Texas A & M University
N - M - R
Newsletter

No. 264

September, 1980

TEXAS A&M UNIVERSITY
DEPARTMENT OF CHEMISTRY
COLLEGE STATION, TEXAS 77843

1 September 1980

MEMORANDUM

TO: Newsletter Participants/Subscribers

FROM: B. L. Shapiro, Editor and Publisher Barry Shapiro

SUBJECT: Size Requirements for TAMU NMR Newsletter Contributions

In order that sufficient margins are left for page numbers, stapling, etc., it is essential that all printed material, drawings, spectral lines, etc. be confined to a maximum area of 7½"* wide by 10"* high, with a full 1/2 inch* margin on all sides.

When material exceeds the above space requirements, it costs us a great deal in time and money, and this we simply cannot afford. Your cooperation will be greatly appreciated.

* For SI freaks+ or afficionados, 19.05 cm. x 25.4 cm., with 1.27 cm. margins.

+ American slang for devotées; no insult implied or intended!

BLS/ks

TAMU NMR NEWSLETTER - ADVERTISERS

TAMU NMR NEWSLETTER - SPONSORS

Abbott Laboratories
Bruker Instruments, Inc.
Eastman Kodak Company
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.)
Shell Development Company
Unilever Research
Varian, Analytical Instrument Division

TAMU NMR NEWSLETTER - CONTRIBUTORS

The British Petroleum Co., Ltd. (England)
E. I. DuPont DeNemours & Company
Intermagnetics General Corporation
The NMR Discussion Group of the U.K.
The Perkin-Elmer Company
Pfizer, Inc.
The Procter & Gamble Co., Miami Valley Labs
Programmed Test Sources, Inc.
Union Carbide Corporation
Xerox Corp., Webster Research Center

DEADLINE DATES: No. 265 6 October 1980
No. 266 3 November 1980

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

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

AUTHOR INDEX - TAMU NMR NEWSLETTER NO. 264

Standard Oil Company (Indiana)
Amoco Research Center
Post Office Box 400
Naperville, Illinois 60566
312-420-5111

July 15, 1980

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

Title: ^{13}C NMR of Ethylene-Butene Copolymers

Dear Barry:

I would like to report some results we recently obtained on ethylene-butene-1 copolymers. We were not able to find any literature references to ^{13}C spectra of these materials other than those where the butene levels were so low that only isolated butene units occurred. We studied polymers containing from 20 to 80 mole-% butene-1. Some samples were prepared with a Ti based catalyst system which should give predominately isotactic butene linkages while others were prepared with a V based catalyst which should give a more random stereochemistry. All samples were run as "melts" -- i.e., polymer with about 10% ODCB to decrease viscosity run at 160°C. A capillary of perdeutero ethylene glycol was used to provide a lock signal. Spectra of copolymers prepared with both a Ti and V catalyst are shown in Figure 1. The darkened peaks in Figure 1B are due to butene units in tail-to-tail as opposed to the normal head-to-tail configurations. As with ethylene-propylene copolymers, the tail-to-tail configurations only occur when a V catalyst is used.

The peak assignments are given in Table 1. The nomenclature used for a methylene resonance is that proposed by Carman[1] where two Greek letters are used to denote the position of a methylene from the nearest two methine carbons in either direction. For example, an $\alpha\gamma$ methylene is one bond (α) from a methine in one direction and three bonds (γ) from a methine in the opposite direction. Assignments were made using the additivity relationships of Lindeman & Adams and by comparison to the ^{13}C spectrum polyethylene containing only ethyl branches and to the ^{13}C spectrum of polybutene-1.

As expected by analogy with ethylene-propylene copolymers, the regions giving the most information about the sequence distribution in ethylene-butene copolymers are the $\alpha\alpha$, ^{t}C and branch-CH_2 regions. Unfortunately, each of these regions has overlap from other peaks. The $\alpha\alpha$ regions is overlapped by the ^{t}C - EBE and the branch CH_2 is overlapped by the $\beta\delta$ methylene. We are presently working with deconvolution techniques in an effort to determine the sequence distributions in these polymers.

Professor Bernard L. Shapiro

The ^{t}C resonance is much more sensitive to sequence distribution than is the CH_3 resonance. Most published spectra of polyethylene containing ethyl branches show that the CH_3 of the ethyl branch has a higher intensity than that of the corresponding ^{t}C peak. Indeed, Axelson, et al[2], report cases where no resonance is observed for the ^{t}C. One explanation for this behavior would be that ethyl branches occur in blocks. The effect of the blocks on the chemical shift of the methyl group is small but the effect on the ^{t}C is large, and peaks due to ^{t}C-BBE and ^{t}C-BBB are obscured by other peaks in low density polyethylene.

Sincerely,

G. J. Ray
Mail Station F-9

GJR/jh
Att.

[1] C. J. Carman & C. E. Wilkes, Rub. Chem. Tech. 44, 781 (1971)

[2] D. E. Axelson, G. C. Levy, and L. Mandalkern, Macromolecules, 12, 41 (1979)

Table I

Observed and Calculated ^{13}C NMR Chemical Shifts for Ethylene-Butene Copolymers and Related Polymers

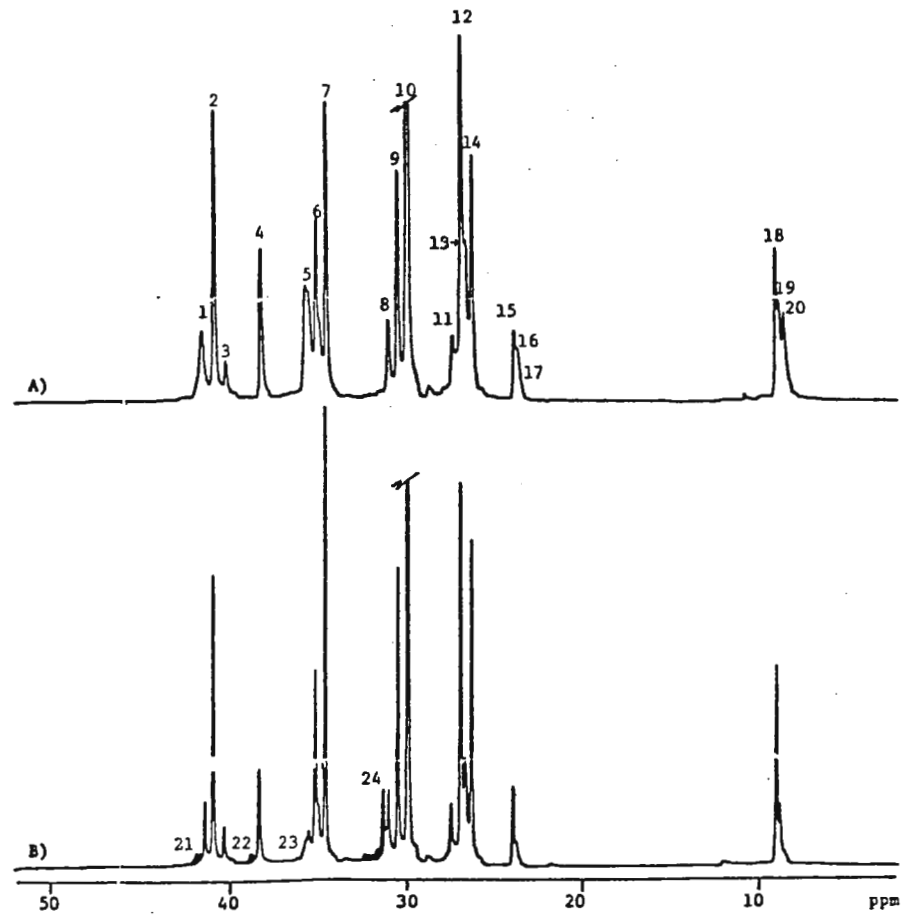
Peak	Carbon	Chemical Shift[a] PE[b]	PB[c]	EB1[d]	EB2[e]	Calc[f]
1	αα BBBB		40.6	40.4	40.5	39.0
2	αα BBBE			39.8	40.0	38.8
3	αα EBBE			39.2	39.6	38.5
6	αγ			34.6	34.9	34.7
7	αδ	34.3		34.1	34.4	34.5
15	ββ EBEBE			24.6	24.9	24.9
16	ββ BBEBE			24.5	24.8	24.8
17	ββ BBEBB			g	g	24.7
12	βδ	27.3		27.3	27.5	27.5
8	γγ			31.0	31.0	30.5
9	γδ	30.4		30.5	30.5	30.2
10	δδ	30.0		30.0	30.0	30.0
2	^{t}C EBE	39.7		39.8	40.0	39.1
4	^{t}C EBB			37.4	37.8	37.0
5	^{t}C BBB		35.5	35.2	35.5	35.0
11	CH_2-BBB		27.9	27.8	28.0	27.7
13	CH_2-BBE			27.2	27.4	27.4
14	CH_2-EBE	26.8		26.8	27.0	27.2
18	CH_3-EBE	11.2		11.2	11.2	11.4
19	CH_3-EBB			11.0	11.1	11.4
20	CH_3-BBB		10.8	10.8	10.8	11.4
23	αβ BB$\overline{B}$			h	32.0	32.0
24	αβ EB$\overline{B}$			h	31.6	31.8
11	βγ			h	28.0	27.8
21	^{t}C B$\overline{B}$E			h	40.9	39.1
22	^{t}C B$\overline{B}$B			h	38.2	37.1

(a) Chemical shifts relative to TMS
(b) Polyethylene prepared with low level butene monomer
(c) Polybutene prepared with Ti based catalyst system
(d) Ethylene butene copolymer prepared with Ti based catalyst system
(e) Ethylene butene copolymer prepared with V based catalyst system
(f) L. P. Lindeman and J. Q. Adams, Anal. Chem., 43 1245 (1971).
(g) Not observed
(h) Not present
(i) $\overline{B}$ represents a butene unit which is bonded tail-to-tail to an adjacent butene unit

GJRay/jh

Figure 1

^{13}C NMR Spectra of Ethylene-Butene Copolymers Prepared with a Titanium Catalyst (A) and a Vanadium Catalyst (B)



JACKSON STATE UNIVERSITY
JACKSON, MISSISSIPPI 39217

DEPARTMENT OF CHEMISTRY
601-968-2171

July 22, 1980

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

Dear Dr. Shapiro:

A recent letter by N.V. Riggs,[1] describes some results of ab initio calculations on amides and imides. It was gratifying that the results briefly mentioned do seem to bear out the qualitative trends found in our earlier calculations using the admittedly less reliable CNDO/2 method.[2] The CNDO/2 calculations also indicate that formimide is planar while there is a very small barrier to inversion in formamide (which is exaggerated in the CNDO/2 calculation), and that there is a preference in formimide for the E,Z configuration. However, it is not true that this latter result is, as stated by Riggs, "in agreement with experimental observations." NMR experiments unambiguously demonstrate that diformamide prefers the E,E configuration in acetone or acetone/toluene. While the existence of the E,Z isomer in the gas phase was demonstrated by Steinmetz,[3] his arguments concluding that it is the principle isomer in the gas phase or in the melt are not at all convincing, especially in view of subsequent NMR results. Admittedly, the energy difference between the two forms of diformamide is quite small, and perhaps we should not be discouraged by this minor lack of agreement between theory and experiment.

---

1. N.V. Riggs, TAMUNMRN, 258, 12 (March 1980).

2. E.A. Noe and M. Raban, J. Am. Chem. Soc., 97, 5811 (1975).

3. W.E. Steinmetz, J. Am. Chem. Soc., 95, 2777 (1973).

Sincerely yours,

Morton Raban /en Eric Noe

Morton Raban
Professor of Chemistry
Wayne State University

Eric A. Noe
Assistant Professor
of Chemistry
Jackson State University

Please credit this contribution to E.A. Noe.

ENC Inc. **Twenty-second Experimental Nuclear Magnetic Resonance Spectroscopy Conference**

Asilomar, California, April 5-9, 1981

August 21, 1980

22nd ENC, Asilomar, California, April 5-9, 1981

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

Dear Barry,

The next (22nd) annual meeting of the Experimental NMR Conference, ENC, will once again be held at Asilomar, California. Registration will begin Sunday, April 5, 1981, and the program will run through noon on Thursday, April 9. While the scientific program has not been completely formulated, sessions in the areas of solid state nmr, multi-quantum transitions, 2-D FTNMR, in vivo studies, NMR imaging, new techniques, computer system designs, and metal NMR in biomolecules are being planned.

While most talks are being arranged by session chairpersons, anyone not contacted who believes he/she has a significant scientific contribution to make may contact me directly. The now firmly established and previously successful poster sessions will continue and anyone interested in presenting a poster should contact Dr. David Dalrymple, Chairperson, at Nicolet Technology Corporation, 145 E. Dana Street, Mountain View, California 94041, before January 15, 1981.

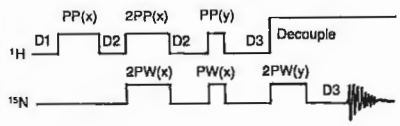
Anyone who attended the ENC's during the period 1976-1980 is on the current mailing list and will receive the registration packet and a copy of the preliminary program by January 1, 1981. Those who believe they are not on the mailing list or who do not receive the registration packet by January 1 should contact directly the ENC Secretary, Dr. A.A. Bothner-By, Department of Chemistry, Carnegie-Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213. The local arrangements for the 22nd ENC will be handled by Dr. Woodrow W. Connover, Nicolet Technology Corporation, 145 E. Dana Street, Mountain View, California 94041.

Sincerely,

Gerd N. La Mar
Chair, 22nd ENC
Department of Chemistry
University of California
Davis, California 95616

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

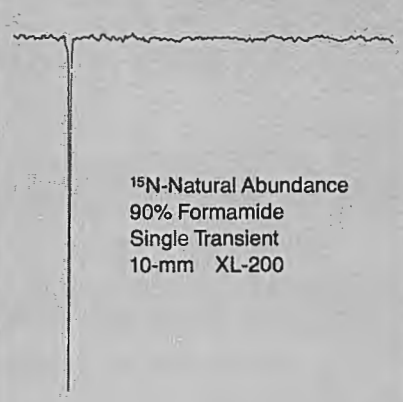
Pulse Diagram

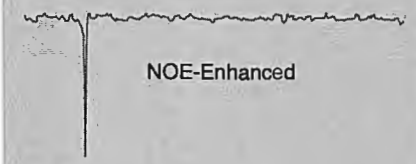


PSG Code

```
"INEPT WITH REFOCUSSING
  AND DECOUPLING
%I(SIMPUL)
PROCEDURE PULSESEQUENCE;
    VAR PP,J,MULT,D3:REAL
BEGIN
    GETVAL(J,'J    ');
    GETVAL(MULT,'MULT   ');
    GETVAL(PP,'PP    ');
    D2:=1.0/(4.0*J);
    PUTVAL(D2,'D2    ');
    IF MULT=3.0
      THEN D3:=1.0/(4.0*J);
      ELSE D3:=1.0/(2.0*J);
    PUTVAL(D3,'D3    ');
    ASSIGN(OPH,V1);
    INCR(V1);
    "EQUILIBRATION"
      STATUS(A);
      DELAY(D1);
    "TRANSFER POLARIZATION"
      STATUS(B)
      DECPULSE(PP,OPH);
      DELAY(D2);
      SIMPULSE(2.0*PW,2.0*PP,
        OPH,OPH,0.0,0.0);
      DELAY(D2);
      SIMPULSE(PW,PP,OPH,V1,0.0,0.0);
      DELAY(D3);
    "START DECOUPLING"
      STATUS(C);
      MOD2(OPH,V2);
      INCR(V2);
      PULSE(2.0*PW,V2);
      DELAY(D3);
    "OBSERVE FID"
      STATUS (D);
END;
```

Refocussed INEPT with Decoupling





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

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

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

Illustrated here is a simple implementation of these ideas.

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

Pulse Sequence Generation

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

PULSE	OFFSET	SPAREON	HLV
OBSPULSE	DELAY	SPAREOFF	DBL
DECPULSE	IFZERO	DECPHASE	ADD
SIMPULSE	LOOP	RCVRON	SUB
STATUS	DECR	RCVROFF	MOD2
ASSIGN	INCR	RND	MOD4

- Ability to specify and vary phase and receiver off-times dynamically
- Use of indirect variables for phase control
- Up to three nested loops for repetitive action
- Ability to execute simultaneous observe and decoupler pulses
- External device control under sequence control
- Use of floating-point parameter format
- User-creation of new delay, pulse, frequency, integer and flag parameters
- Flexible branching within sequences
- Ability to phase-shift within a pulse with no dead times
- Use of math statements for sequence timing calculations
- Complete separation of sequence code from parameter sets
- Dynamic variable calculations
- Use of indirect parameter labels in sequence code
- User control of parameter display characteristics
- **Example sequences**
  Standard two-pulse
  Carr-Purcell-Meiboom-Gill T2
  Quadrupole echo
  Cross-polarization
  Miltiple-contact cross-polarization
  Selective excitation
  Quadrature selective excitation
  INEPT
  INEPT with refocussing and decoupling
  PREP
  J-Cross polarization
  Refocussed J-cross polarization
  Noise off-resonance spin echo
  Inversion-recovery spin echo
  Multiple quantum 2D
  Proton-carbon correlated 2D
  Heteronuclear enhanced 2D
  Double quantum ^{13}C-^{13}C spectroscopy

Acquisition Processor

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

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

Standard Features

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

Accessories

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

Data System

- PASCAL language
- State-of-the-art operating system
- Disk-based using modular design software concept
- Concurrent and sequential PASCAL
- Floating-point data and math format
- Multitasking-simultaneous acquire, plot, print, display, parameter entry
- Queuing of acquisitions, plots, prints and calculations
- Spooling of plots and prints
- Disk-resident data tables
- Separate FID and spectral storage
- System resident PASCAL compiler for user programming
- User access to data files
- Expandable user-defined command and parameter architecture
- Floating-point or integer transform
- Convolution difference/gaussian apodization functions
- Parameter set libraries
- 2D transform
- Plot graphics
- T1, T2, 3-parameter least-squares-fit analysis programs
- Spin simulation
- LAOCOON with magnetic equivalence
- User-definable disk libraries
- PASCAL system source code availability
- NOE calculation
- Add-subtract-convolution spectral manipulation

varian/instrument group • 611 hansen way, palo alto, california 94303 u.s.a.
679 springvale road, mulgrave, victoria, australia 3170 • 45 river drive, georgetown, ontario, canada L7G 2J4
3rd matsuda bldg., 2-2-6 ohkubo, shinjuku-ku, tokyo 160, japan • steinhauserstrasse, CH-6300, zug, switzerland
other sales offices and dealers throughout the world

varian

MAG-2842 (Printed in U.S.A.)

Monsanto

PHYSICAL SCIENCES CENTER

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

August 20, 1980

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

MAGIC ANGLE SPINNING SPEED MONITOR

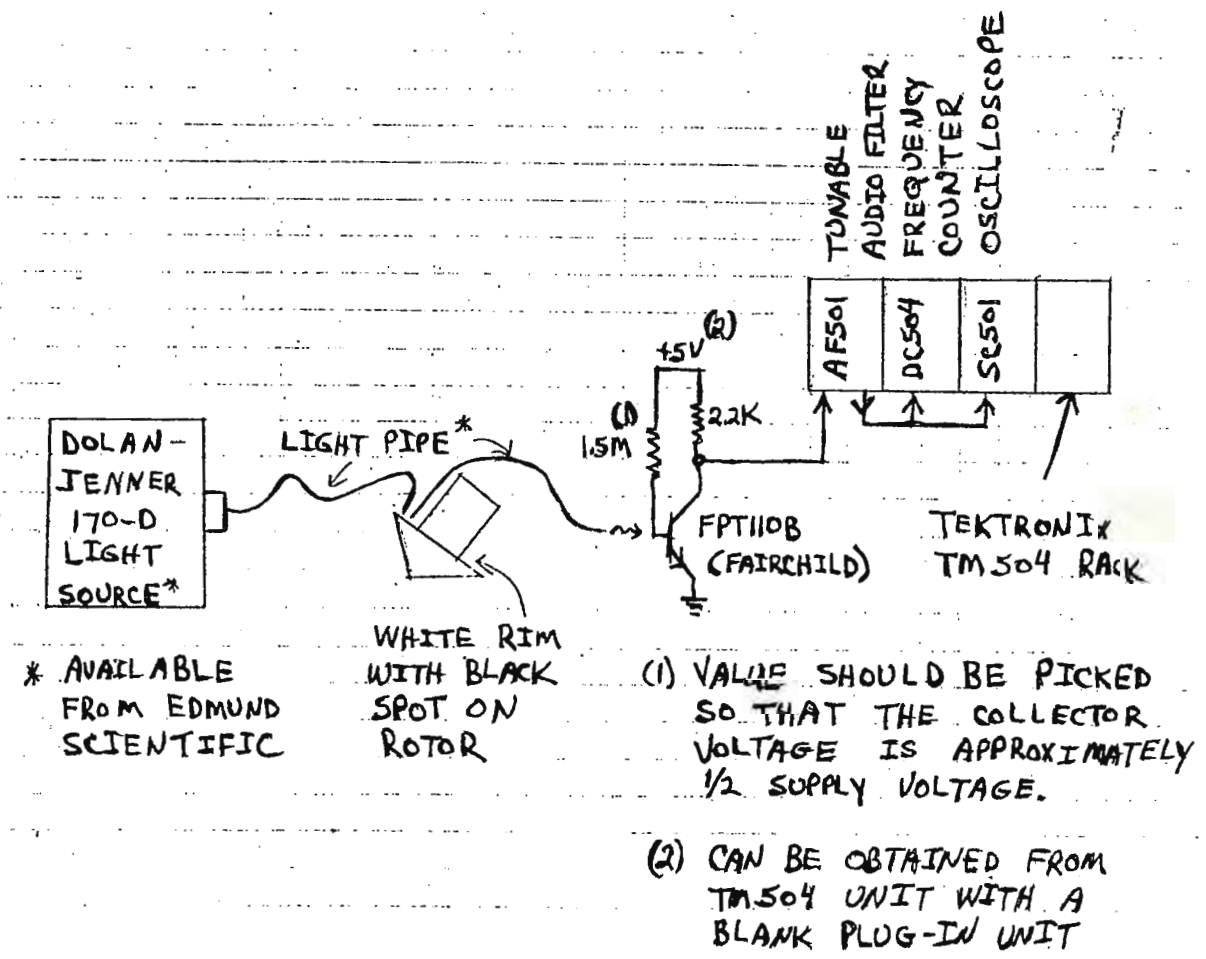
Dear Barry:

I enclose a diagram illustrating a technique whereby the spinning frequency and stability of a magic-angle rotor in a magnet can be monitored in situ. Please credit this contribution to the Monsanto subscription.

Sincerely,

Robert A. McKay

Robert A. McKay



EESTI NSV TEADUSTE AKADEEMIA

KEEMILISE JA BIOLOOGILISE FÜÜSIKA INSTITUUT

200104 Tallinn, Lenini puiestee 10
Tel. 44-06-40, 60-57-29, 60-57-93
Arve 6 112 260 Riigipanga Lenini osakonnas Tallinnas

АКАДЕМИЯ НАУК ЭСТОНСКОЙ ССР

ИНСТИТУТ ХИМИЧЕСКОЙ И БИОЛОГИЧЕСКОЙ ФИЗИКИ

200104 Таллин, бульвар Ленина, 10
Тел. 44-06-40, 60-57-29, 60-57-93
Расч. счет 6 112 260 в Ленинском отделении Госбанка, г. Таллина

July 31, 1980 Ref. No. 24

Teie nr.
На Ваш №

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

Magic rolling of rocks

Dear Prof. Shapiro:

With the solid state high resolution NMR highly popular and still gaining, it was indeed high time to look for ever harder tasks for it to master. We turned to stones as the hardest and most solid objects readily available. It appears that ^{29}Si high resolution NMR spectra of all kinds of stones, rocks, minerals, glasses, cements, zeolites, catalysts, etc., whether amorphous or microcrystalline, consist often of sharp (20 to 120 Hz) lines with chemical shifts that are regular and easy to interpret. We used our CXP-200 and CXP-200/300 Bruker spectrometers for this job, both in the high power decoupling and cross-polarization modes. Magic angle spinning at about 3 kHz was used in both cases. The ^{29}Si *rf* pulse length was 4 to 10 μsec and the repetition rate from 2 to 30 sec^{-1}. The measuring time varied from a few minutes to overnight runs. The samples were provided by the Tallinn Technical University, Tartu State University and, most importantly, by Dr. G.Engelhardt in the Central Institute of Physical Chemistry, Berlin.

The ^{29}Si chemical shifts of silicates depend upon the type of condensation of the [SiO_4] tetrahedra. The ^{29}Si shift ranges are quite distinct and do not overlap (-65 to -75 ppm from liquid TMS in monosilicates, -77 to -83 in disilicates and chain end groups, -84 to -90 in the chain middle groups, -95 to -100 in the branching sites and -103 to -112 in the quartz-like three-dimensional frameworks). These solid-state

shift ranges are close to those in soluble silicates and are not sensitive to the presence and nature of large cations (Na, K, Ca, Mg, Zn, etc.).

In the case of the three-dimensional aluminosilicates the ^{29}Si chemical shift depends primarily on the degree of silicon substitution by aluminum in the lattice. Each additional aluminum atom (or rather $[A\ell O_4]$ tetrahedron) that shares an oxygen atom with the given Si atom in the $[SiO_4]$ tetrahedron shifts this particular ^{29}Si resonance by about 5 ppm to low field. In the spectra of synthetic zeolites NaA ($Si/A\ell = 1$), NaX ($Si/A\ell = 1.18$ and 1.35) and NaY ($Si/A\ell = 2.5$) with a very flimsy bubble-like structure, up to 5 separate ^{29}Si signals with very different intensities can be found. The line intensities are close to those predicted from the $Si/A\ell$ ratio and the known zeolite structure. The signal in the low field (-84 ppm from TMS) corresponds to $[SiO_4]$ tetrahedra that are directly connected to four $[A\ell O_4]$ tetrahedra (in our designation Si(4 Aℓ)). The other four signals at about -89 ppm, -94 ppm, -99 ppm and -103 ppm correspond to the less substituted Si(3 Aℓ), Si(2 Aℓ), Si(1 Aℓ) and Si(0 Aℓ) units, respectively. Quite surprisingly, the single sharp signal from NaA zeolite is shifted from the expected value for Si(4 Aℓ) units (always at -84 ppm, particularly in thomsonite, sodalite, chlorosodalite, nepheline, and other $Si/A\ell = 1$ zeolites) to -89 ppm, which is typical for Si(3 Aℓ) units. An A-type zeolite with a regular distribution of $[SiO_4]$ tetrahedra, each connected to 3 $[A\ell O_4]$ tetrahedra, is possible, but only if a symmetrically distributed pattern of SiOSi and AℓOAℓ pairing in the double four-rings, connecting the cubooctahedra, is present. The existence of such AℓOAℓ bridges violates the well-known Loewenstein rule, which disapproves of any sharing of oxygen atoms by two four-coordinated aluminum atoms in aluminosilicates. We tend to believe that there might be loopholes to every rule and so the aluminums should be allowed to be as gay as they please if they so insist. We try to find out what they are really up to.

Sincerely

E. Lippmaa M. Mägi A. Samoson M. Tarmak

E.Lippmaa, M.Mägi, A.Samoson, M.Tarmak, G.Engelhardt

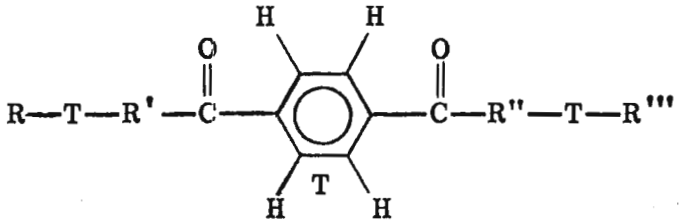
August 8, 1980

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

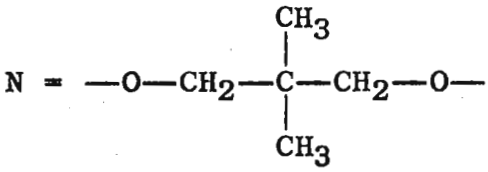
Dear Barry:

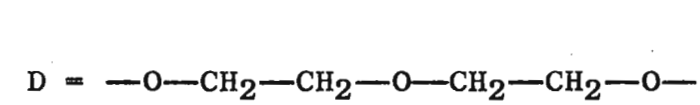
Long-Range Chemical-Shift Effects in Polymers

Recently, we have found that the chemical shifts of the aromatic protons in copolyesters of terephthalic acid (T) with neopentyl glycol (N) and diethyleneglycol (D) are influenced by chemical differences at surprisingly long distances down the polymer chain. As can be seen in the figure, nine different resonances for the aromatic protons are resolved at 600 MHz. These signals derive from the different combinations of glycols around the terephthalic acid as shown below. The assignments of groups of terephthalate signals to structures involving only the nearest diols are shown in the figure.



R, R', R'', R''' = N or D





Nonequivalent protons giving AA'BB' patterns are possible for some of the above combinations, but apparently the A and B protons have essentially the same chemical shifts. A very similar, less-resolved pattern occurs at 400 MHz, for example, contrary to what one would expect if coupling effects were present.

As far as we know, chemical-shift effects relating to the second group of glycols down the chain have never been found before in polyesters. In some cases here, we are seeing chemical-shift differences from structural differences 17 to 21 bonds from the

Professor B. L. Shapiro, Texas A and M University
August 8, 1980

observed protons. Of course, through-space distances (or average distances) are probably more relevant than bond distances; we are exploring whether the shifts can be used to get conformational information. We expect to be submitting a publication on this work in the near future. We thank Professors Dadok and Bothner-By for allowing us to obtain the 600 MHz spectra.

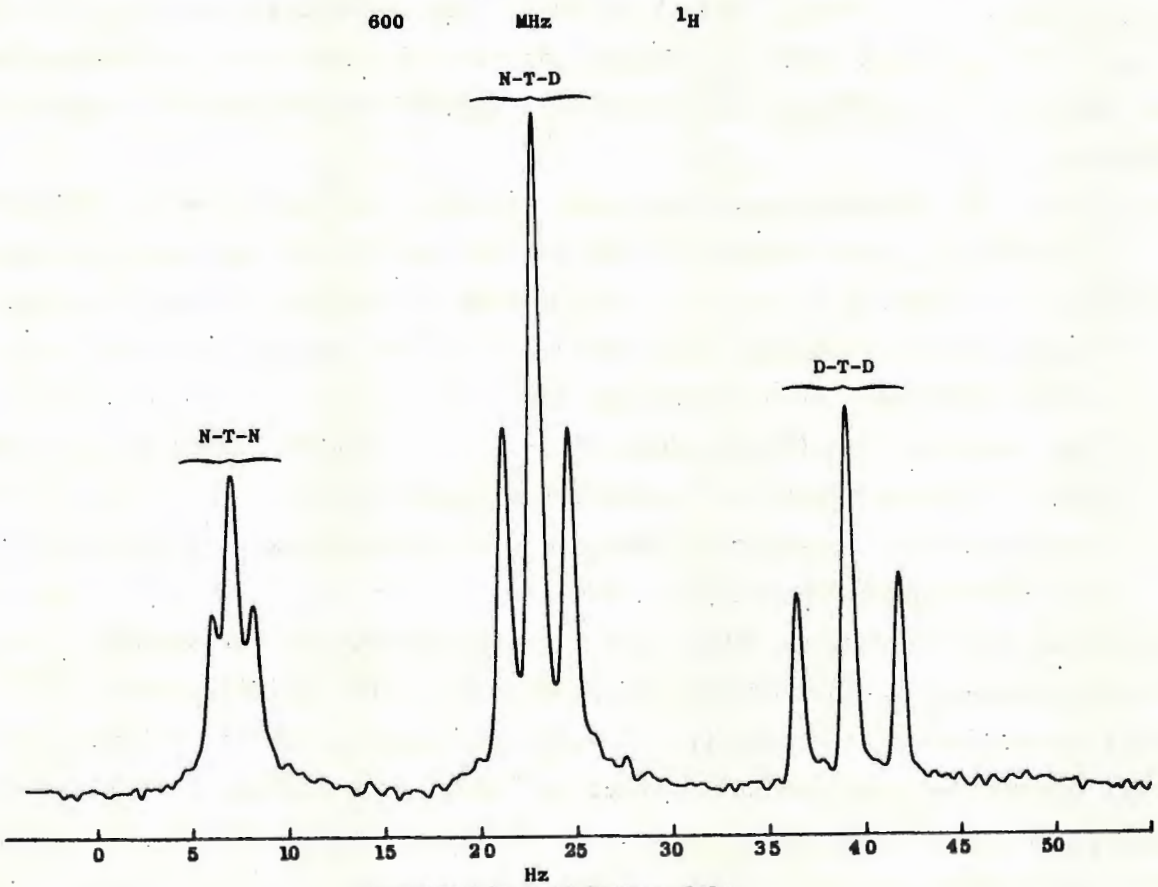
Sincerely yours,

Mark Mike

PMH/JMH/nc

P. M. Henrichs
Chemistry Division
Research Laboratories

J. M. Hewitt
Chemistry Division
Research Laboratories



Terephthalic Acid Protons Only

264-13

The University of Connecticut

STORRS, CONNECTICUT 06268

THE COLLEGE OF
LIBERAL ARTS AND SCIENCES
Department of Chemistry

August 13, 1980

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

Dear Professor Shapiro:

While trying to interpret observed quadrupolar splitting patterns ($\Delta\nu_i$ vs. carbon #i) for labeled liquid crystals using polymer chain statistics, I've arrived at a prescription for handling the intra- and extramolecular motional averaging of the relevant electric field gradient tensors which can be applied to completely flexible solute molecules in nematic solvents. Figure 1a shows the DMR spectrum of n-octane-d_{18} dissolved in Merck Phase V at 300K. The quadrupolar and dipolar splittings employed in the computed spectrum (Figure 1b) were obtained via a configurational average wherein the following conditions were imposed on the model of molecular reorientation:

a) intra- and extramolecular motional averaging is separable (a configuration lifetime is long compared to the overall rotational correlation time);

b) the order matrix S of each configuration is diagonal in the molecular fixed frame that diagonalizes the moment of inertia tensor I (the magnitude and biaxiality of S is derived from I);

c) the energetic constraints imposed on a given configuration by the nematic mean field are generated by the interactions of each atom with the wall of a hypothetical cylinder of radius r (the cylinder axis is concident with the minor principal moment of inertia).

As the normal internal energy parameters are well documented for alkanes, the only adjustable parameter in this scheme is r. Moreover, the optimized value for r indicates that in the case of alkanes dissolved in nematics, other configurational dependent properties (rms end-to-end vector, "kink" probabilities, etc) are only slightly perturbed by the constraints of the nematic mean field from the values computed for isotropic systems ($r = \infty$). This simple model of chain dynamics is readily extended to other situations (model bilayers) and preliminary comparisons of experiment with calculations are very encouraging.

Very truly yours,

Ed Samulski

Edward T. Samulski

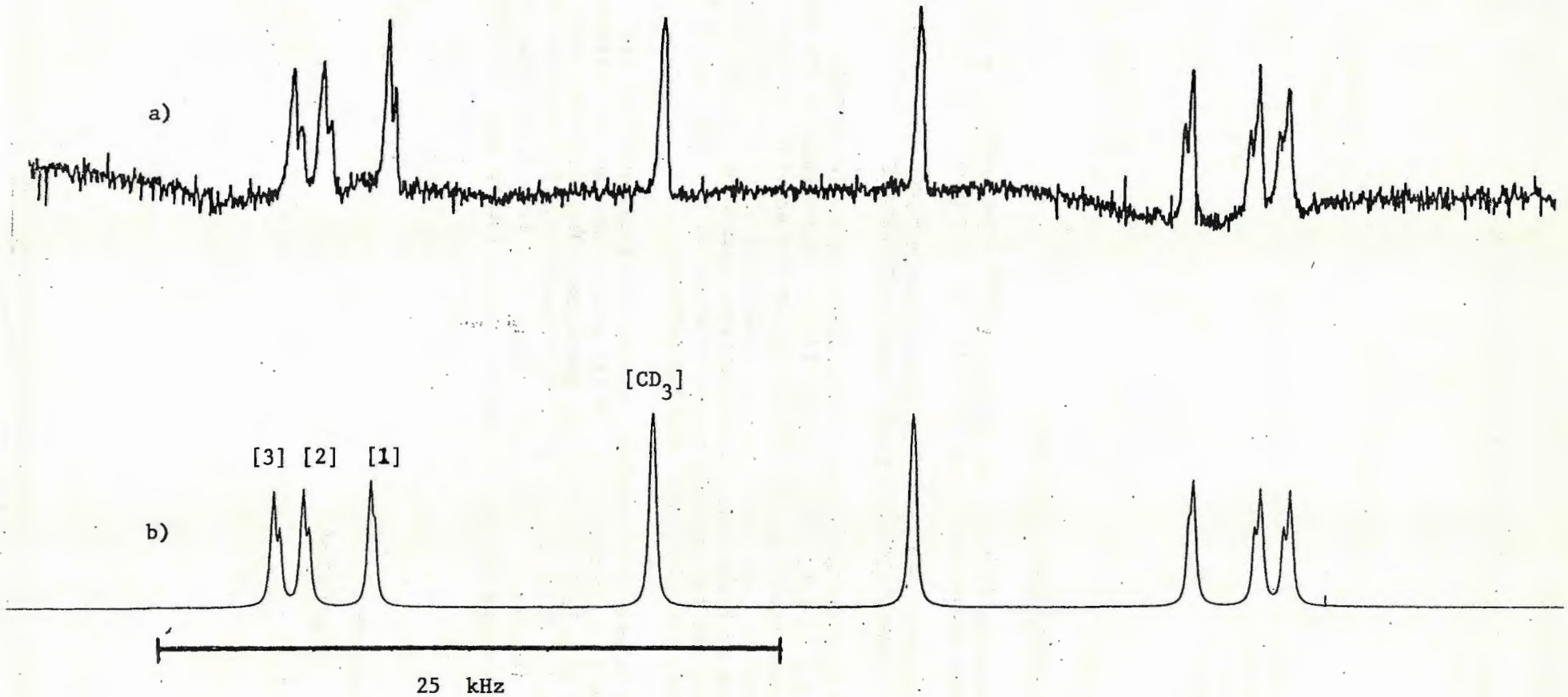


FIGURE 1. DMR spectrum of n-octane-d_{18} in nematic solvent. a) Experimental spectrum; b) Calculated spectrum with r = 4.58Å. The assignment [i] is derived from the calculation and commences with the penultimate carbon with increasing i toward the center of the octane molecule.

varian associates limited
28 Manor Road/Walton-on-Thames/Surrey/KT12 2QF
Telephone Walton-on-Thames 43741/Cables Varian Walton/Telex 928070

varian

Your Reference:
Our Reference: CT/drs

15th August 1980

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

Dear Professor Shapiro,

MULTIPLET SELECTION EXPERIMENTS WITH INEPT

I have recently been using Freeman and Morris's INEPT experiment as a kind of rival to off-resonance decoupling on my XL-200. The sequence I use is:-

^{1}H D1-90°(x,-x)-D2-180°(Y)-D2-90°(Y)-D3-180°(X)-D3-DECOUPLE
^{13}C 180°(X)-D2-90(X,Y)-D3-180°(X,Y)D3ACQUIRE

I enclose a partial spectrum of Menthol. The bottom trace is an INEPT experiment with D3 set to 1/6J (D2 is always 1/4J). Above this is the single frequency off resonance spectrum with the decoupler set so that the three quartets did not overlap. This off-resonance decoupled spectrum illustrates the familiar problems of broadening and distortions caused by second-order effects. By contrast the top two INEPT spectra where D3 has been set to 1/4J and 3/8J respectively, provide a much simpler picture.

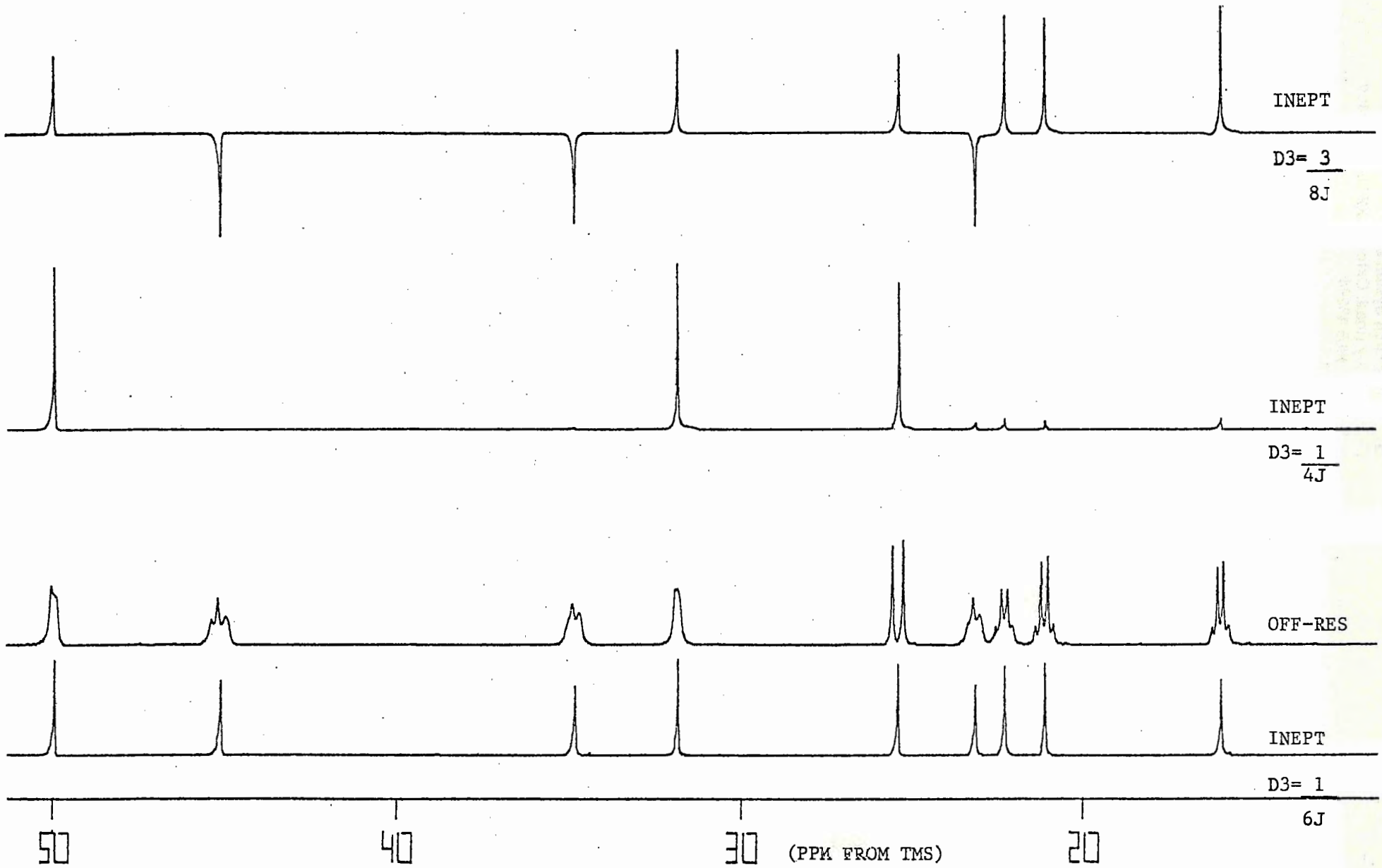
With D3 set to 1/4J we see only doublets, the triplets and quartets are certainly suppressed by a factor of 10. While with D3 set to 3/8J triplets appear out of phase with both doublets and quartets. Obviously the phase angle is also dependent on the one bond carbon-proton coupling constant but the method can tolerate changes of about ±10%. While this is a disadvantage of the method, its major advantage is that it is, of course, faster than off-resonance decoupling.

Yours sincerely,

C J Turner

C. J. Turner

Encl.



C. J. TURNER Carbon spectra of Menthol observed by the INEPT pulse sequence

264-17

Oxford Research Systems
Ferry Hinksey Road, Oxford OX2 0DT, England
Telephone 0865 43294
Telex 83413

OXFORD
RESEARCH SYSTEMS

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

DATE 20 August 1980

OUR REF. DS/SIE

YOUR REF.

Dear Barry,

May I introduce a new subscriber and a new technique to your Newsletter. Topical Magnetic Resonance (TMR) is a new technique for acquiring ^{31}P high resolution NMR spectra from a selected, localized place within a sample. This localization process involves carefully profiling the main magnetic field, B_o, solely with static magnetic field gradients. TMR is aimed primarily at studies of the biochemistry of living systems and although in principle TMR may be used for any nucleus, we have selected ^{31}P because of its established value in the study of animal metabolism. In keeping with the current vogue we derived our name from ancient Greece - Τοπος = a place.

We have proved the technique both with phantoms, e.g. concentric spheres with each compartment containing different solutions and also by obtaining ^{31}P spectra uniquely from the liver of a live, intact animal (you can check that this is working because the liver contains no phosphocreatine, and so when you decrease the size of the sensitive volume down to the size of the liver, that peak disappears).

We have obtained spectra from individual muscles of human limbs, and followed the time course of metabolite concentrations when the blood supply is stopped. Attached are some spectra, which I hope your readers will find interesting, which show the expected effects, such as the increase of inorganic phosphate, decrease of phosphocreatine, etc. These spectra were obtained on an Oxford Research Systems TMR 32 Spectrometer.

Details of the technique and our preliminary applications work have been submitted for publication. Preprints and further details on the technique are available from Oxford Research Systems on request.

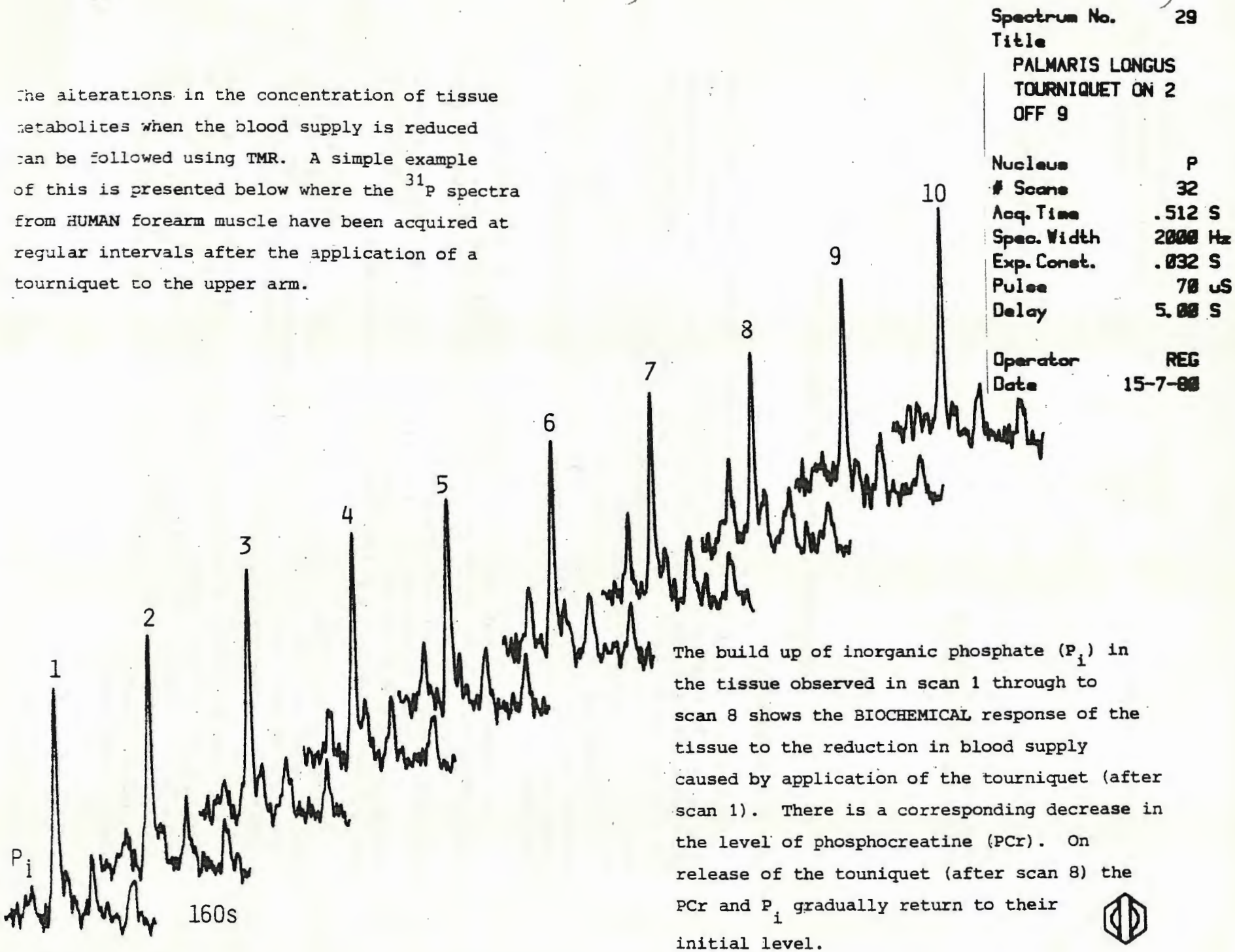
Best Wishes.

Yours sincerely,

DR. DEREK SHAW
Marketing Manager

Enc.

The alterations in the concentration of tissue metabolites when the blood supply is reduced can be followed using TMR. A simple example of this is presented below where the ^{31}P spectra from HUMAN forearm muscle have been acquired at regular intervals after the application of a tourniquet to the upper arm.



The build up of inorganic phosphate (P_i) in the tissue observed in scan 1 through to scan 8 shows the BIOCHEMICAL response of the tissue to the reduction in blood supply caused by application of the tourniquet (after scan 1). There is a corresponding decrease in the level of phosphocreatine (PCr). On release of the touniquet (after scan 8) the PCr and P_i gradually return to their initial level.

HARVARD MEDICAL SCHOOL

JEAN L. DELAYRE, Ph.D.
Research Associate in Biophysics

25 Shattuck Street
Boston, Massachusetts 02115
617 · 732-1878

Dr. B.L. Shapiro
Dept. of Chemistry
Texas A&M University
COLLEGE STATION, TX 77843

22 August 1980

SODIUM NMR IMAGES OF A PERFUSED RAT HEART

Dear Dr. Shapiro,

Most of the work of acquiring NMR images has been done looking at proton (i.e. water) in various media. Some experiments have been carried out on phosphorus, although low sensitivity and several lines in the spectrum which may overlap are the main drawbacks to obtaining phosphorus images. On the other hand, sodium offers good sensitivity, comparable to proton and a single line spectrum which eases the image reconstruction program.

The recording of a two-dimensional cross-section is based on the application of linear magnetic field gradients in two perpendicular directions and one alternating gradient in a direction perpendicular to the two others.

The images shown here were obtained using a Nicolet NT-360 Wide-Bore NMR spectrometer (8.2 T) which has been modified in the following way:

- three computer-controlled DAC's were added to vary the currents of the first order gradient shim coils;
- several patches to NTCFT were written to provide these controls during acquisition of the NMR data as well as to allow the reconstruction and the display of the image from the different projections.

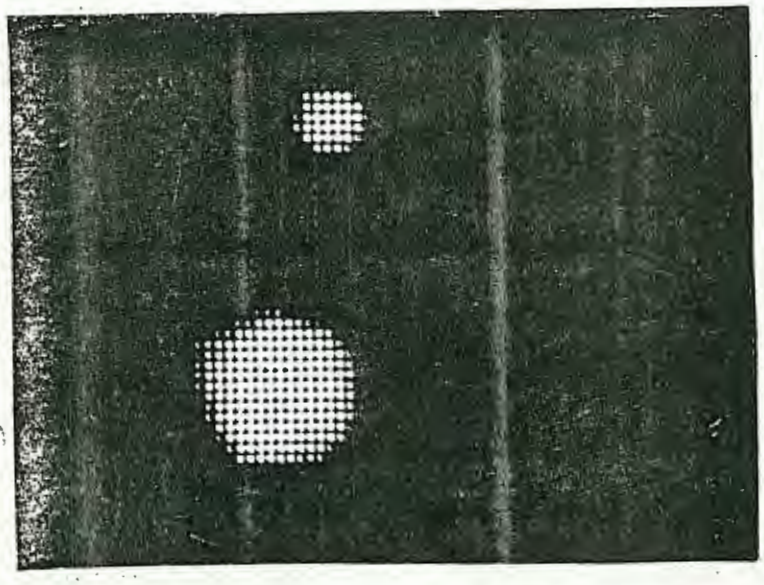
The system was tested using a phantom consisting of a 20 mm sample tube full of water in which a 5 mm and a 2 mm tubes filled with an physiologic solution have been inserted and slightly off-centered. The image (64x64 pixels) was reconstructed from twelve projections, one every 15 degrees.

The cross-section of a perfused rat heart at the level of the left ventricle was obtained under the same experimental conditions. In order to get a "still" picture, the acquisition of each FID was triggered by the heart beat. One image shows the heart during diastole (the heart is relaxed and full of "blood"), the second shows the same heart during systole (the heart is contracted).

With this type of data, one can calculate the ejection fraction (EF) which gives an idea of how 'good' the heart is (a normal EF is usually between 60% and 85%). In this particular case, EF was found close to 56%.

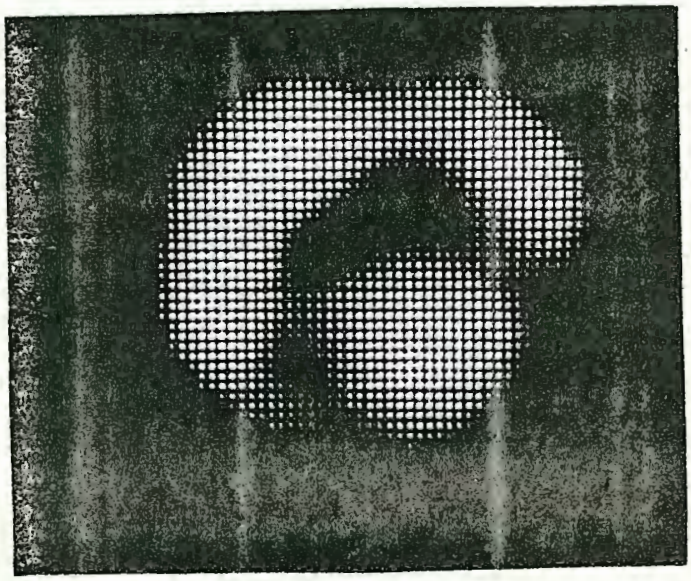
Yours sincerely,

Jean L Delage

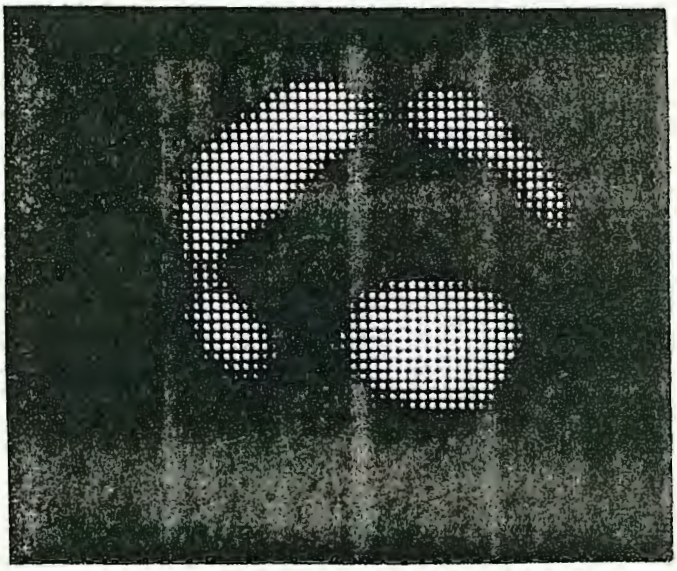


Phantom
<-

DIASTOLE



SYSTOLE



מכון ויצמן למדע
THE WEIZMANN INSTITUTE OF SCIENCE

REHOVOT · ISRAEL רחובות · ישראל

ISOTOPE DEPARTMENT מחלקת איזוטופים

July 31, 1980

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

Dear Prof. Shapiro:

Proton NMR with deuterium decoupling in liquid crystals

Proton NMR Spectra in liquid crystal solvents of molecules containing more than 6 or 8 magnetic nuclei are usually very complex, poorly resolved and difficult to interpret. As an example consider the spectrum of cyclopentane (C_5H_{10}) in dihexyloxyazoxybenzene (110°C) shown in Fig. 1. To overcome this difficulty, Snyder and Meiboom suggested several years ago (J. Chem. Phys. 58, 5089, 5096, 1973) to use partially deuterated compounds and record the proton spectrum under condition of deuterium decoupling. Efficient and complete decoupling can best be obtained by irradiating the deuterium with a single frequency at exactly its Larmor frequency. This requires an extra stable irradiation channel locked to the proton frequency of the spectrometer. We perform such experiments routinely on the WH-270 Bruker spectrometer of our chemical services unit without any irreversible modification or major interference with its electronic circuitry, by using the lock channel of the proton probe as the decoupling channel. This is possible because the stability of the cryomagnet is sufficient to permit accumulation of spectra over long period of times without a lock.

An example of this application is shown in Fig. 2. The upper trace in this figure corresponds to the spectrum of 1,2,2',5,5', pentadeutero cyclopentane ($C_5H_5D_5$) at 82°C in the same solvent as for C_5H_{10} of Fig. 1. The middle trace shows the deuterium decoupled spectrum and the lower one is the corresponding calculated spectrum using the following value (H_z): $D_{33'}$=1730; D_{34}(Cis)=-305; $D_{34'}$ (trans)=-7; D_{13}(Cis)=-150; $D_{13'}$ (trans)=-50; J_{34}(Cis)=8.5; $J_{34'}$ (trans)=6.0.

The experimental set up consists of a PTS-160 synthesizer, locked to the 10 MHz frequency of the WH-270 console, which provides the 41.457 MHz deuterium frequency. The rf irradiation is amplified with a broad band power amplifier (ENI model 350L) and applied through a variable attenuator (Teleonic TG 950A) and watt meter (Bird Electronic Corp., model 4314) to the lock connector of the probe. In our experiments the rf decoupling power was less than 10 watts and 3-5 watts were usually sufficient for complete decoupling. Power above 15 watts must be avoided to prevent damage to the matching circuit of the probe.

CABLE ADDRESS: WEIZINST (Israel) : מען למברקים PHONE: (054) 82111-83111 : טלפון TELEX: 31900 : טלקס

A complete conformational analysis of cyclopentane in terms of the experimental dipolar couplings will be published at a later date together with H. Zimmerman (Max Planck Institute for Medical Research, Heidelberg, W. Germany) and Z. Luz of this Institute.

Sincerely yours,

R. Poupko

R. Poupko

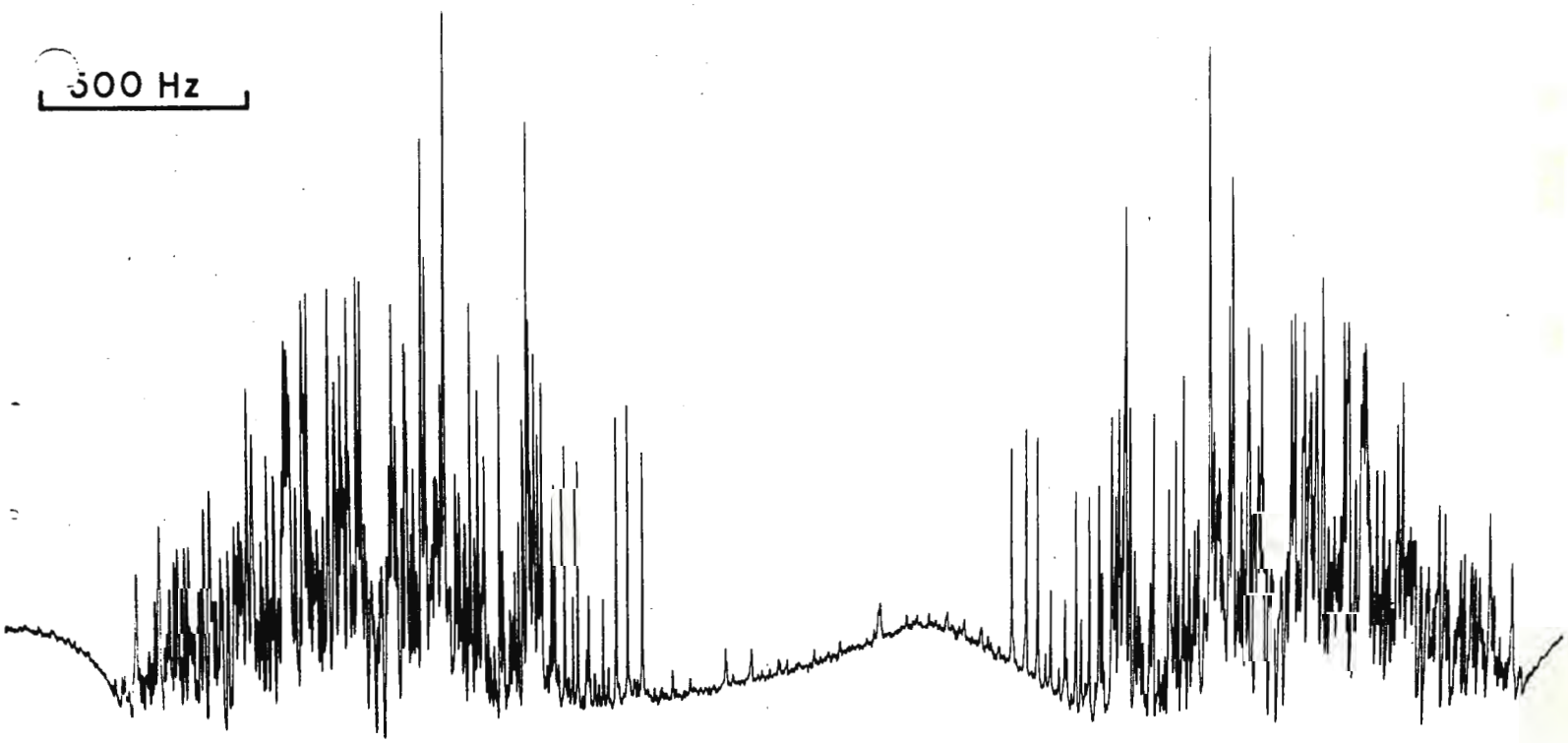


Fig. 1

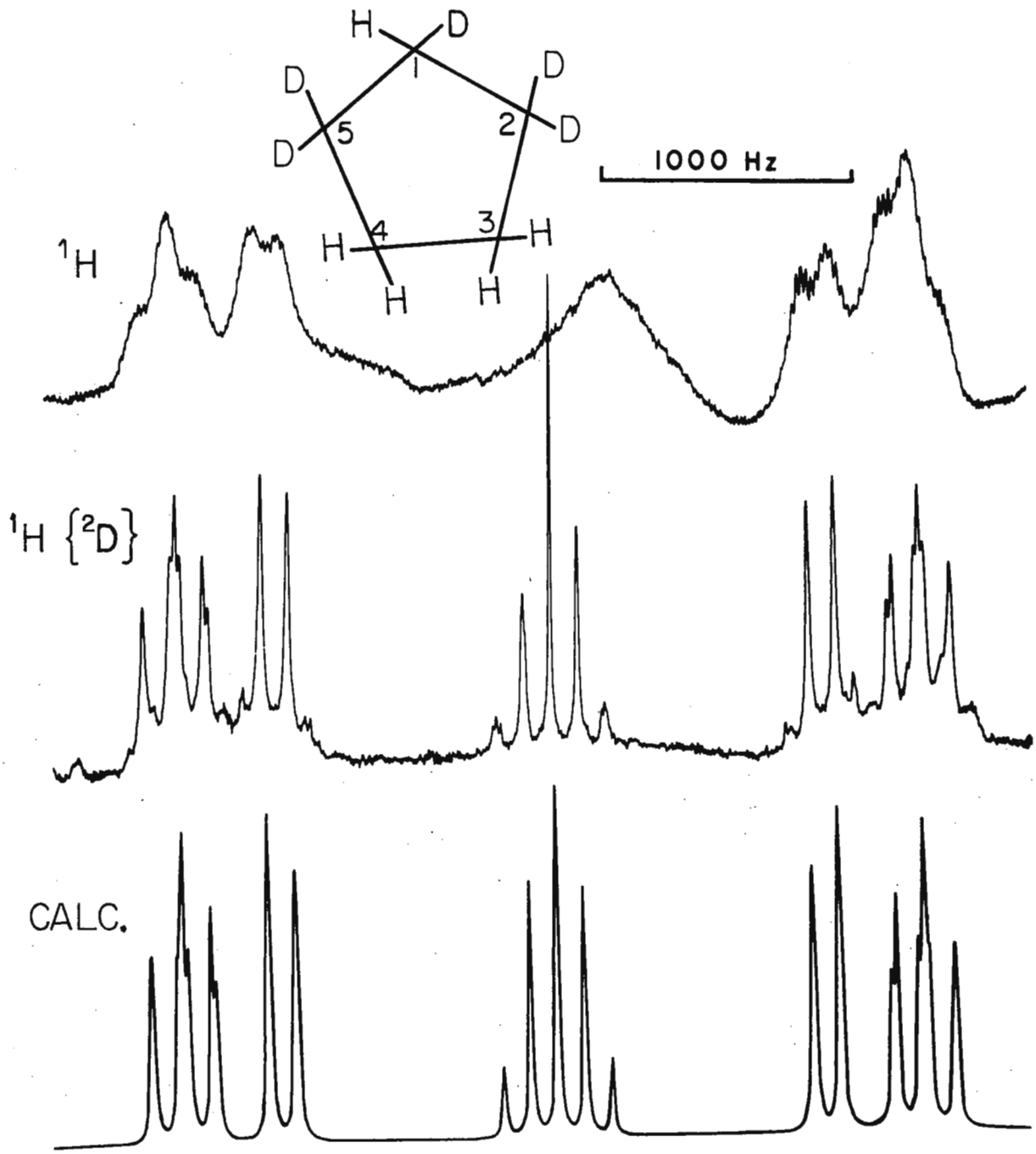
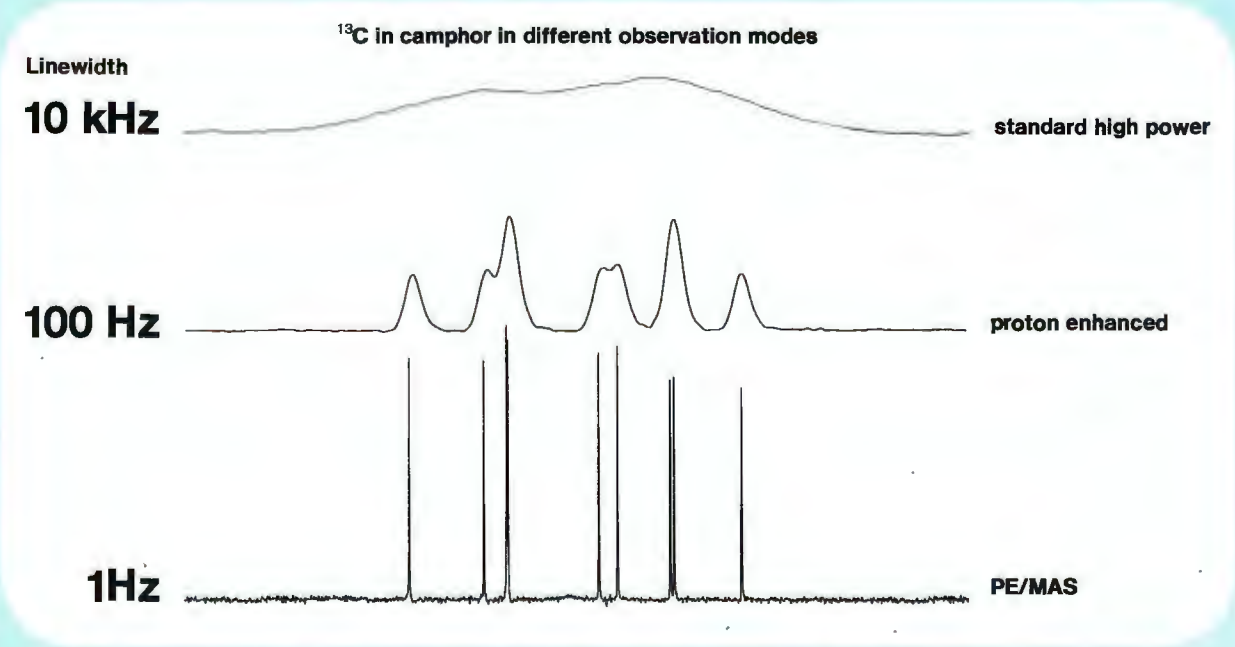


Fig 2

Bruker ≡ NMR
NMR ≡ Bruker

Should you intend to run high-resolution NMR spectra of true solids, the only real choice is a BRUKER CXP:

CXP 100
CXP 200
CXP 300



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

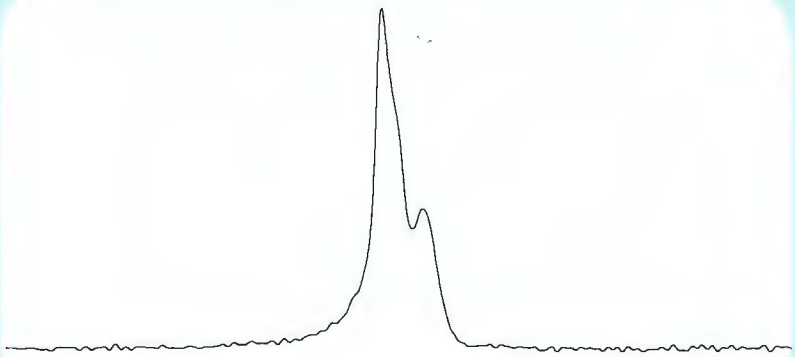
Unique features of the CXP spectrometer line for cross-polarization / magic angle sample spinning experiments comprise:

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

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

Polyethylene

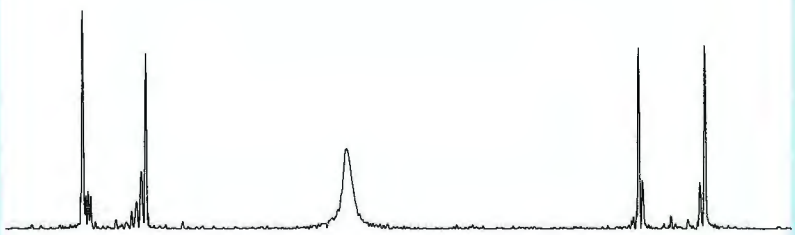
The resolution shown in the spectrum of this highly crystalline polymer required a decoupling field of 20 Gauss.



Cured Neoprene with Carbon Black *)

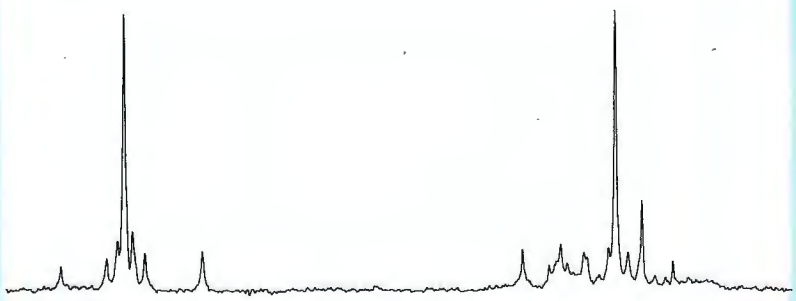
Soft plastics afford excellent S/N and resolution even in the absence of cross polarization and using low decoupling power (35 W, BB-decoupling, 263 transients at 3.5 s recycle time, Gaussian resolution enhancement).

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



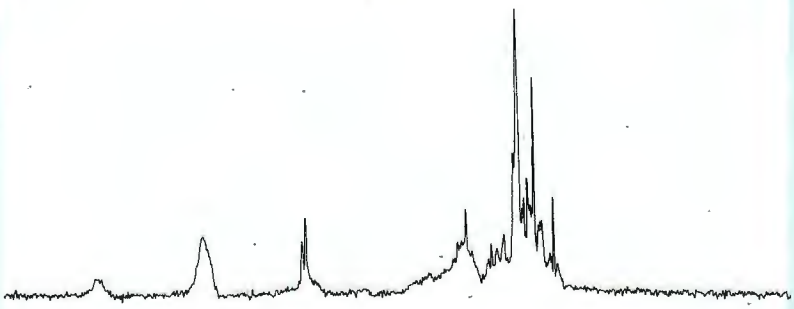
Styrene Butadiene Polymer

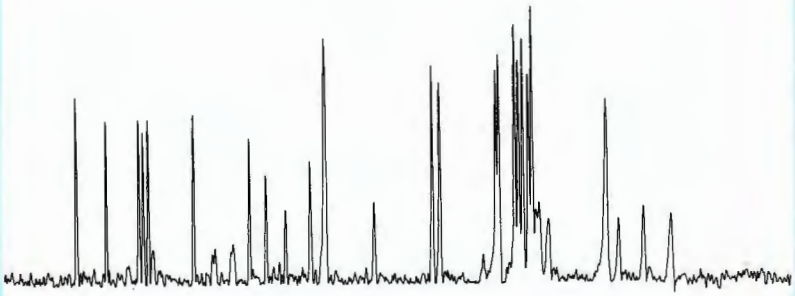
This complex polymer system afforded well separated interpretable lines in 30 minutes experimental time.



Erythrocyte Ghosts

Even this highly complex biological sample gave well resolved resonances.



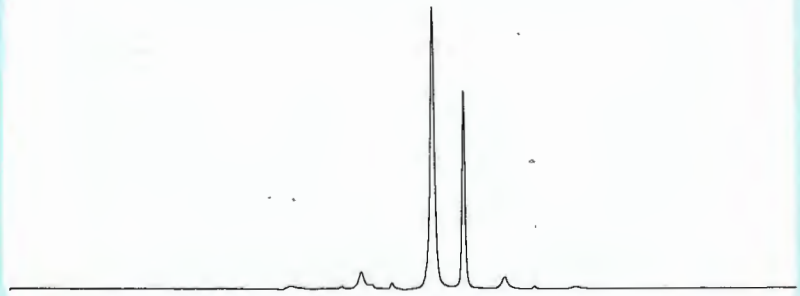


Reserpine

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

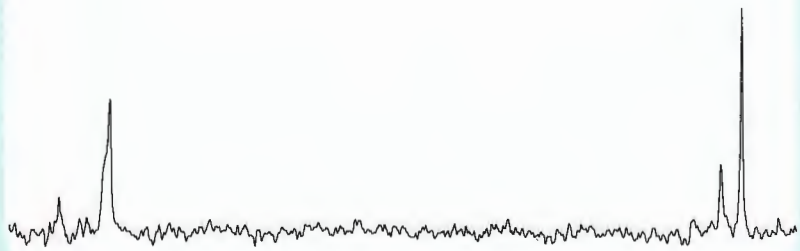
Ammonium Dihydrogen Phosphate

Magic angle spinning reduced the ^{31}P linewidth from 34 to 1.4 ppm.



Mixture of Sodium Chloride and Sodium Nitrite Crystals

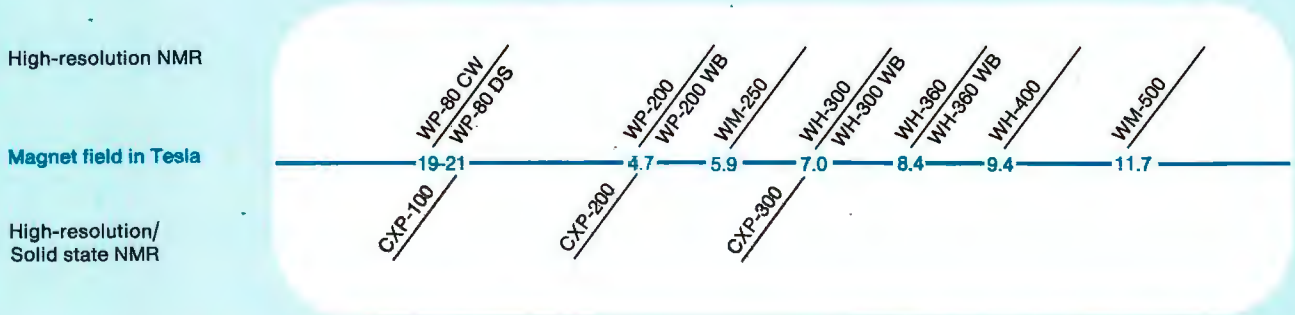
This spectrum shows the chemical shift dispersion of ^{23}Na in the solid state. Magic angle spinning narrowed the lines to 2 ppm.



Ammonium Nitrate

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

Whether your NMR needs are governed by scientific demands or budgetary constraints, Bruker is the only real choice. No other manufacturer offers as complete a product line as we do:



For further information, please contact your nearest BRUKER representative:

WEST-GERMANY
BRUKER ANALYTISCHE MESSTECHNIK GMBH
Silberstreifen, 7512 Karlsruhe-Rheinstetten
Tel. (0721) 5 11 85, Tx. (07) 826 836

USA BRUKER INSTRUMENTS, INC.
Manning Park, Billerica, Mass. 01821
Tel. (617) 667-9580, Tx. 94-7125

USA BRUKER INSTRUMENTS, INC.
201 San Antonio Circle, Suite 152
Mountain View, Calif. 94 040, Tel. (415) 9413804

CANADA BRUKER SPECTROSPIN LTD.
2410 Dunwin Drive, Unit 4 L5L 1J9, Mississauga,
Ontario, Canada, Tel. (416) 828-2830, Tx. 06-961 446

AUSTRALIA BRUKER SELBY
352 Ferntree Gully Rd., Notting Hill, Victoria
Tel. 544 4844, Tx. 30889

JAPAN BRUKER JAPAN
Garden Park Bld. 405 27, Kanda Sakumacho
3-chome, Chiyoda-ku, Tokyo, Tel. (03) 866-0968

ENGLAND BRUKER SPECTROSPIN LTD.
Unit 3, 209 Torrington Avenue
Coventry CV49HN, Tel. (0203) 46 37 70

SWITZERLAND SPECTROSPIN AG
Industriestr. 26, 8117 Zürich-Fällanden
Tel. (01) 8 25 48 55, Tx. 54 850

NETHERLANDS BRUKER SPECTROSPIN NV
Bruynvisweg 18, 1530 AB Wormer
Tel. (75) 28 52 51, Tx. 19 197

SCANDINAVIA BRUKER SPECTROSPIN AB
Vasavägen 11, S-184 00 Åkersberga
Telephone 08-7 32 90 40

FRANCE BRUKER SPECTROSPIN SA
Rue de l'industrie, (67160) Wissembourg
Tel. (88) 00 33 88 - 94 98 77, Tx. 87 639

BELGIUM BRUKER SPECTROSPIN S.A./N.V.
Rue du Vindictive-Straat, 2
1040 Bruxelles, Tel. (02) 7 36 11 38, Tx. 25.797

ITALY BRUKER SPECTROSPIN SRL.
Via Pasquale Migliorelli, 2, 20161 Milano
Tel. (02) 64 64 261, Tx. 37 263

Koninklijke/Shell-Laboratorium, Amsterdam

Shell Research B.V.

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

Uw ref.:

Onze ref.: AG

Amsterdam, 8 August 1980
Postadres: Postbus 3003, 1003 AA Amsterdam
Tel. via telefoniste (020) 20 91 11
Tel. rechtstreeks (020)
Hr/Mw

Dear Barry,

COATED BORON NITRIDE MAGIC ANGLE SPINNERS

Until recently we have used Delrin, Kel-F or perdeuterated polymethyl methacrylate (PMMA) as materials for our hollow Andrew type magic angle spinners on our Bruker CXP-300 spectrometer. There have been drawbacks to each of these. Delrin, although having excellent spinning properties (easily in excess of 4.5 kHz), unfortunately gives a large background signal, whose spinning side bands interfere with both aliphatic and aromatic carbon signals at a field of 7.05 T. There are also some impurity signals which further confuse the aliphatic carbon region. Kel-F has poor spinning qualities in our spinner configuration and we have never achieved spin rates better than 2.5 kHz. Its advantages as a material with a clean background are therefore lost. The perdeuterated PMMA which we have received has tended to be soft and become easily damaged; we suspect low molecular weight compounds to be present, which weaken the material. In any case, there is a residual PMMA spectrum, which interferes with the aliphatic and carbonyl carbon signals. Moreover, the product is rather expensive!

Not exactly in desperation, but close to it, we turned to boron nitride following an article by Yannoni et al.[1]. This material, grade HP from Carborundum, gives a very clean background since it contains no carbon. It is machinable, but only with some difficulty, because it is rather soft. The spinning characteristics are good and spin rates in excess of 4 kHz can be readily achieved. Above 5 kHz, however, there is a tendency to self-destruction! Furthermore we found that there was considerable wear of the mushroom head caused by contact with the aluminium stator during the deceleration process. Our solution to these problems was to coat the head with a methacrylate polymer "X-60" from Hottinger Baldwin Mess Technik. The procedure consisted in degassing the adhesive at low temperature, then using a dummy stator to hold the still cold adhesive, and pressing the boron nitride spinner into the stator to obtain a uniform film over the head of the rotor. The flutes needed for spinning were then machined into the coating but not the boron nitride.

We observe no background signal from these coated spinners, and their lifetime is in general better than 100 hours at spinning rates between 4 and 5 kHz. The coating can be renewed when wear becomes excessive.

As a simple demonstration of the advantage of coated boron nitride spinners we have included a spectrum of sucrose, together with one recorded in a Delrin spinner by way of comparison.

Its very satisfying to have a contribution ready before we get any warning notice from you. Hopefully we can continue in this way!

Yours sincerely,

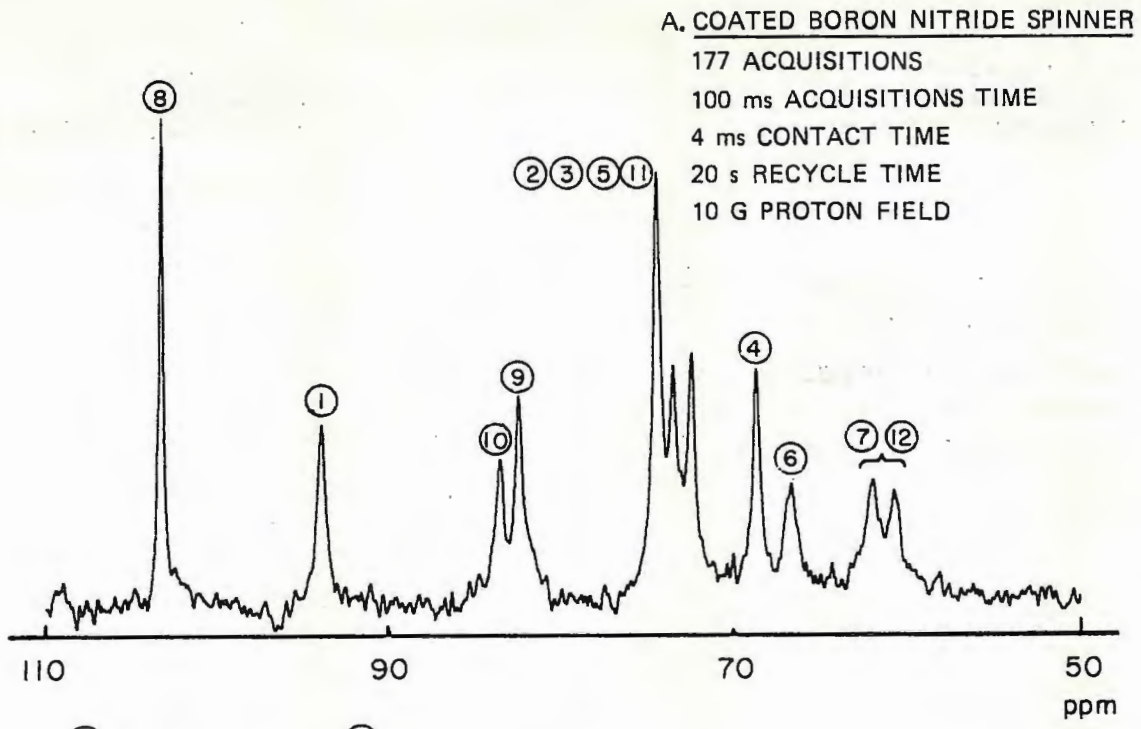
KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM

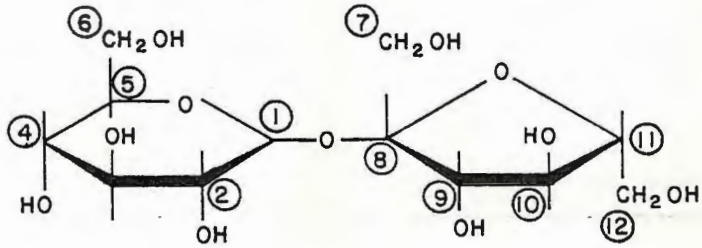
M. de Wit R. Huis G.R. Hays A.D.H. Clague

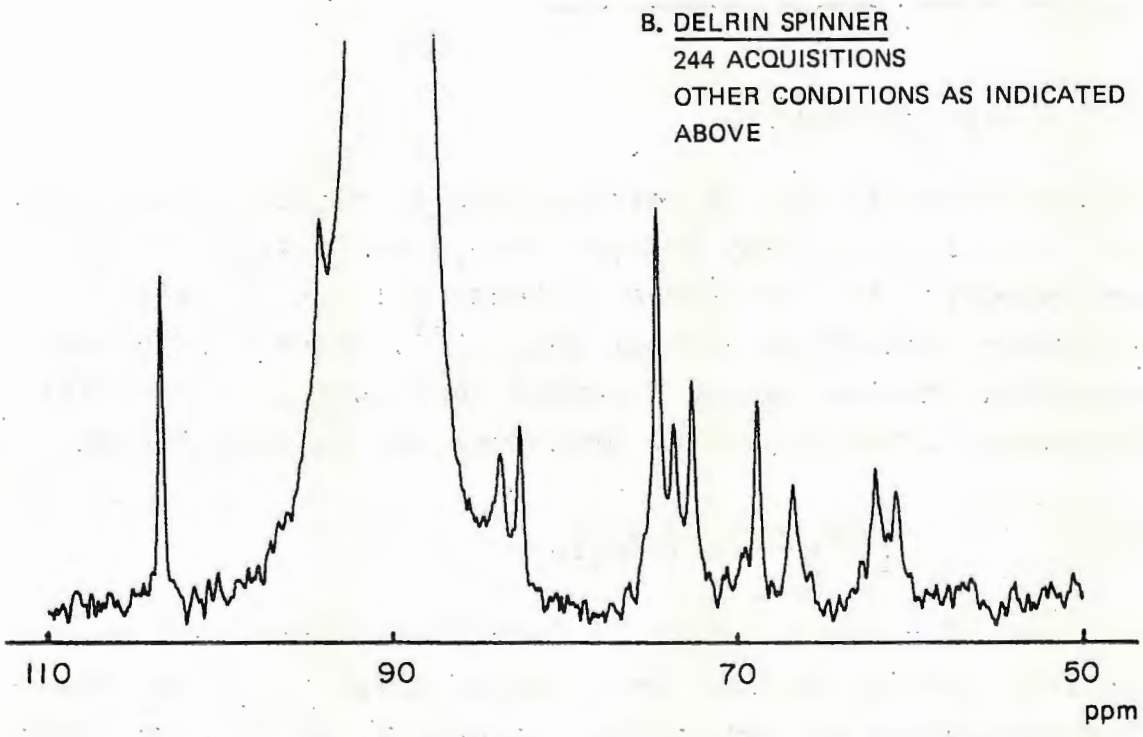
Enclosure

1. C.A. Fyfe, H. Mossbruger and C.S. Yannoni, J. Magn. Reson., 36, 61 (1979)

PUBL. 80.075







CPMAS ^{13}C SPECTRA OF SUCROSE

DRAWN Dk
DWG 80.08.1008

Prof. Dr. D. Leibfritz
Universität Bremen
Fachbereich Chemie/Biologie

NW 2 Leobenerstraße
2800 Bremen 33
Telefon (04 21) 218-2818/28 41 / 2550

Bremen, den 05.08.1980

Prof. B.L. Shapiro
Dept. of Chemistry
Texas A&M-University
College Station
Texas 77843
USA

Selective Peak Suppression in C-13 NMR

Postdoctoral Position available

Dear Professor Shapiro,

In some cases it may be advantageous to eliminate one or more signals in a C-13 NMR-spectrum, for instance in complex spectra, in the case of intense solvent signals or compounds bound to a polymer support[1]. Since a C-13-homodecoupling device is not a common accessory of commercial instruments, the following procedure may be used instead.

$$\left[(P1,\ T1)_n\ ,\ P_{rf}\right]_m$$

A series of n short pulses P1 (one microsecond long at our machine) applied before the sampling pulse P_{rf} gives selective saturation at the carrier frequency. An average number of n is 1000. The intervall T1 should be as short as possible, since it causes side bands of its reciprocal value. The side-

bands may be used to suppress a further line or may be placed outside the spectrum. The technique is applied to an off resonance spectrum of cholesterol, where the lines of the carbons 7/8 are eliminated (see fig.). The procedure works also for saturation transfer experiments. With lower n values the method resembles a reversed DANTE-experiment [2], where a selective 90°-Puls could be followed by a nonselective 90°-pulse; but it can be more easily done. A detailed report on the applications is in preparation.

Yours sincerely

M. Feigel

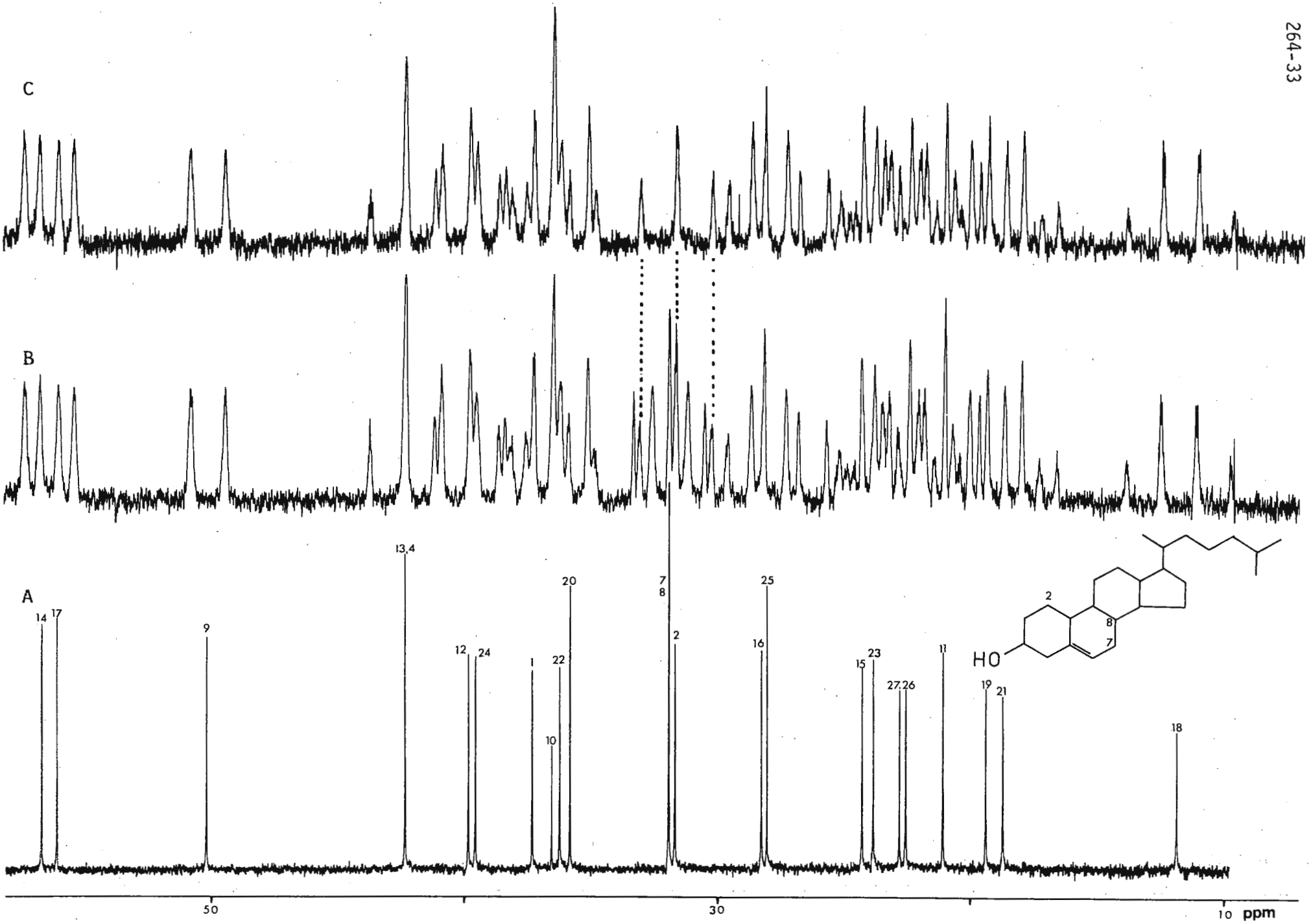
D. Leibfritz

References

1) D. Leibfritz et al Tetrahedron 34, 2045 (1978)
2) G. Bodenhausen, R. Freeman and G. Morris, J. Magn. Res. 23, 174 (1976)

Postdoctoral Position open

A postdoctoral position is available in my lab to carry out NMR studies on peptides. We are equipped with a Bruker 360 MHz multinuclei spectrometer. The salary is $ 17.000/year. Some experience in 2D NMR is prefered.



C-13 spectra of cholesterol: decoupled(a); off resonance(b); off resonance with selective suppression(c)

JEOL (U.S.A.), INC. • ANALYTICAL INSTRUMENTS DIVISION
235 BIRCHWOOD AVENUE • CRANFORD, NEW JERSEY 07016
TELEX NO. 13-8840 • (201) 272-8820

August 21, 1980

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

Dear Barry:

^{13}C and ^{31}P: Magic, Morphology, and Metals, Solid Evidence

As we run more and more solids spectra, we have observed some unusual results (although not unexplainable to an after-the-fact a priori theorist), and we believe that sharing these data may encourage others to pursue similar experiments.

The first result is the ^{13}C solid NMR of vitamin-C (L-ascorbic acid) which gives 9 lines for the 6 carbons (and some Fourier ringing from the truncated FID). However, the epimer, D-araboascorbic acid, gives the expected 6 lines (fig. 1a & b). The crystal structure of vitamin-C[1] shows 4 molecules per unit cell (2 pairs of symmetry related molecules) and, hence, 3 carbons become nonequivalent in the solid state. In a similar fashion, vanillin (a model compound for lignins), shows nonequivalent carbons in the ^{13}C solid state spectrum while iso-vanillin does not (fig. 1c & d).

In ^{31}P solid NMR, we have been looking at metal-phosphine

complexes and have have observed both ^{31}P - ^{183}W coupling and ^{31}P - ^{195}Pt coupling (fig. 1e & f), however, the Platinum compound shows two distinct ^{31}P resonances with associated Pt satellites and both sets of resonances have different $T_{1\rho}$'s indicating different molecular species (or at least different orientations).

Both the ^{13}C chemical shifts and the ^{31}P coupling are only slightly different in the solid state versus solution.

	SOLID	SOLUTION
$^{1}J_{PW}$	260 Hz	276 Hz
$^{1}J_{PPt}$	1898/1879 Hz	1797 Hz

The ^{13}C spectra in Fig. 1a and b are 2000 Hz width (133 ppm) while 1c through f are 4000 Hz (267 ppm ^{13}C and 166 ppm ^{31}P). The metal-phosphine samples were courtesy of Gary Gray (currently at J. T. Baker) and we are in the process of further investigating metal-phosphorus coupling in the solid state.

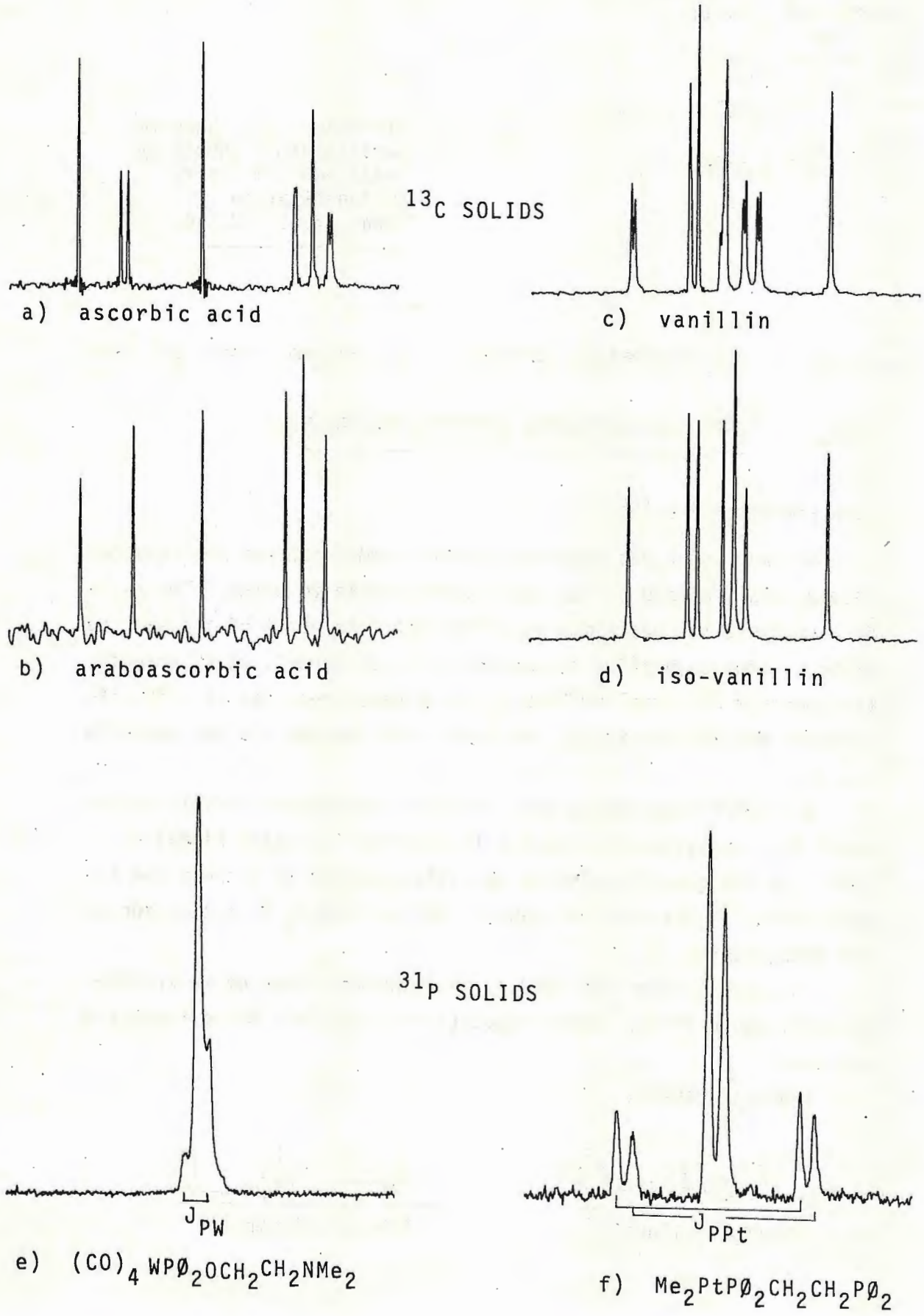
Sincerely,

Dr. Michael J. Albright

MJA/mjd

1. Hvoslef, J., ACTA. CHEM. SCAND., 18, 841 (1964).

FIGURE 1 ^{13}C and ^{31}P SOLID NMR DATA



GRUPPO LEPETIT spa

anno di fondazione 1868
sede in Milano . capitale sociale L. 29.363.000.000
trib. Milano N. 22049 . C.C.I.A. Milano 95669
codice fiscale e partita IVA N. 00795960152

Research Laboratories
Via Durando, 38
20158 Milano, Italy
20124 Milano . Via R. Lepetit, 8
27771 centralino
telefoni: 2777 selezione passante
279735.6.7 interurbano
telegrammi: Lepetit . Milano
telex: 311054 LEPMI
conto corrente postale N. 00589200
casella postale 3698 . 20100 Milano

destinatario:

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

nostro riferimento: Physicochemical Service data: Milano, August 25, 1980

Title: WATER IN DEUTERATED DIMETHYL SULPHOXIDE

Dear Professor Shapiro,

we have sometimes observed in the ^{1}H NMR spectrum of vials of DMSO-d_6 the presence of two peaks attributable to water. The ratio between these two peaks may vary from batch to batch of the same supplier or from a supplier to another one. We report, as an example, the spectrum of a vial of DMSO-d_6 99.8% Merck recorded at 20°C with a Bruker WH-270 (insert A). The separation between the two peaks is 6.5 Hz.

At higher temperature the signals of water move upfield and at about 80°C coalesce; in insert B is reported the water signal at 120°C. In the graph is plotted the difference in Hz between the highest water signal and the highest peak of DMSO-d_6 as a function of the temperature.

It appears then that DMSO-d_6 contains two kinds of water differently bound to it. Other suggestions to explain these facts are welcome.

Yours sincerely,

Edoardo Martinelli Ambrogio Ripamonti

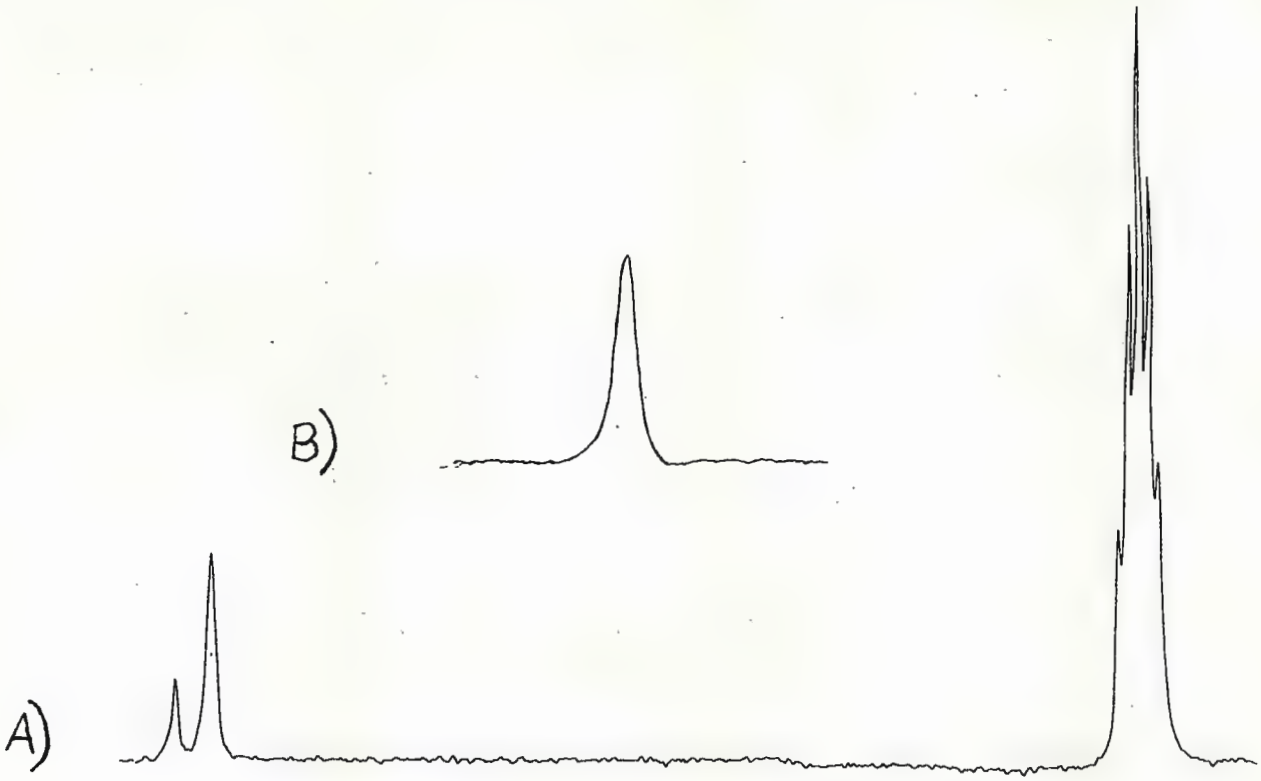
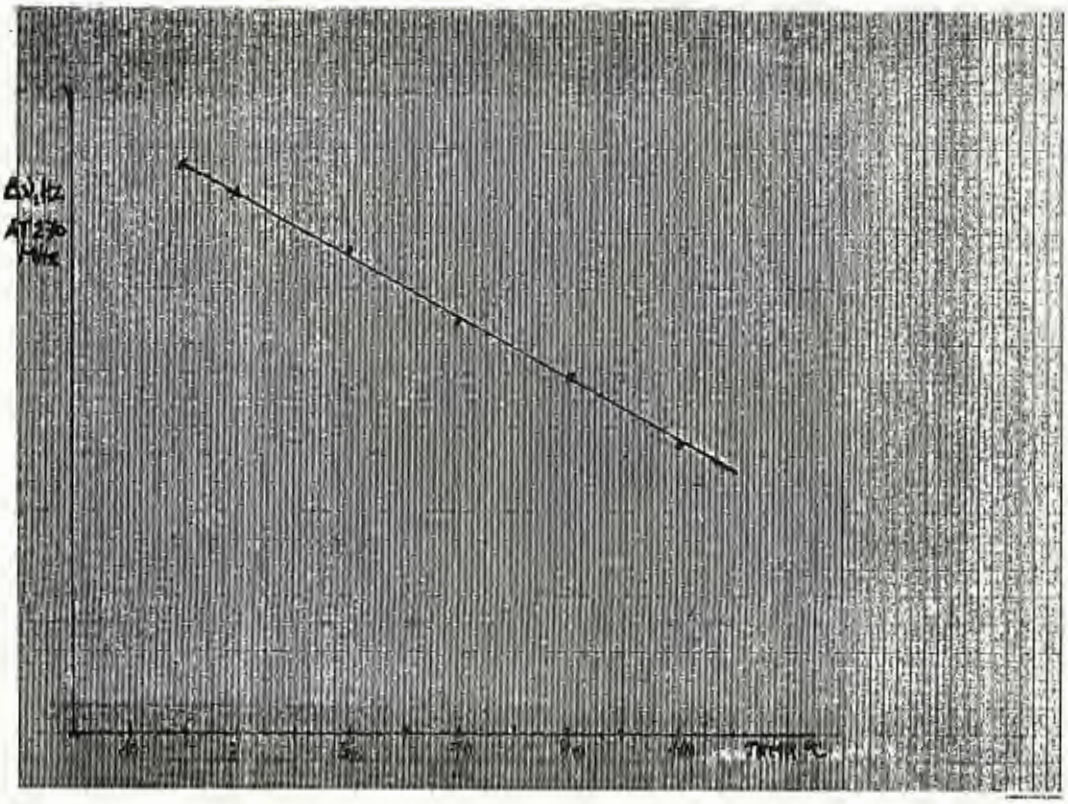


Fig. ^{1}H NMR spectra of DMSO-d_6 99.8% Merck - A) at 20°C
B) at 120°C.



ETH EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE
ZÜRICH

Laboratorium für anorg. Chemie

Universitätstrasse 6
Telefon 01 326211
Dr. P. S. Pregosin

Postadresse:
Laboratorium für anorg. Chemie
ETH-Zentrum
CH-8092 Zürich

August 18, 1980

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

^{75}As NMR Linewidths in $AsEt_4^+$ Salts

Dear Prof. Shapiro,

Of the group V NMR nuclei, arsenic seems to have been somewhat neglected. Admittedly, ^{75}As is a quadrupolar nucleus and therefore less attractive; nevertheless, it is possible to obtain useful information from its measurement. For example: shown below are linewidth data from the PhD thesis of Giovanni Balimann (current address: Spectrospin AG, Zürich-Fällanden) which suggest that this NMR probe may have importance in the area of ion pairing. A full report on this subject is in preparation.

Please credit this contribution to the account of Prof. L. M. Venanzi.

^{75}As Linewidths for $[AsEt_4]K$ Compounds (DMF, ∿ 25°C)

X	Δν 1/2, Hz
Cl^-	1450
Br^-	885
I^-	520
BF_4	450

Sincerely
Paul Pregosin

Suggested title: ^{75}As NMR Linewidths in $AsEt_4^+$ Salts.

NT-Series Fourier Transform Superconductive Magnet NMR Spectrometers

The NT-Series has been conceived and designed to provide optimum performance while being fully adaptable to new techniques with minimal cost and difficulty. More than just a collection of instruments, the NT-Series represents a *completely modular approach* to FT-NMR instrumentation that allows the user to expand his system as his research needs grow and to easily accommodate new experimental techniques as they develop.

Outstanding NT-Series features include these:

- **A full range of superconductive magnets from 3.5T to 11.7T in both wide-bore and narrow-bore configurations.**
- **Multinuclear observation with a wide variety of fixed-tune and broadband probes.**
- **Simultaneous acquisition, processing, and plotting for greater sample throughput.**

- **Simplified control of spectrometer operations and parameters by using easy keyboard commands.**
- **Advanced Nicolet-1180 Data System with the most comprehensive FT-NMR software package available.**
- **Extended dynamic range performance with 40-bit acquisition and floating-point processing.**
- **An expandable pulse-sequence library, including T_1, T_2, Redfield, 2D-FT, etc.**
- **Convenient computer-control of field shimming, observe and decoupling frequencies, sample temperature.**
- **Precise digital plotting with full annotation of spectral parameters and flexibility of hard-copy format.**

The multiple-technique NT-Series spectrometers provide the user with the ability to easily adapt to the newest techniques and experimental configurations.

Some of these are:

- **High-resolution studies of solids with Waugh-Pines cross-polarization and magic-angle spinning**
- **High-sensitivity wide-bore ^{13}C studies of high molecular weight polymers.**
- **Automated T_1 and T_2 measurements.**
- **Chemical dynamics studies.**
- **Temperature-programmed experiments.**
- **^{31}P experiments on living organs.**

NICOLET TECHNOLOGY CORPORATION
145 East Dana Street
Mountain View, California 94041
Telephone: 415/969-2076

FX SERIES
OF
FT NMR SYSTEMS

FX-90Q
OMNI Probe™ System
10mm, 5mm, micro inserts

FX-60Q
Solids Probe (^{13}C) with
Magic Angle Spinning
High Resolution Probe ($^{13}C/^{1}H$)

FX-200
Dual Probe ($^{13}C/^{1}H$)
Broad Band (^{15}N to ^{31}P)
50 KHz Spectral Width

System Features

- Light Pen Control System
- Foreground/Background
- Digital Quadrature Detection
- Multi Frequency Observation
- Programmable Multi Pulser
- Module Performance Indicator Lights
- Comprehensive Auto Stacking
- T_1-rho
- Double Precision (32 bit word length)
- Floppy; MH Disc Storage
- 50KHz Spectral Width
- CPU Expansion to 65K

JEOL

USA Inc., Analytical Instruments Div.
235 Birchwood Ave., Cranford, NJ 07016
201—272-8820