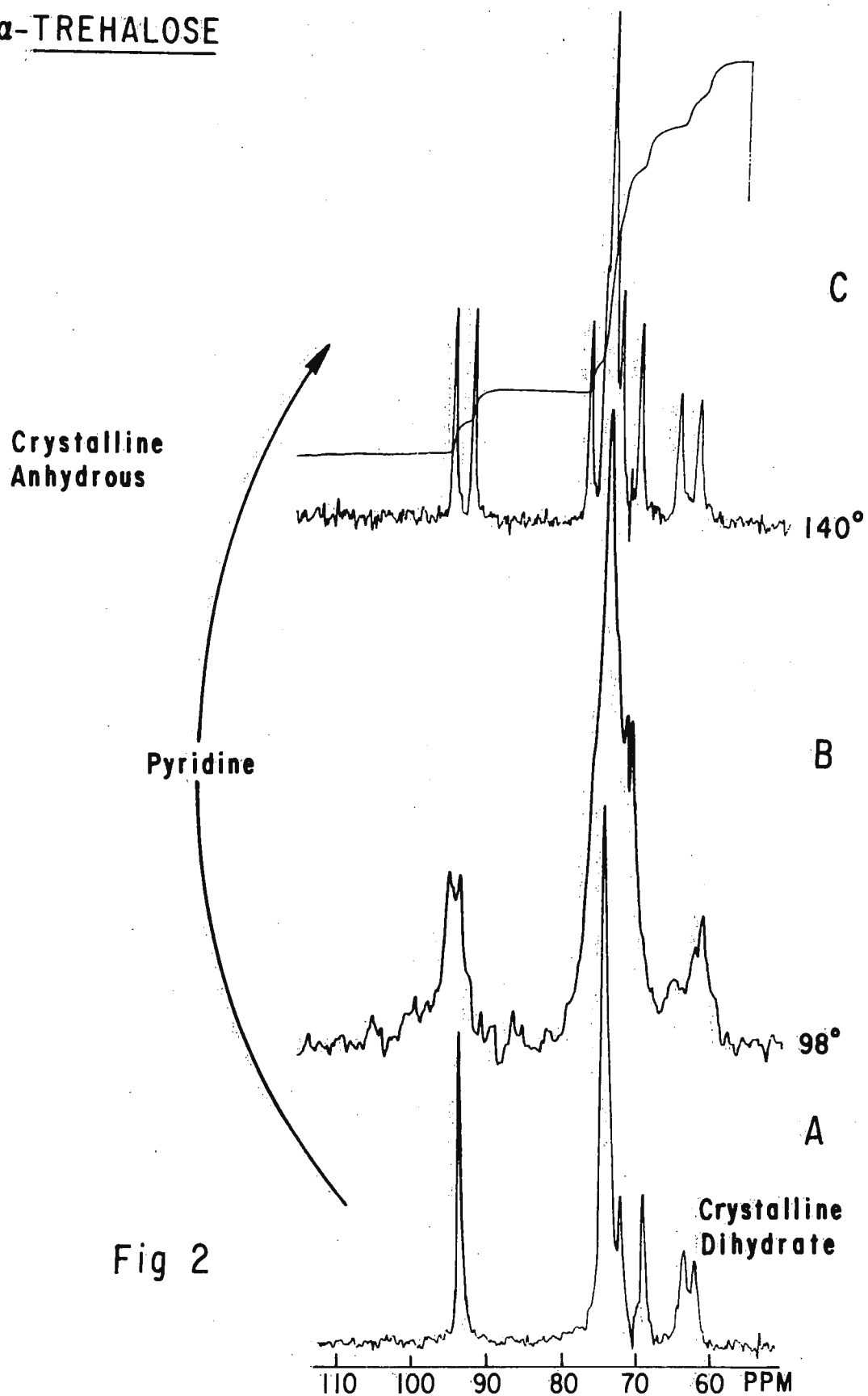
Prof. Dr. D. Leibfritz
Universität Bremen
Fachbereich Chemie/Biologie

NW 2 Leobenerstraße
2800 Bremen 33
Telefon (04 21) 218-2818/28 41

August 4, 1982/t

Prof. B.L. Shapiro

Texas A & M University

Dept. of Chemistry

College Station, Texas 77832

USA
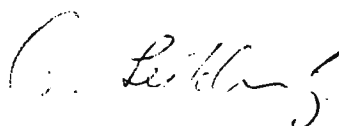
Title: Vacuum leakage in the magnet housing

Dear Prof. Shapiro,

Because of an increase in the helium consumption we had to warm our
magnet (WH-360) with an Oxford magnet. It turned out, that the aluminum
of the bottom plate was slightly corroded. Especially the circular groove,
which contains the large O-ring, showed a significant corrosion on the
surface. It has been necessary to mill off one milimeter of the alu-
minum plate in order to obtain a reasonably good vacuum again.

In my opinion the corrosion is mainly due to condensed water, which
drops down from the liquid nitrogen outlet. In order to avoid water
to get into the small slot between the magnet housing and the bottom
plate we sealed the slot with sealing silicone. We used ordinary
cartridges with silicone, which are used to tighten windows, glass etc.

Yours sincerely,

(Prof. Dr. D. Leibfritz)

National Research Council   Conseil national de recherches
Canada   Canada

Division of Chemistry   Division de chimie

Ottawa, Canada
K1A 0R6

August 26, 1982

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

Dear Barry:

Re: Removal of ^{13}C signals from deuterated solvents

Occasionally there is interference in a ^{13}C spectrum
from a signal or signals arising from the solvent. This is
normally overcome by using deuterated solvents which are
depleted in ^{13}C. It is possible to get similar suppression of
the solvent signals from normal deuterated solvents with the
pulse sequence of Figure 1. One subtracts alternate FID's.
This is a simple pulse sequence since it does not require any
phase shifting of either radio frequency nor very short pulses
from the decoupler. Of course, there is distortion of the
spectrum but even quaternary carbons are usually nearly visible
because of long range carbon-proton spin coupling. In
Figure 2(a) is a normal spectrum of 2 methylbutene-2 in
deuteratetrahydrofuran, while Figure 2(b) shows the spectrum
with the new sequence. Residual solvent lines are from those
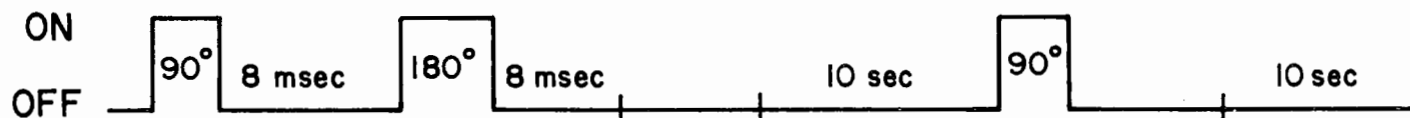solvent molecules which are not completely deuterated.
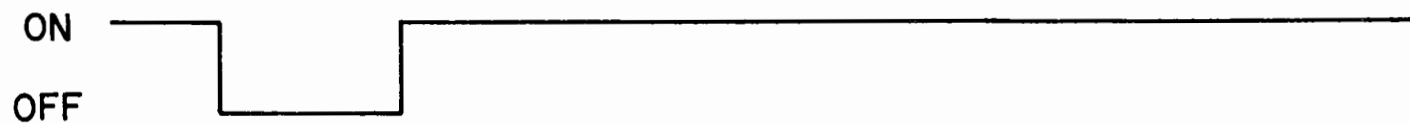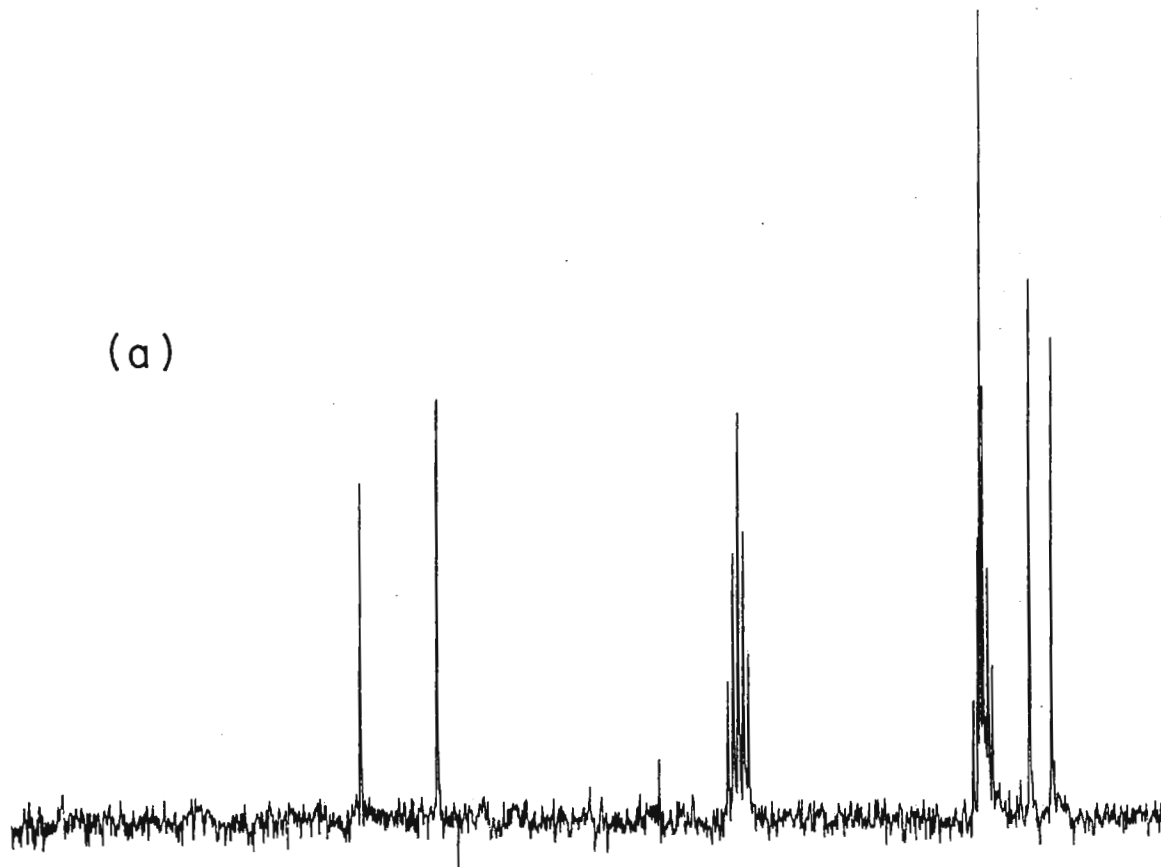
Yours truly,

S. Brownstein

SB/ar
Encl.

Canada
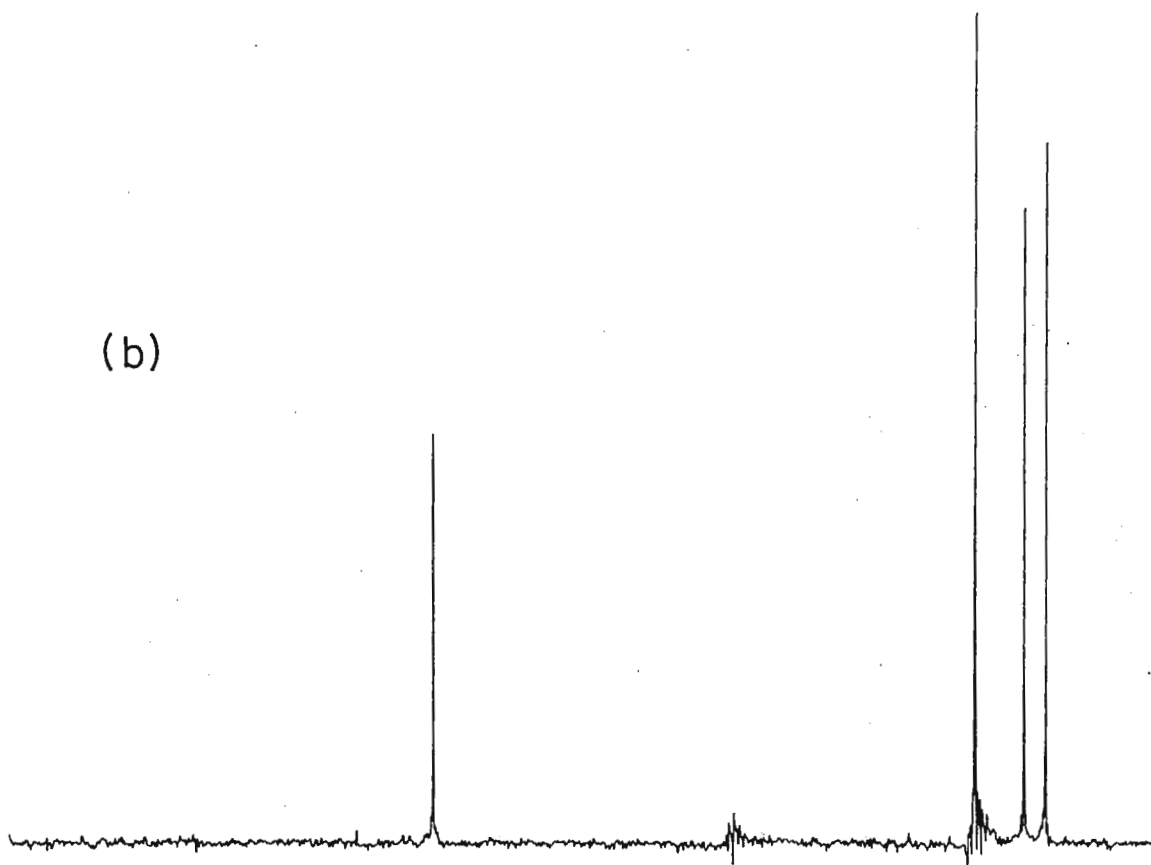
(a)

(b)

varian / instrument group
25 hanover road / florham park / new jersey 07932
telephone (201) 822-3700

August 10, 1982

Dear Barry,

19F DECOUPLING USING MLEV-16

One first tends to think of MLEV-16 as a method of obtaining equally efficient decoupling at reduced power levels, but another equally important aspect of this experiment is the ability to decouple over wider ranges for a given YH2. An obvious application is 19F decoupling at high fields.

Shown below are three spectra for the compound

CF3-(CF2)5-CH2-CH2-OH

The 19F spectrum, shown on the left, covers a range of nearly 10000 hz. With a YH2 of 6000 Hz, conventional (swept square wave) decoupling fails totally to give an acceptable spectrum (upper right). MLEV-16 (lower right), by contrast, shows complete decoupling of the C-F couplings (the downfield carbon shows two- and three-bond couplings to protons).

Each of these spectra were obtained and output on the XL-200, as was this letter!

Sincerely,

Steve Patt
NMR Applications Chemist

OBSERVE 19F:
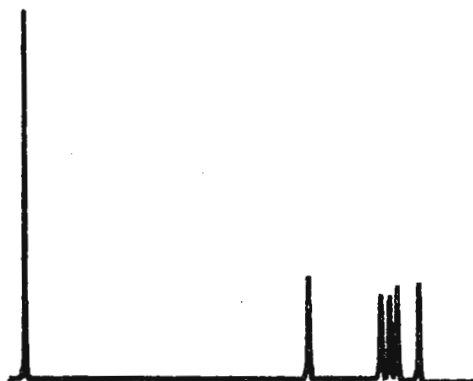
OBSERVE 13C,
DECOUPLE 19F:

BROADBAND

MLEV-16

CASE WESTERN RESERVE UNIVERSITY · CLEVELAND, OHIO 44106

August 23, 1982

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

Re: $^{13}C\{^2H\}$ INEPT for Labelling Studies

Dear Prof. Shapiro:

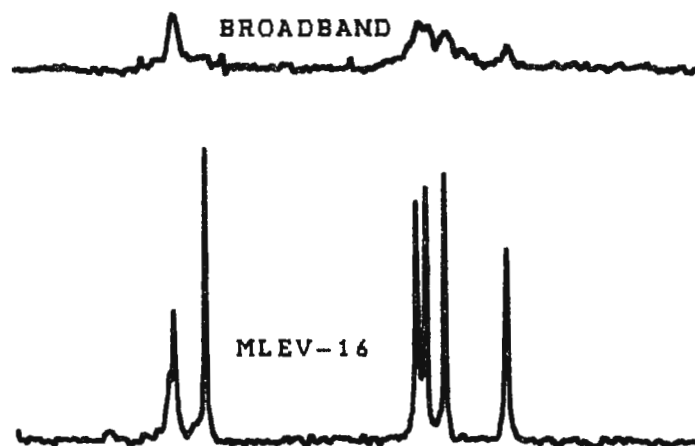To analyze a specific carbon location, ^{13}C labelling is unequivocal, but often difficult and expensive. If the site can be deuterated more easily, then observation of the ^2H nmr spectrum is an alternative means of identifying the position of the label. However, ^2H nmr spectra of isotropic liquids suffer from the disadvantage of low spectral dispersion.

Advantage can be taken of both the ^{13}C spectral dispersion and the expediency of ^2H incorporation by observing deuterated carbons using a $^{13}C\{^2H\}$ INEPT[1,2] experiment.
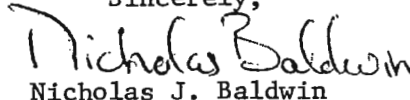
Besides the synthetic work, it does require some modifications of most spectrometers. On our Varian XL-200, we switched the ^2H transmitter from the lock to decoupler channel (but routed the signal through the double-tuned broad band observe coil) and added a double stage 30.7 MHz narrow band filter to the observe line.

With these changes we were able to pick out the deuterated aromatic peaks of phenylethanol in a 5% solution in chloroform(protonated) as shown in Figure 1.
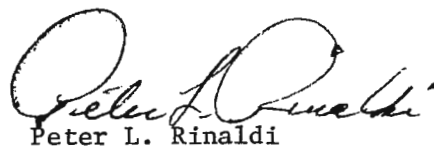
While polarization transfer from ^2H to ^{13}C is not favorable (compared to the normal ^{13}C spectrum with NOE) for a single acquisition, the faster repetition rate allowed by the faster relaxing ^2H more than compensates for the loss of signal.

Please credit this letter to Bill Ritchey's account.

Sincerely,

Nicholas J. Baldwin

Research Assistant

Peter L. Rinaldi

Assistant Professor
of Chemistry

References:
(1) Morris, G. A.; Freeman, R. M., Am. Chem. Soc., 1979, 101, 760-762.

(2) Morris, G. A.; J. Am. Chem. Soc., 1980, 102, 428-429.

Department of Chemistry
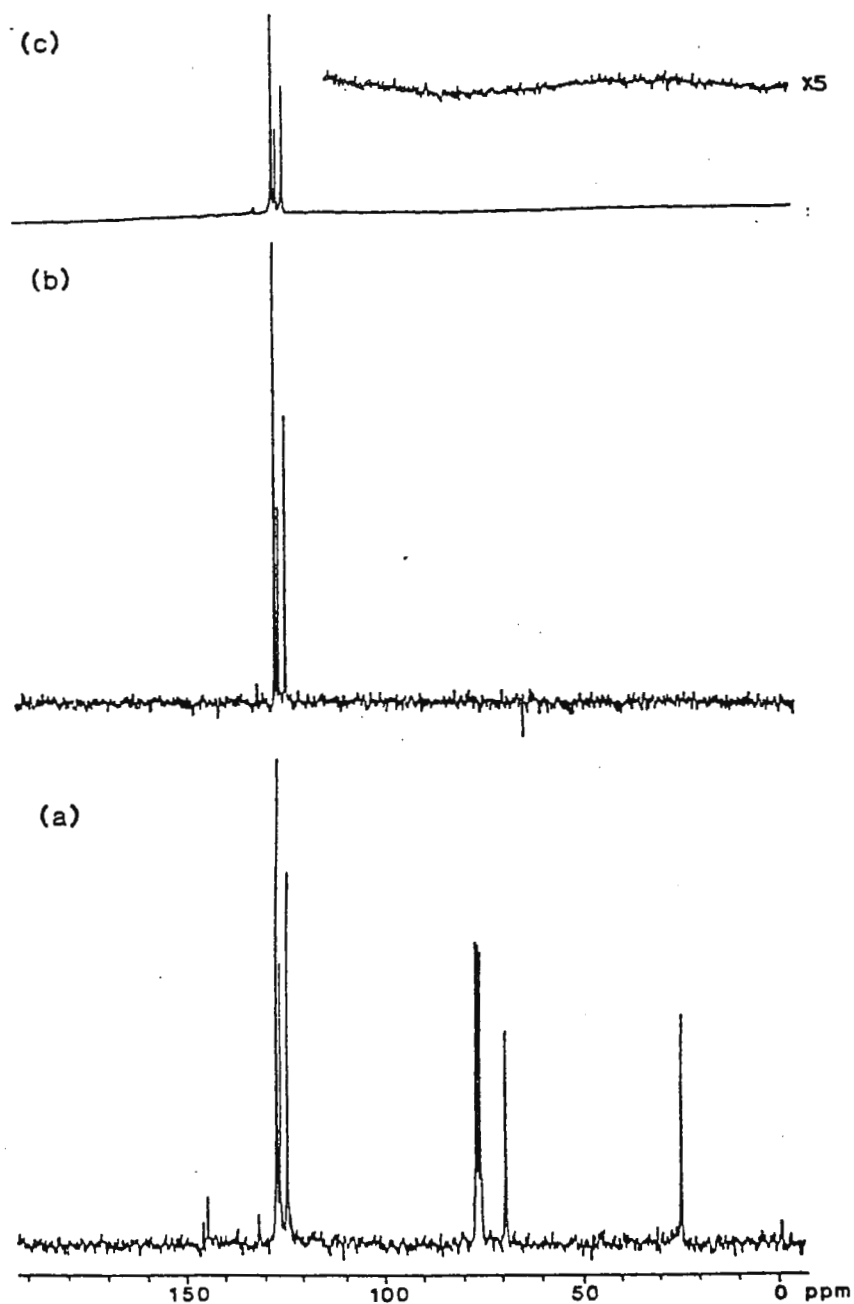
Figure 1 -- ^{13}C nmr spectra of 1-phenylethanol (1-PE) in chloroform, obtained
using a spectral window of 5,000 Hz, acquisition time of 0.4 sec,
and an exponential weighting of 3.5 Hz: a) normal proton decoupled
spectrum of 5% 1-PE in CDCl$_3$, obtained with a total experiment
time of 4 min., 4 transients, repetition time 6s, 90° pulse;
b) ^{13}C{^{2}H} INEPT spectrum of 1-PE-d$_5$ (deuterated in the aromatic
position) in CHCl$_3$ obtained with a total experimental time of
4 min., 240 transients, and 1s repetition time; c) same as b
but with 1% 1-PE-d$_5$ in CHCl$_3$, 20,000 transients, and 1.4s repeti-
tion time.

CONSIGLIO NAZIONALE DELLE RICERCHE

ISTITUTO DI CHIMICA DELLE MACROMOLECOLE

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

20133 MILANO, August 12, 1982
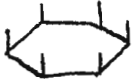VIA ALFONSO CORTI N. 12
TEL. 29.28.93 - 29.30.97 - 29.36.04 - 29.37.91
29.52.78 - 29.54.82 - 29.60.71 - 23.53.10

No. Esr. Prot. N. .... Ring Reversal of Hexakismethoxycarboxyl cyclohexane

Dear Professor Shapiro,

we have recently measured by complete line shape analysis of
the carbon-13 NMR spectrum the kynetic parameters for ring reversal
of hexamethyl ester of cyclohexane 1,2,3,4,5,6-hexacarboxylic acid
in both cis and muco isomers.The results are the following:

	cis	muco
ΔG^{*}_{cb} at 25 C	16.68 ± 0.07	12.14 ± 0.10 kcal/mol
ΔH^{*}_{cb}	14.79 ± 0.32	11.79 ± 0.5 kcal/mol
ΔS^{*}_{cb}	-6.33 ± 0.08	-1.2 ± 2.0 e.u.

The value of ΔG^{*} for the cis form is relatively high and
comparable to that measured for inositol and hexamethylcyclohexane.
The lowering of the barrier of the muco isomer can be due to an
increase of the ground state and /or to a decrease in that of the
transition state. However the latter contribution seems more reasonable
considering the higher stability of the muco isomer relative to the cis
previously reported by Angyal for the inositols. The lower energy
of the muco activated state can be ascribed in part to the effect
of the non-bonding interactions of the eclipsed substituent groups,
molecular models showing that in the cis activated state corresponding
to a conformation with five ring carbons(C-5,C-6,C-1,C-2 and C-3) in
a plane, the three vicinal substituents on C-6,C-1 and C-2 are eclipsed.
Meanwhile in the muco activated state this interaction is no longer
present because of the change of configuration at C-1.

Very truly yours

G. Gatti

G. Gatti

Carleton University
Ottawa, Canada K1S 5B6

August 18, 1982.

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

^{15}N NMR of Inosine Metal Ion Binding

As part of her doctoral thesis research Mary-Jane Bell is starting to put our XL-200 through its paces in the title work, using INEPT and nOe suppressed experiments.

Inosine, below, contains the rare base hypoxanthine, which occurs primarily as part of the anticodon triplet in a number of t-RNA species.
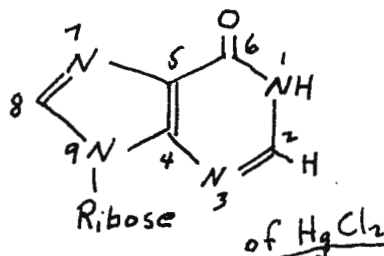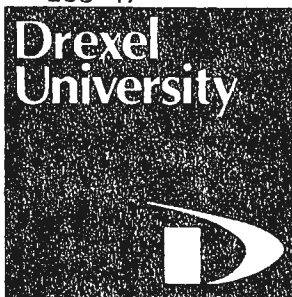

Addition of 0.5 molar equivalents of $HgCl_2$ to a DMSO-d_6 solution of inosine causes N-7 to move upfield by ca 5 ppm. Resonances for N-1 and N-3 are essentially unaffected, while the N-9 resonance moves downfield by ca 2 ppm.

We attribute these shifts to N-7 metallation. Zn^{+2} causes similar effects, while "hard" metals appear not to bind at nitrogen. Recently we've used ^{199}Hg shifts to further probe these phenomena - hopefully more about that in future contributions.

Sincerely,

G.W. Buchanan,
Professor of Chemistry.

mcs

Department of Chemistry ☐ Steacie Building ☐ (613) 231-2760

Drexel University

Drexel University • Philadelphia, Pennsylvania 19104

College of Science
Department of Chemistry
(215) 895-2638, 2639

August 24, 1982

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

Dear Barry,

Nitroxide Spin Labels;   A Polymer Perturbation?

Stable free radicals covalently attached to polymer chains can often be used to study dynamics of polymers where NMR is not conveniently used.[1] The question often posed in conjunction with the use of spin labels is, "does the label significantly perturb the motion of the polymer molecule?" To answer this question we compared ^{13}C and ^2H (enriched at the methyl group) NMR spectra with ESR spectra of the nitroxide spin labeled poly(vinyl acetate)-PVAc in various diluents. The spin label used was 2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl-3-carboxylic acid, which was added to the polymer side chain via ester interchange. The labeled polymer typically contained 1-10 nitroxides/molecule ($M_w=2.10^5$).

Shown in the figure are the spectra in chloroform as a function of concentration. As can be seen from all three techniques, there is a large change in the mobility of the polymer over a small concentration range (64 to 72%). From linewidth studies, results for the "effective" correlation times have been calculated for the side chain for all three techniques. The numerical results from all three are in agreement. Even though the calculations are crude (assuming a single exponential correlation time and Kivelsons Theory holds), we feel that in this system the nitroxide spin label is an accurate reporter group for the side chain polymer motion. With other diluents results from NMR and ESR are also in agreement and we feel, in general, that the nitroxide spin label is not a perturbation of polymer motion because of the qualitative and semi-quantitative agreement of NMR and ESR results. Further results will be forthcoming.

Cheerfully yours,

Wilmer G. Miller
Professor of Chemistry
University of Minnesota
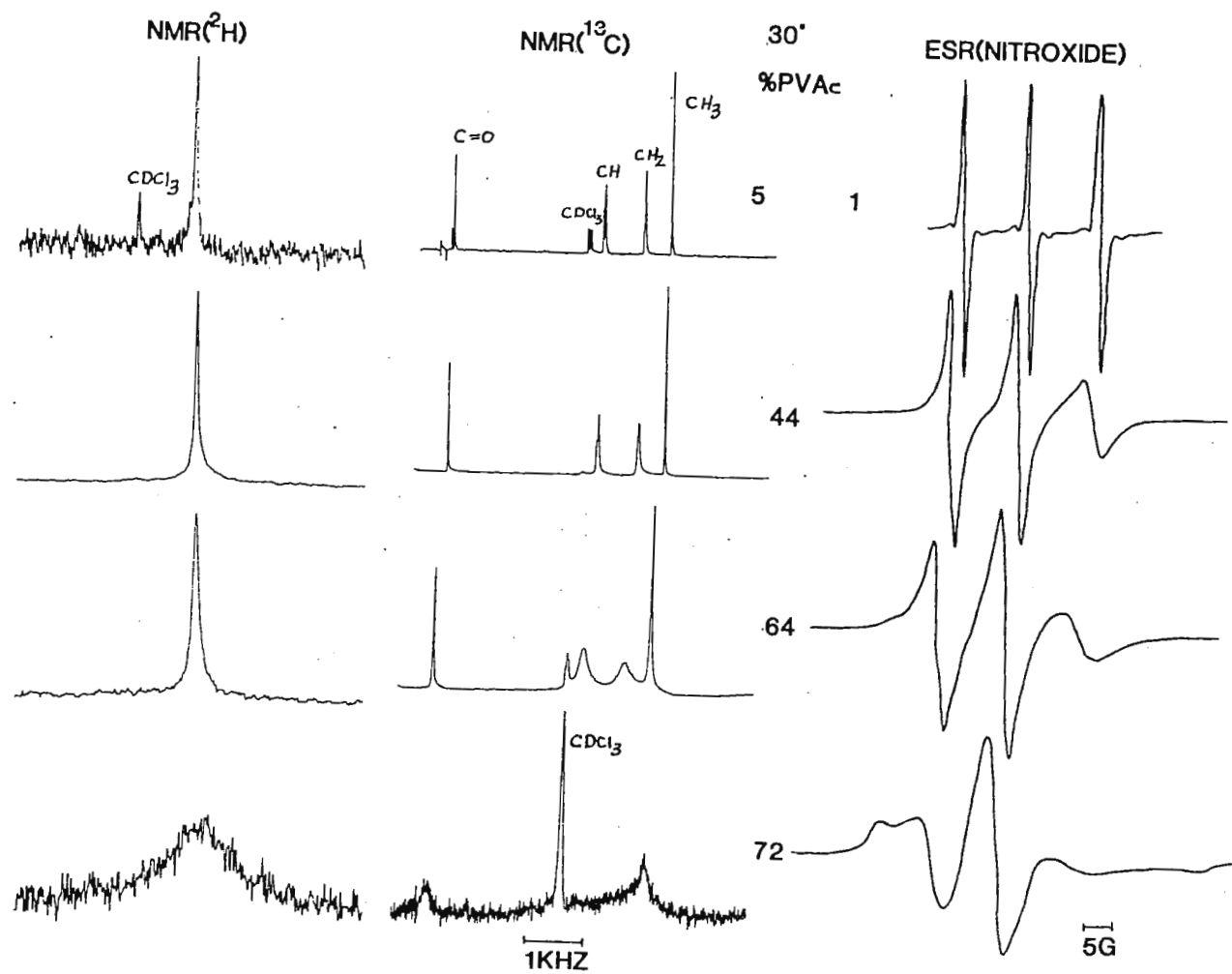
Frank D. Blum
Assistant Professor
of Chemistry

1. W.G. Miller, Spin Labeled Synthetic Polymers, in "Spin Labeling II.", L. Berlinner, Ed., Academic Press, New York, 1979.

POLY(VINYL ACETATE)–CHLOROFORM

Monsanto

_____ PHYSICAL SCIENCES CENTER

Monsanto Company
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

August 27, 1982

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

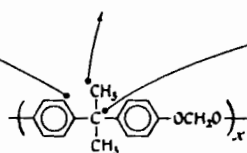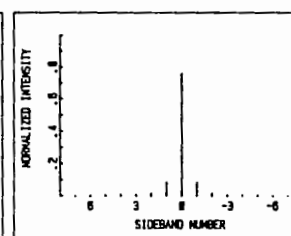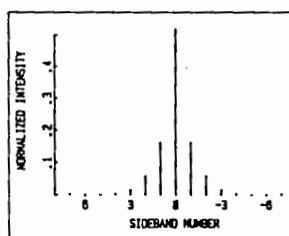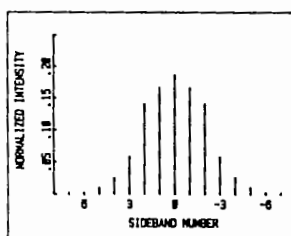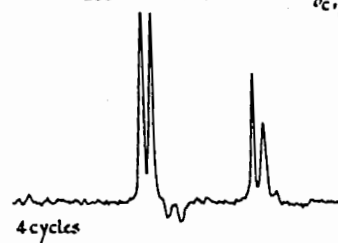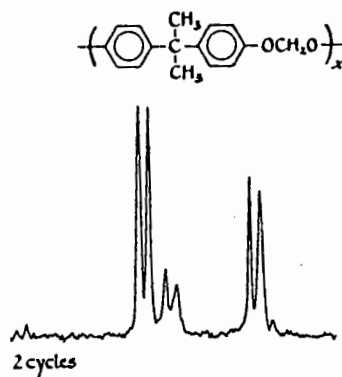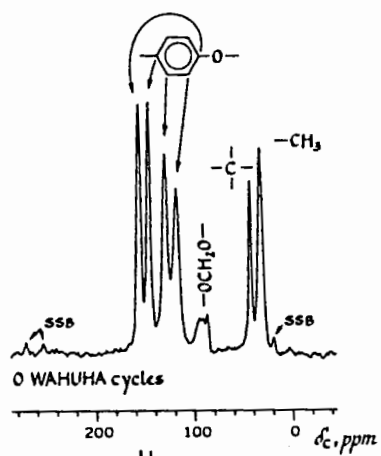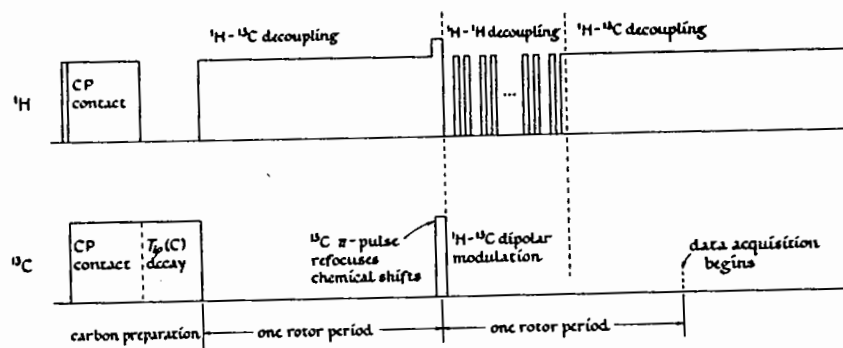Dipolar Ratational Spin-Echo C-13
NMR of Polymers

Dear Barry:

The reduction in the strength of the CH dipolar interaction
by molecular motion (of frequency comparable to or greater
than the dipolar interaction) is a measure of the amplitude
of the motion. We can detect the time evolution of the
cross-polarization carbon magnetization under the influence
of $^1H-^{13}C$ coupling exclusively in a solid sample rotating
at the magic angle using the pulse sequence shown at the top
of the figure. This experiment is similar to one introduced
by Munowitz and Griffen. The most important difference is
that we perform the experiment at low field so that spinning
sidebands from chemical shift anisotropy are not a problem.
The spectra shown in the middle of the figure were obtained
with dipolar evolution occuring for times measured by integral
numbers of WAHUHA 4-pulse repetitions. The centers of various
lines in the spin-echo spectra are then Fourier transformed
with respect to the dipolar evolution time. This is a 16-point
Fourier transform resulting in a 16-point frequency spectrum
in the dipolar dimension. Examples are shown at the bottom
of the figure. Dipolar lineshapes are broken up into side-
bands separated by the spinning frequency of 2 kHz. Broad
dipolar sideband patterns appear for carbons with strong CH
coupling. Details of the lineshapes can be interpreted in
terms of molecular motion in much the same way that ^2D
quadrupolar spin-echo lineshape patterns are now routinely
interpreted. In fact, for protonated (or deuterated) carbons,
^{13}C and ^2D experiments can be devised which contain identical
information about motion. The motivation for doing the carbon
experiment is that it is performed at natural abundance and
so is well suited for those systems which are labeled only
with difficulty.

Sincerely

Jake

Jacob Schaefer

^{1}H — ^{13}C decoupling

^{1}H — ^{1}H decoupling ^{1}H — ^{13}C decoupling

^{1}H

CP contact

CP contact $T_{1\rho}(C)$ decay

^{13}C

^{13}C π-pulse refocuses chemical shifts

^{1}H — ^{13}C dipolar modulation

data acquisition begins

carbon preparation — one rotor period — one rotor period

0 WAHUHA cycles   —CH$_3$ —OCH$_2$O—   —C—   SSB   SSB

2 cycles

200   100   0 δ_C, ppm

4 cycles   16 cycles

NORMALIZED INTENSITY   SIDEBAND NUMBER

NORMALIZED INTENSITY   SIDEBAND NUMBER

NORMALIZED INTENSITY   SIDEBAND NUMBER

UNIVERSITY OF CALIFORNIA, SAN DIEGO

BERKELEY · DAVIS · IRVINE · LOS ANGELES · RIVERSIDE · SAN DIEGO · SAN FRANCISCO   SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY, B-014
LA JOLLA, CALIFORNIA 92093

August 27, 1982

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

Spectral Densities of Motion from Carbon
Lineshapes of CD and CD2 Groups

Dear Barry,

Though lineshape calculations may seem to some to be as old as the hills – or the shape of old hills – our recent calculations and experiments should rejuvenate some interest. We recently completed calculations which allow us to determine <u>individual</u> spectral densities of motion, $j(w_o)$ and $j(2w_o)$, for deuterium from the ^{13}C spectra of CD or CD2 groups.

The lineshape of the ^{13}CD triplet is determined by the scalar coupling constant and the spectral densities $j(w_o)$ and $j(2w_o)$ (where w_o is the deuterium Larmor frequency). We have used this calculation to determine spectral densities from best fit spectra of monodeuterated MBBA in the isotropic phase at several different temperatures. A sample spectrum and corresponding best fit theoretical spectrum are shown in fig. A.

Our experimental work on MBBA is progressing rapidly and is yielding highly interesting results. A more thorough description of this work will be coming soon to a journal near you!

We have also done lineshape calculations of a ^{13}CD2 group, as a function of six spectral densities and and a coupling constant, using a computer. We hope to measure some experimental quintet spectra in the near future.

Sincerely,

Joel   Bob   Girte
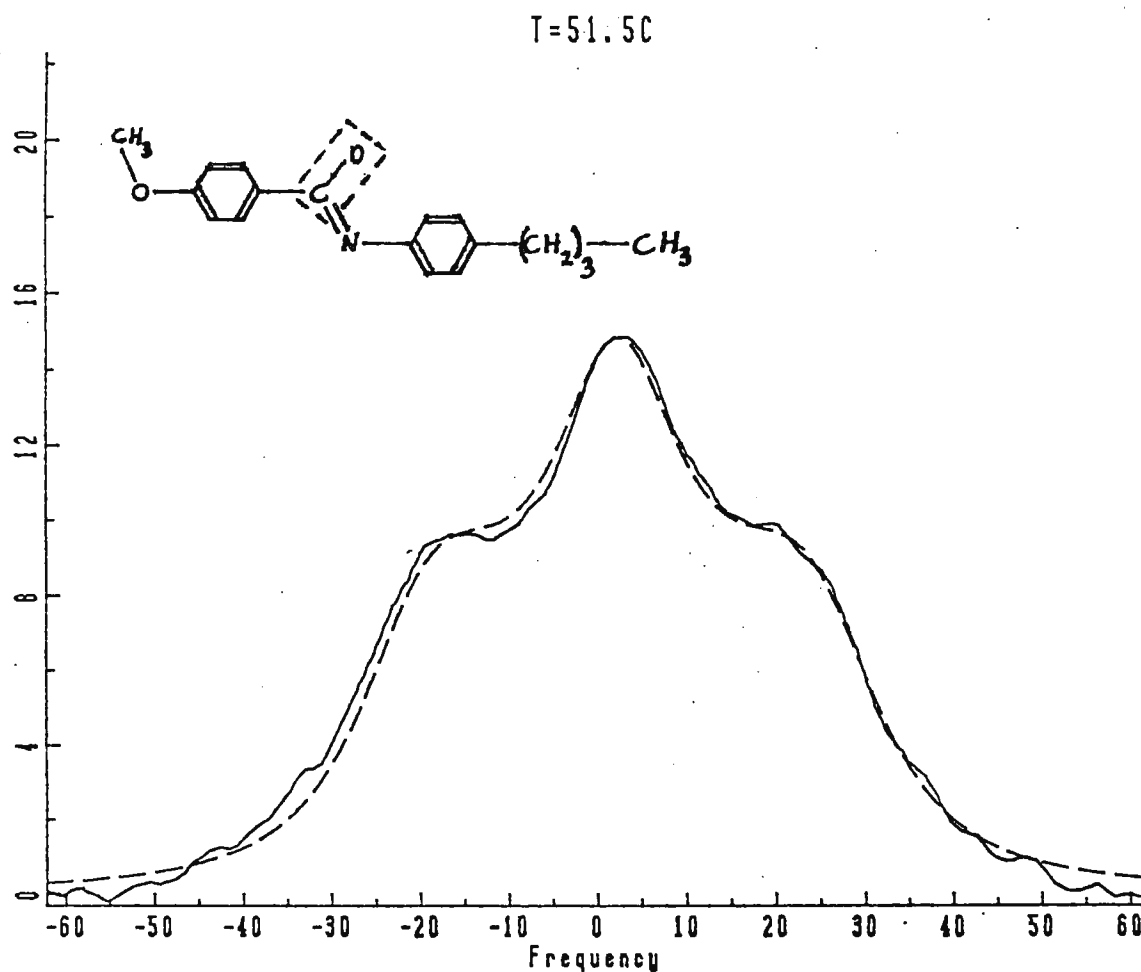
Joel F. Martin, Robert L. and Regitze R. Vold

Fig. A   Carbon-13 spectrum of the CD triplet of
linkage deuterated MBBA in the isotropic phase
(solid line) and the corresponding calculated
spectrum (dashed line). The field strength was
23.49 kG and the temperature was 51.5C.

Spectral densities of $j_1(w_0)$ = 55.5 ps and
$j_2(2w_0)$ = 40.1 ps were calculated using a
coupling constant of 24 Hz.

BRUKER Instruments, Inc.

MANNING PARK
BILLERICA, MASSACHUSETTS 01821
(617) 667-9580

August 27, 1982

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

"Course in 2D and DEPT Techniques"

Dear Barry:

Bruker is pleased to announce that we will be presenting
a course titled "High-Resolution Heteronuclear Multipulse Nmr
in Liquids" in cooperation with Drs. David Doddrell and R.
Bendall of Griffith University, the week of October 18-21, 1982.
The course will consist of two mornings of lectures, and two
afternoons of spectrometer and instrumentation examples.
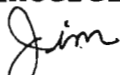
The topics to be covered will be:

1. Development of a vector Approach to Heteronuclear Multipulse Nmr:

> Effect of rf pulse amplitude and phase, and of hetero-
> nuclear coupling. Vector diagrams for CH, CH2 and CH3
> systems. Refocusing pulses. Double-rotating frame,
> effect of pulse on second nucleus.

2. Spin Echo Sequences:

> Proton flip, gated decoupled, off-resonance
> gated-decoupled and 1H randomization methods. A
> general sequence for quaternary carbons only.
> Applications to spectral editing. Discussion of
> errors involved. 2D J-spectroscopy.

3. Polarization Transfer vectors and INEPT sequence.

> Signal enchancement applications. Other polarization
> transfer sequences. 2D applications.

4. Correlated Motion: the vector description of heteronuclear
quantum coherence.

> Sequences involving correlated motion. 2D applications.
> Polarization transfer plus correlated motion. The EPT
> sequence.

5. The DEPT sequence.

> Signal enhancement, spectral editing and 2D applications.

The course will be held on the campus of the University of Wisconsin-Milwaukee so as to be centrally located for the greatest number of attendees. The cost of the course is $200 and lodging is available near the conference site at the Park East Hotel.

Those wishing to attend should contact Dr. Leo Brown of our Chicago office as soon as possible, even if you will require later travel approval, so that you can reserve a space in this popular course. Dr. Brown will also coordinate lodging arrangments. If there is substantial interest the course will be given twice. Registration will be limited to 25 members per course. Our phone number there is 312-668-4441.

Sincerely,

James W. Cooper, Ph.D.
Vice President for Software Development

JWC/c

SYRACUSE UNIVERSITY

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

August 10, 1982

Professor Barry Shapiro
Department of Chemistry
Texas A β M University
College Station, TX 77843
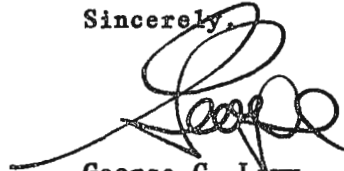
Postdoctoral or Senior Researcher Position

Dear Barry,

We have an opening in our laboratory for a postdoctoral or senior researcher specializing in the application and development of 2D NMR methods. Our main interests in this area are two fold: 1) we are interested in developing new 2D methods and 2) we are interested in applying these methods to several biochemical problems. Our in-house computer (Data General MV/8000) has already been used to develop a powerful general purpose 2DFT data processing system. This software is capable of rapidly processing extremely large data arrays. New capabilities can be easily added to the system and a successful candidate will be expected to contribute to the development of this software (although not necessarily as a programmer). Biochemical projects include an ongoing study of DNA motional dynamics and the effect of certain carcinogenic agents on DNA conformations and metabolic studies using ^{31}P and ^{13}C (with enriched substrates).

Syracuse University is an equal opportunity employer and all interested applicants should send their resume as soon as possible.

Sincerely,

George C. Levy
Professor

Charles L. Dumoulin, Ph.D.
Operations Manager

GCL/CLD:jrd

GEORGE C. LEVY, DIRECTOR   (315) 423-1021   RESOURCE COMPUTER: (315) 422-3443, (315) 422-3447